CAMBRIDGE CARES

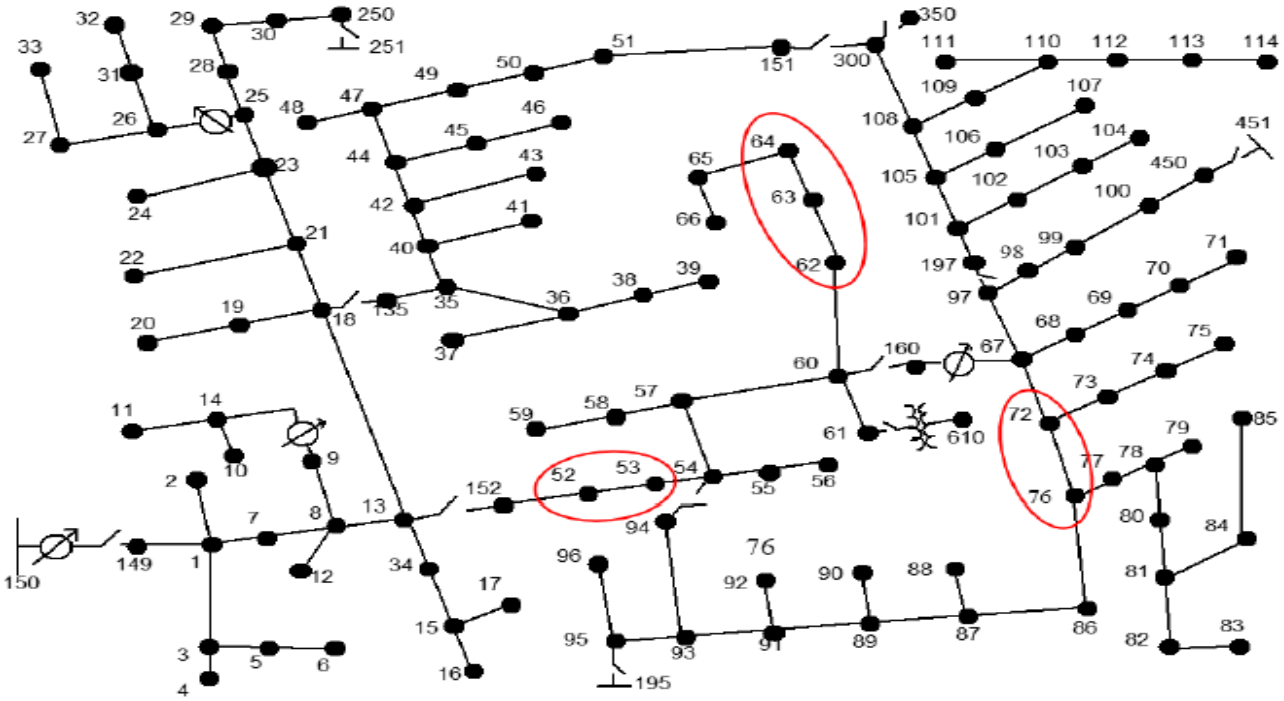
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH AND EDUCATION IN SINGAPORE LTD.

Biannual Research Report

May 2017 — October 2017

CAM.CREATE C4T

Cambridge Centre for Carbon Reduction in Chemical Technology



CREATE

Centre for Reseach Excellence and Technological Enterprise

University of Cambridge

Nanyang Technological University

National University of Singapore

Cover figure: Finding exhaustive solutions for Optimal PML Placement: A intermediate step where the nodes in the network are categorized following specific rules (CARES C4T IRP4)

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CAMBRIDGE CENTRE FOR ADVANCED RESEARCH AND EDUCATION IN SINGAPORE LTD.
Registration No. 201302109Z
1 Create Way, #05-05 CREATE Tower, Singapore, 138602

cares@hermes.cam.ac.uk
http://www.cares.cam.ac.uk

3 Foreword

Prof. Markus Kraft,

CARES Director.

October 2017

I am very pleased to present the 7th Biannual Research Report of the Cambridge Centre for Carbon Reduction and Technology (C4T), the first programme managed by the Cambridge Centre for Advanced Research and Education in Singapore (CARES).

PIs in residence

Since April both Prof MACIEJOWSKI (IRP4) and Dr. FISHER (IRP2) have successfully completed their six month stays in Singapore. This has deepened the existing Cambridge-Singapore collaborations further and given excellent opportunities for the Cambridge PIs to interact with the Singapore-based researchers on a day-to-day basis. Prof Alexei LAPKIN has now started his six month stay at CARES. We are delighted that he has also had the opportunity to serve as an Adjunct Professor at NUS where he gives lectures to undergraduates on advanced reaction engineering. This new course covers many aspects of the work going on in C4T and hopefully will encourage more excellent young researchers to join the field in the future.

Intra CREATE

In the last report I mentioned that CARES had submitted a number of proposals to the Intra CREATE grant calls. I am now very pleased to announce that CARES was successful in securing funding for a large Intra CREATE project. The work will be carried out together with University of California, Berkeley; BEARS, NTU and NUS. The title of the successful proposal is: ”A table top chemical factory for the reduction of CO_2 to value added chemicals”. The work will contribute to filling the gap between the fundamental research which is currently going on in CARES and BEARS and commercially successful technology. The project’s lead principal investigators are Professor Alexei LAPKIN (Cambridge; CARES) and Joel AGER (University of California, Berkeley; BEARS). The grant is of the order of SGD 5M and will last 36 months. We are excited that we have this unique opportunity to work together. The CARES-hosted project was one of only four selected from over 70 applications. In addition to this large Intra CREATE grant we are proposing various work streams for the second round of the Intra CREATE seed funding. This funding instrument is directed to members of the programme who are at the early stages of their academic career. CARES will submit on topics including air quality sensing in Singapore (CARES/BEARS) and smart grid energy storage (CARES/NTU).

Highlights

We mentioned in our last Biannual Report that CARES had received the Inaugural BCA Green Mark for Laboratories Platinum Award. On the 13th June Prof Markus Kraft was presented with the BCA certificate at the annual BCA Awards ceremony. This annual meeting is the social highlight of the Building and Construction Authority and is attended by several hundred people, so was a great opportunity to advertise our programme.

I am also delighted to report that C4T researchers have received a number of awards and accolades for excellence in recent months. These include Prof ZENG Hua Chun (PI, NUS, IRP1) who received the Outstanding Researcher Award from AICHE Singapore and Prof Martin PUMERA (Co-I, NTU, IRP2) and Prof LEE Jim Yang (PI, NUS, IRP2) who were both named “Highly Cited Researcher 2017” by the publishers of Web of Science. Dr Jithin John VARGESE (RF, NTU, IRP1) received the Exxon Mobil Poster Award at the SE Asia Catalysis Conference 2017 for work on the contribution of nickel and oxygen vacancies in altering surface reactivity of NiO for C-H activation. A team including members of IRP4 (Dr. Joymala Moirangthem (RF, NUS, IRP4), Prof. S.K. Panda (PI, NUS IRP4), and Prof. Gehan Amaratunga (PI, Cam IRP4) won a best paper award with their JPS-inspired paper “Electrical Grids of the future: GIS-integrated Power-flow as an Online Service”. Prof XU Rong (Co-PI, NTU, IRP3), Prof John Robertson (Co-I, Cam, IRP3/4), Shuyang Wu (PhD student, NTU, IRP3) and a team including myself produced an article (“Investigating the Role of Tunable Nitrogen Vacancies in Graphitic Carbon Nitride Nanosheets for Efficient Visible-Light-Driven H2 Evolution and CO_2 Reduction”), which was ACS Editor's Choice. Each day ACS Editors' Choice features an article selected from across all ACS journals by ACS editors for its potential broad public interest.

A special highlight of the past six months for me personally was Prince Andrew, the Duke of York's visit to the British High Commission in Singapore on 13th June. In a private display for Prince Andrew we demonstrated J-Park Simulator, our C4T signature project, which was also part of the 'Science is Great' event hosted at the British High Commission in celebration of the Commonwealth Science Conference which was held in Singapore this year.

Conferences

As in every reporting period our programme members presented the fruit of their work at various conferences. I will mention only a small selection. The Department of Chemical Engineering and Biotechnology (CEB) Research Conference, 26 - 27 June 2017 in Cambridge was organised by Prof Alexei Lapkin (PI, IRP1, Cam). Many Cambridge CARES students from Singapore attended this conference which strengthened the collaboration between CARES and CEB. We also took part in the second Commonwealth Science Conference (CSC) which was organized by the Royal Society and National Research Foundation, Singapore from 13th to 16th June 2017 in Singapore. This was a unique conference where the top researchers and policy makers from nations around the world came together and discussed the key events like Paris Climate agreement, Britain leaving the EU (Brexit), the role of India and China in the global economy and their effects on the future of mankind. Eight members of C4T attended the 9th International Conference on Applied Energy (ICAE 2017) which was held in Cardiff from 21 August to 24 August this year. The theme of ICAE 2017 was "Energizing the future" and all C4T presentations received excellent feedback.

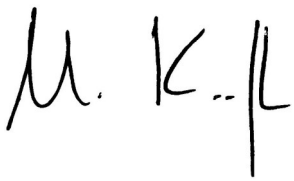
Visitors

Although we had no senior academic visitors during this period we were fortunate to have a number of young talents working with us. Laura PASCAZIO visited from Prof Andrea D'ANNA's group at the University of Naples and HOU Dingyu from Prof YOU Xiaoqing's research group from Tsinghua University in Beijing. Both are working with members of IRP3 on fundamentals of carbon nanoparticle formation in flames. YU Haiyan from Beijing University of Chemical Technology and Harshiyot SINGH from NUS are both working on topics in IRP2. Anira PERERA and Yehia AMAR both students at Cambridge, and John ATHERTON from the University of Queensland in Australia were working on IRP1 and IRP4 topics, respectively.

Features

In this edition of research report you will find two pieces that explain the potential impact of our research, which I highly recommend to you. Dr Quang Thang TRINH (Research Fellow, IRP1, NTU), explains how in-silico design of efficient catalysts for the conversion of methane can lead to higher value chemicals and ZHANG Chuan (PhD Student, IRP3, NTU) investigates the importance of waste heat exploitation in future energy systems as an efficient way to cut down the overall CO_2 emissions. A feature that focuses more on fundamental science by ZHANG Shengliang (PhD Student, NUS, IRP2) answers the question: what are electronic smart windows? I would like to thank all authors for putting in this additional effort to communicate their exciting research to our readers.

In closing, I hope I have been able in this brief overview to encourage you to examine the contents of this report more closely. Please get in touch if you have questions or find some common ground for collaboration.



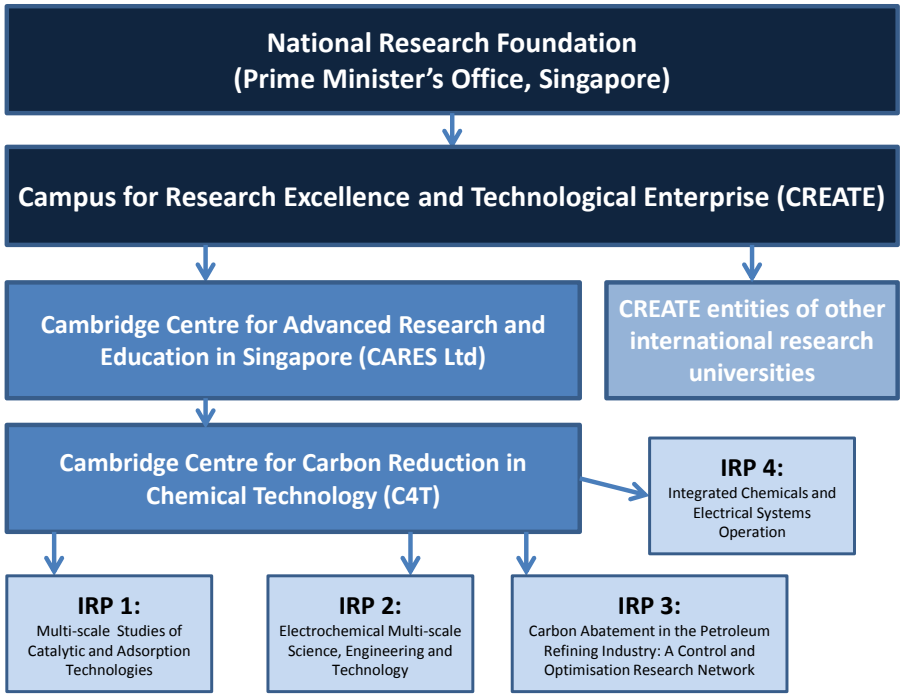
Prof. Markus Kraft, CARES Director

1.1 Structure and Organisation

The Cambridge Centre for Advanced Research and Education in Singapore (CARES) is a wholly-owned subsidiary of the University of Cambridge. CARES is funded by the National Research Foundation, as part of CREATE (Campus for Research Excellence and Technological Enterprise) and hosts a number of research collaborations between the University of Cambridge, Nanyang Technological University, the National University of Singapore and industrial partners.

CARES is guided strategically by a Governing Board comprised of senior representatives from the three partner universities (the University of Cambridge, Nanyang Technological University and the National University of Singapore), from the National Research Foundation and from industry. Scientific oversight is provided by a global Scientific Advisory Board.

The first programme administered by CARES is the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T). The C4T programme is a world-leading partnership between Cambridge and Singapore, set up to tackle the environmentally relevant and complex problem of assessing and reducing the carbon footprint of the integrated petro-chemical plants and electrical network on Jurong Island in Singapore. It brings together researchers from Chemical Engineering, Biotechnology, Chemistry, Biochemistry, Information Engineering, Electrical Engineering, Materials Science and Metallurgy.



The motivation for the C4T project is to integrate materials design and selection (i.e. for adsorbents and catalysts) with advances in process design to achieve improved selectivity and conversion. Such improvements will provide a reduced carbon footprint and energy demand for both established and new processes. Lowering the cost of CO_2 capture, and technologies and strategies for waste heat utilisation are also underlying drivers in the research. The reduction of the carbon footprint from a

wider systems perspective through integration of chemical process related loads within the electrical power network is also addressed.

C4T addresses the complex problem of carbon abatement in chemical technologies by focusing on four fundamental aspects. These four collaborative Interdisciplinary Research Programmes (IRPs) combine state-of-the-art experimental analysis with advanced modelling research from Cambridge and Singapore. Whilst each IRP has clearly-defined milestones and deliverables, denoted as work packages (WPs), there is significant interactions among the IRPs.

- IRP 1: Multi-Scale Studies of Catalytic and Adsorption Technologies (MUSCAT)
- IRP 2: Electrochemical Multi-scale Science, Engineering and Technology (EMSET)
- IRP 3: Carbon Abatement in the Petroleum Refining Industry: A Control and Optimisation Research Network (CAPRICORN)
- IRP 4: Integrated Chemicals and Electrical Systems Operation (ICESO)

2.1 IRP1: 'A Multi-objective Optimization Including Results of Life Cycle Assessment in Developing Bio-renewables-Based Processes'

Daniel Helmdach, Dr Polina Yaseneva, Dr Parminder K. Heer, Artur M. Schweidtmann, Prof Alexei A. Lapkin

DOI: 10.1002/cssc.201700927

Abstract:

A decision support tool has been developed that uses global multiobjective optimization based on 1) the environmental impacts, evaluated within the framework of full life cycle assessment; and 2) process costs, evaluated by using rigorous process models. This approach is particularly useful in developing biorenewable-based energy solutions and chemicals manufacturing, for which multiple criteria must be evaluated and optimization-based decision-making processes are particularly attractive. The framework is demonstrated by using a case study of the conversion of terpenes derived from biowaste feedstocks into reactive intermediates. A two-step chemical conversion/separation sequence was implemented as a rigorous process model and combined with a life cycle model. A life cycle inventory for crude sulfate turpentine was developed, as well as a conceptual process of its separation into pure terpene feedstocks. The performed single- and multiobjective optimizations demonstrate the functionality of the optimization-based process development and illustrate the approach. The most significant advance is the ability to perform multiobjective global optimization, resulting in identification of a region of Pareto-optimal solutions.

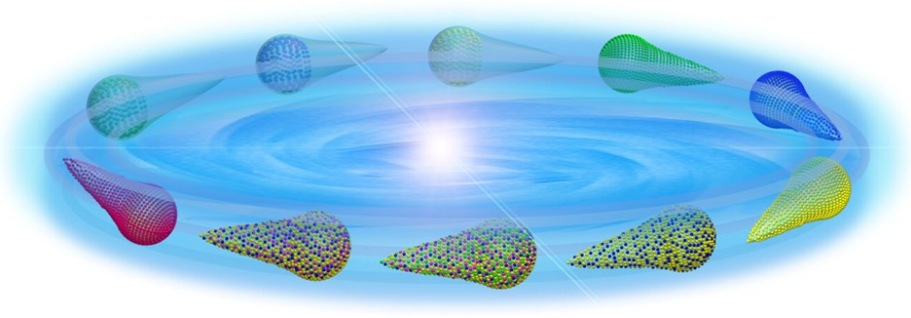
'Smart Nanocatalysts with Streamline Shapes'

Zhan Guo Wu, Zeng Hua Chun

DOI: 10.1021/acscentsci.7b00216

Abstract:

Particulate catalysts with streamline shapes have important impacts on fluid-related reactions, and they need to be properly characterized. However, utilization of streamline-shaped catalysts for heterogeneous catalysis has remained an unexplored area due to the lack of easy-to-use techniques to produce such shaped catalysts, especially at the small length scale of the submicron to micron regime. Herein, we report our recent development of a class of prototype nanocatalysts with streamline shapes. In this research, the kinetic control is adapted to obtain streamline-shaped supports, followed by functionalizing such supports

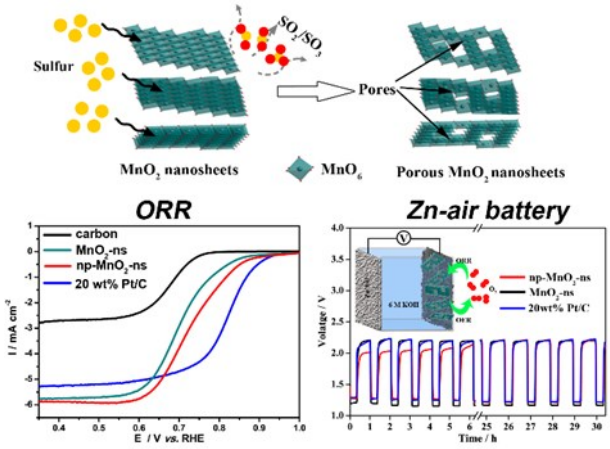


with catalytically active metal nanoclusters (e.g., Au, Pd, Pt, and Ag or their combinations) in a stepwise manner. Advantages related to the streamline morphology of catalysts have been demonstrated with a number of solid–solution systems such as alcohol oxidation, olefin hydrogenation, and Suzuki–Miyaura coupling. We believe these findings will promote new research on the design and synthesis of functional materials with additional fluid-advanced features.

2.2 IRP2: 'Improving the Electrochemical Oxygen Reduction Activity of Manganese Oxide Nanosheets with Sulfurization-Induced Nanopores'

Tianran Zhang, Xiaoming Ge, Zhao Zhang, Nguk Neng Tham, Zhaolin Liu, Adrian Fisher and Jim Yang Lee

DOI: 10.1002/cctc.201701192R1

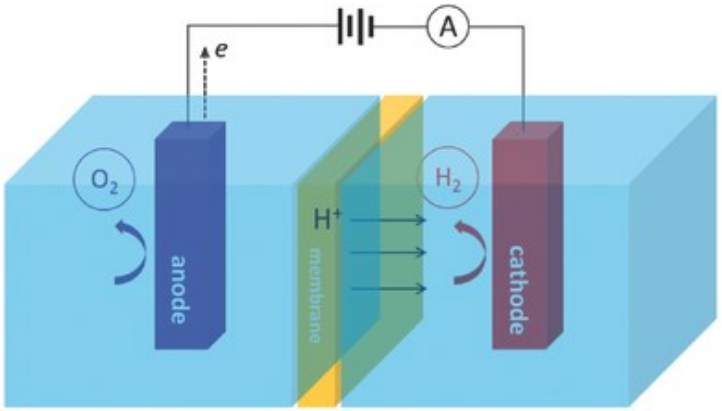


Abstract: Low cost and high activity electrocatalysts for oxygen reduction reaction (ORR) are necessary for the development of fuel cells and metal-air batteries. Manganese oxide would be a good candidate for its low cost, abundant supply and environmental benignity; if not for its relatively low activity compared with the noble metals. To improve the ORR activity of manganese oxide, we developed a sulfurization process to create pores in two-dimensional (2D) manganese oxide nanosheets. The nanoporous MnO_2 nanosheets (np-MnO_2-ns) prepared as such contain 7 nm pores in the nanosheets; and its half-wave potential (0.73V) are 40 mV more positive than pore-free MnO_2 nanosheets (MnO_2-ns, 0.69V). The higher ORR activity of np-MnO_2-ns may be attributed to the combination of a large surface area; and the presence of high ORR activity $Mn^{3+/4+}$ sites. The np-MnO_2-ns also show enhanced OER activity and delivered a good performance in rechargeable Zn-air batteries.

'Recent Methods for the Synthesis of Noble-Metal-Free Hydrogen-Evolution Electrocatalysts: From Nanoscale to Sub-nanoscale'

Jiong Wang, Hua Zhang, Xin Wang

DOI: 10.1002/smtd.201700118



Abstract:

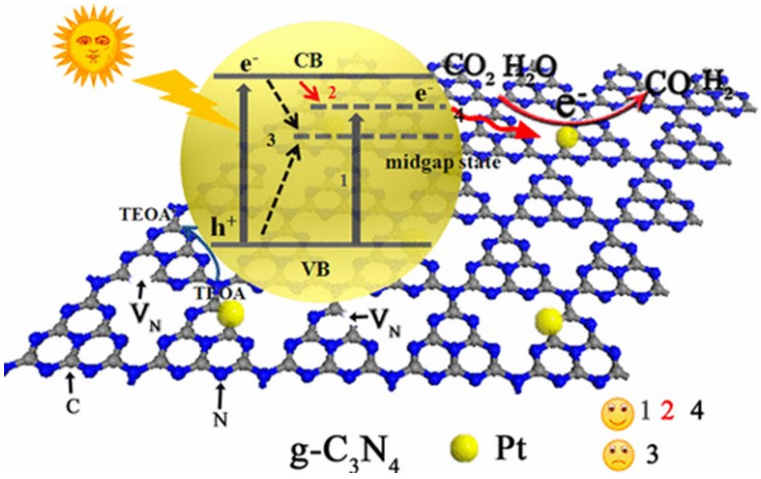
Electrochemical splitting of water into hydrogen is a promising approach for energy conversion and storage. The development of efficient and low-cost electrocatalysts is crucial for realizing the wide application of this technology. Here, recent advances in the synthesis of various electrocatalytic structures toward the hydrogen-evolution reaction (HER) are summarized, centering on several

important examples of nonprecious-metal nanostructures, molecular clusters, and single-atomic/molecular catalysts. The central strategy to achieve high electrocatalytic activity is discussed, namely, maximizing the utilization efficiency of all active sites through downsizing and merging the gap between homogeneous and heterogeneous catalysis. To close, the current challenges and future opportunities are discussed.

2.3 IRP3: 'Investigating the Role of Tunable Nitrogen Vacancies in Graphitic Carbon Nitride Nanosheets for Efficient Visible-Light-Driven H2 Evolution and CO_2 Reduction'

Wenguang, Tu, You, Xu, Jiajia, Wang, Bowei, Zhang, Tianhua, Zhou, Shengming, Yin, Shuyang, Wu, Chnmei, Li, Yizhong, Huang, Yong, Zhou, Zhigang, Zou, John, Robertson, Markus, Kraft, Rong, Xu

Doi:10.1021/acssuschemeng.7b01477



Abstract:

Vacancy engineering, that is, self-doping of vacancy in semiconductors, has become a commonly used strategy to tune the photocatalytic performances. However, there still lacks fundamental understanding of the role of the vacancies in semiconductor materials. Herein, the g-C3N4 nanosheets with tunable nitrogen vacancies are prepared as the photocatalysts for H2 evolution and CO_2 reduction to CO. On the basis of both experimental investigation and DFT calculations, nitrogen vacancies in g-C3N4 induce the formation of midgap states under the conduction band edge. The position of midgap states becomes deeper with the increasing of nitrogen vacancies. The g-C3N4 nanosheets with the optimized density of nitrogen vacancies display about 18 times and 4 times enhancement for H2 evolution and of CO_2 reduction to CO, respectively, as compared to the bulk g-C3N4. This is attributed to the synergistic effects of several factors including (1) nitrogen vacancies cause the excitation of electrons to midgap states below the conduction band edge, which results in extension of the visible light absorption to photons of longer wavelengths (up to 598 nm); (2) the suitable midgap states could trap photogenerated electrons to minimize the recombination loss of photogenerated electron–hole pairs; and (3) nitrogen vacancies lead to uniformly anchored small Pt nanoparticles (1–2 nm) on g-C3N4, and facilitate the electron transfer to Pt. However, the overintroduction of nitrogen vacancies generates deeper midgap states as the recombination centers, which results in deterioration of photocatalytic activities. Our work is expected to provide new insights for fabrication of nanomaterials with suitable vacancies for solar fuel generation.

IRP3: 'Design of Computer Experiments: A Review'

Sushant Garud, Iftekhar A. Karimi, and Markus Kraft

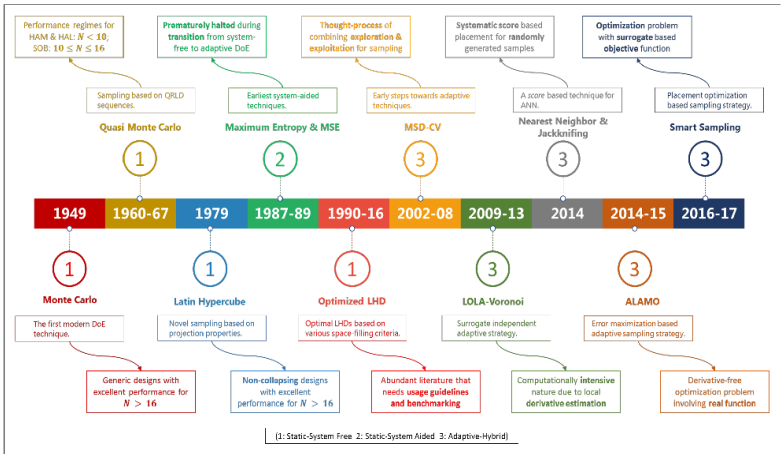
https://doi.org/10.1016/j.compchemeng.2017.05.010

Highlights:

- Modern DoE techniques are comprehensively reviewed.
- A detailed classification and chronological evolution of the modern DoE research is presented.
- Our numerical and visual analyses revealed the excellent high dimensional performance of SOB3.
- Rapidly growing class of adaptive DoE is critically discussed.
- Several potential opportunities for future research in modern DoE are discussed.

Abstract:

In this article, we present a detailed overview of the literature on the design of computer experiments. We classify the existing literature broadly into two categories, viz. static and adaptive design of experiments (DoE). We begin with the abundant literature available on static DoE, its chronological evolution, and its pros and cons. Our discussion naturally points to the challenges that are faced by the static techniques. The adaptive DoE techniques employ intelligent and iterative strategies to address these challenges by combining system knowledge with space-filling for sample placement. We critically analyze the adaptive DoE literature based on the key features of placement strategies. Our numerical and visual analyses of the static DoE techniques reveal the excellent performance of Sobol sampling (SOB3) for higher dimensions; and that of Hammersley (HAM) and Halton (HAL) sampling for lower dimensions. Finally, we provide several potential opportunities for the future modern DoE research.



2.4 IRP4: 'Optimal power flow solutions incorporating stochastic wind and solar power'

Partha, Biswas, Ponnuthurai, Suganthan, Gehan, Amaratunga

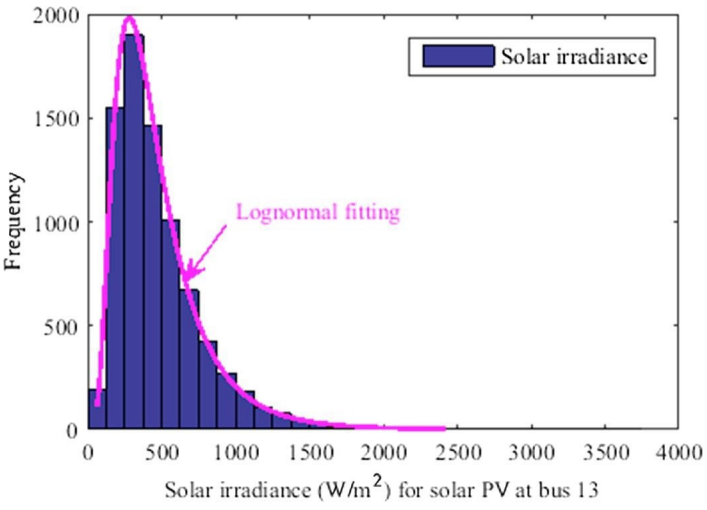
DOI: 10.1016/j.enconman.2017.06.071

Highlights:

- Optimal power flow problem incorporates wind generators and solar photovoltaic.
- Uncertain wind and solar power are appropriately modelled.
- Generation cost is optimized with optimal scheduling of all sources.
- Emission cost is also included in objective function.
- Adaptive differential evolution with proper constraint handling method is applied.

Abstract:

Generations from several sources in an electrical network are to be optimally scheduled for economical and efficient operation of the network. Optimal power flow problem is formulated with all relevant system parameters including generator outputs and solved subsequently to obtain the optimal settings. The network may consist of conventional fossil fuel generators as well as renewable sources like wind power generators and solar photovoltaic. Classical optimal power flow itself is a highly non-linear complex problem with non-linear constraints. Incorporating intermittent nature of solar and wind energy escalates the complexity of the problem. This paper proposes an approach to solve optimal power flow combining stochastic wind and solar power with conventional thermal power generators in the system. Weibull and lognormal probability distribution functions are used for forecasting wind and solar photovoltaic power output respectively. The objective function considers reserve cost for overestimation and penalty cost for underestimation of intermittent renewable sources. Besides, emission factor is also included in objectives of selected case studies. Success history based adaptation technique of differential evolution algorithm is adopted for the optimization problem. To handle various constraints in the problem, superiority of feasible solutions constraint handling technique is integrated with success history based adaptive differential evolution algorithm. The algorithm thus combined and constructed gives optimum results satisfying all network constraints.



2.5 Focus on Impact

In the third of a CARES C4T series of short articles focusing on the potential real world impact of the programme's research, Dr. Quang Thang TRINH (Research Fellow, IRP1, NTU), explores the application of computational catalysis in guiding the design of more efficient catalyst for methane conversion to chemicals and ZHANG Chuan (PhD Student, IRP3, NTU) investigates the importance of waste heat exploitation in future energy systems.

Focus on Impact: Computational design efficient catalyst for non-oxidative coupling of methane

Dr. Quang Thang TRINH received his Bachelor and Master of Science in Chemical Engineering from Hanoi University of Science and Technology, Vietnam in the year 2002 and 2005, respectively. After a few years working as a Lecturer in the School of Chemical Engineering at Hanoi University of Science and Technology, Vietnam, he came to Singapore to pursue and completed his Ph.D. in 2014 from the Department of Chemical Engineering, National University of Singapore. He has worked as a Research Fellow in a group of Prof. Samir H. Mushrif at the School of Chemical and Biomedical Engineering, Nanyang Technological University since 2014 and joined the CARES C4T program in 2016. Dr. TRINH's research interests involve the application of first principle calculations in understanding the properties of nanomaterials, studying the surface chemistry and evaluating catalytic activity of heterogeneous catalysis in methane activation, CO_2 reduction and biomass conversion.

Methane is the main component of many commercially exploitable resources such as natural gas, shale gas and gas hydrates. It has huge potential to become an important feedstock for the synthesis of fuel and value added chemicals. Despite its tremendous potential, methane still remains hugely underutilized. Majority of methane (> 90%) is used to supply heat and electricity via burning, producing lots of CO_2. Current utilization of methane via the conversion to syngas and subsequently to hydrocarbons via Fischer-Tropsch synthesis requires high temperature and pressure conditions and are therefore energy and capital intensive. Direct conversion of methane to chemicals (via non-oxidative coupling, partial oxidation, oxidative coupling) could be more economical and has been studied for decades; however it remains to be a commercial success and the lack of active and selective catalysts is one of the key reasons for it.

Active transition metals (Ru, Pt, Ir, Rh) can activate the very stable C-H σ bonds in methane; however, they are expensive and also lead to the thermodynamically more favourable and undesired deep dehydrogenation of methane to carbon which also deactivates the catalyst. Therefore, there is a strong incentive to find cheaper and more abundant catalysts. Controlling C-H activations is believed to be the most crucial aspect in the design of an effective catalyst for the utilization of methane. To promote the synthesis of C_2 hydrocarbons from methane, the strategy is to activate the first and second C-H bonds, while suppressing further dehydrogenation to preserve the precursors of the coupling reaction. Several recent success stories have been reported on Science and Nature journals, substantiating this strategy. However, experimental monitoring and tuning those elementary steps on heterogeneous catalyst is very challenging.

First principles calculations provide powerful tools to study and design heterogeneous catalysts, especially for complicated, multi-step reactions. The typical scale to study catalytic reactions is the molecular scale, which is difficult to access experimentally. First principles based molecular modelling on the other hand is best placed to investigate molecular level effects and can greatly help to guide and validate the chemical intuition on the molecular scale. Our recent works on the design of Oxygen reduction reaction catalyst, the investigation on the solvent effect during the conversion of fructose to 5-hydroxymethyl-furfural, the understanding of the adsorption and reaction of aldoses sugars on transition metals surface or the insights into the selective oxidation of glucose to gluconic acid on CuO catalyst… illustrate how first principles based modelling is able to shed light into the mechanism and guide the design of heterogeneous catalysts with improved activity, selectivity and stability. In CARES, we are applying computational simulations in guiding the design of more efficient catalyst for methane non-oxidative coupling reaction. Recently, we have succeed in employing density functional theory calculations to evaluate the structure and activity of the novel boron

doped Cu catalyst (called B-Cu) in methane activation and conversion follow the above-mentioned strategy. Our comprehensive study has been able to (i) elucidate the most stable microstructure of the catalyst, (ii) investigate the activity and selectivity of the catalyst and (iii) explain the role of boron in altering the activity and selectivity. Our calculations suggest that, unlike the conventional Cu catalyst, methane would not undergo complete dehydrogenation to produce carbon on the B-Cu catalyst and that high selectivity towards the formation of ethylene is expected. Our claims about the high selectivity of ethylene on the proposed novel catalyst are also substantiated by the fact that kinetic barriers and reaction free energies computed for the novel B-Cu catalyst proposed in this work are very similar to those computed for the *state of the art* iron based and palladium based catalysts, which have experimentally demonstrated high selectivity towards ethylene. This example illustrates the ability of computational catalysis in providing a framework to guide either the design of catalysts or reaction conditions to help advance our command over this fiendishly difficult problem. It is also applicable to design catalyst for other processes to reduce the CO_2 footprint, e.g water splitting, CO_2 methanation and biomass conversion.

Chuan Zhang a PhD student in IRP3 under the supervision of Prof Alessandro Romagnoli and Prof Markus Kraft. He got his master degree of Mechanical Engineering from Shanghai Jiao Tong University China in 2012 before joining CARES. His current work in CARES is mainly about thermal energy management of eco-industry park. This work includes modelling and optimization of various waste heat recovery technologies, semantic representation and ontology design of simulation models, intelligent system development.

Focus on Impact: The importance of waste heat exploitation in future energy systems

Most of the time, when people talk about energy, they take it for granted that energy is electricity, which obviously is not true. Although electrification is becoming the fashion for primary energy utilization, whereas direct conversion of primary energy, particularly fossil fuel, into heat still plays an important role in current energy system. Indeed, International Energy Agency reports that 50% of final energy consumption globally is used in the production of heat. For such heat-oriented utilization, Waste Heat Recovery (WHR) is always an interesting issue. Waste heat refers to the energy that is generated without being put to practical use and WHR is the process of capturing heat discarded by existing process and convert the heat into a productive end-use. In practice waste heat are generated by kilns, furnaces, ovens, turbines, engines, and other equipment. It is estimated that from the total industrial energy consumption, approximately 20–50% of energy consumption is being discharged as waste heat. Given such huge potential, waste heat as an important energy source, should be valorised in existing and future energy systems.

Recovering waste heat can be achieved via numerous methods, the most common technologies are Waste Heat to Power (WHP) and waste heat to thermal energy. Waste heat to thermal energy use (district heating, combustion air preheater etc.) would always be the most economical and efficient way of using waste heat, where possible. However, most waste heat cannot be used for thermal use due to no localized heating or cooling requirements at the waste heat site; hence the use of WHP technologies to either use the electricity onsite or distributing it through the grid becomes a more popular solution. WHP technologies have two mechanism: power generation via mechanical work or via direct electricity conversion. Common technologies for power generation via mechanical work include steam Rankine cycle, organic Rankine cycle and turbo compounding; whereas direct electricity conversion includes thermoelectric generation, piezoelectric generation and thermionic generation. The selection of WHR technologies will depend on key factors such as the temperature, phase, and chemical composition of the exhaust stream, as well as the nature of the desired end-use for recovered heat.

Another important issue when talking about WHR is the quantification of waste heat potential. To give some figures, the industrial waste heat from USA, China, Germany, and UK are 13 billion GJ/year, 7.6 billion GJ/year, 313 million GJ/year, and 386 million GJ/year respectively. Out of such amount of waste heat, it is estimated that around 5000MW and 4000MW electricity can be harvested in the case of US and China respectively. Moreover, the Levelized Cost of Electricity (LCOE) of WHP technologies are usually much lower than conventional and renewable power generation.

To summarize, improving energy efficiency by focusing on waste heat exploitation is definitely one pressing issues to tackle. We believe that through synergistic cooperation of energy researchers, we are going to find solutions in sufficient time to make full use of our waste heat in the future energy landscape.

ZHANG Shengliang (PhD Student, NUS, IRP2) has graduated from Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences in 2015.. His research interest: Tunable Plasmonic Semiconductor Nanocrystals for Smart Windows

2.6 Focus on Fundamental Science: What are electronic smart windows?

Smart windows can dynamically control the transmittance of solar irradiation into buildings by switching reversibly between a transparent state and a blocking state. They have emerged as a viable technology to reduce building energy consumption for heating, ventilation, and air conditioning (HVAC), while providing glare reduction, unobstructed views, and natural daylighting.[1] Currently, As much as 30 to 40% of the primary energy supply in the world are spent in buildings for HVAC and lighting. A large fraction of this energy is wasted simply because most building fenestration technologies are either not energy efficient or not adaptable to dynamic climates. Smart windows can tune the transmittance of sunlight to provide variable solar heating and daylight according to the changing weather and personal preferences; as one of the elements of energy-efficient buildings. Previous simulation studies have shown that smart windows can reduce a building's energy needs by up to 40% relative to static windows.[2] In addition, there is a large market potential for smart windows because millions of square feet of windows are installed annually in the world.

Smart windows may be classified into three main categories based on their underlying operating principles: electrochromic, photochromic and thermochromic windows. Electrochromic windows change transmittance upon an externally applied voltage, while photochromic and thermochromic windows respond to environmental stimuli by altering their transmittance with the change of light intensity and temperature, respectively. Among them, electrochromic windows are the most versatile because they provide dynamic modulations over a broad spectral range, and can be user controlled to meet personal preferences. By comparison photochromic and thermochromic windows cannot be user controlled since their response are entirely dependent on the environment.

Electrochromism refers to the special functionality of materials whose optical properties can be reversibly and persistently changed by the application of a small electric field. Generally, electrochromic smart windows have a multilayer structure consisting of an active electrochromic electrode layer, a counter electrode layer, an electrolyte layer separating the two electrodes, and two transparent conducting layers serving as the electrical leads and supporting substrates. The electrochromic materials are the most critical component in the electrochromic windows. Many inorganic and organic materials are electrochromically active, such as transition metal oxides (WO_3, MoO_3, V_2O_5, TiO_2, Nb_2O_5), Prussian blue, viologens, conducting polymers, just to name a few.[3] Among them, tungsten oxide (WO_3) has been investigated the most extensively. It is identified as one of the most promising inorganic electrochromic materials based on its high optical modulation, fast switching time, and high reversibility and coloration efficiency. WO_3 is a periodic structure consisting of edge- and corner-sharing WO_6 octahedral; with open tunnels of interstitial sites which facilitate ionic motion and intercalation. When WO_3 is cathodically charged, the intercalated cations (H^+, Li^+, Na^+) are charge compensated by the injected electrons, reducing the tungsten cations from W^{6+} to W^{5+}. Concurrently, the material changes from a clear, transparent state to a dark blue color. Although the coloration mechanism is not fully understood, it is widely accepted that the optical absorption is attributed to the intervalance charge transfer from W^{5+} to W^{6+} sites for amorphous WO_3, and intraband transitions in the case of crystalline WO_3.

An ideal smart window which is universally applicable across building types and climate zones, should be able to independently control the transmittance of visible sunlight and solar heat into a building. These two parameters directly affect a building's energy use and influence occupant comfort. For this reason, independent control of the visible and near-infrared (NIR) regions of the solar spectrum is a key target for next-generation advanced electrochromic devices, and would contribute to optimize the energy efficiency across a building's heating, cooling, and artificial lighting systems. Unfortunately, most of the current electrochromic smart windows cannot selectively control the visible light and NIR. In most of the instances both spectral responses are simultaneously blocked. In 2013, the Millrion group[4] reported a breakthrough in spectrally-selective electrochromic smart windows, where a ITO-NbO_x composite was used to dynamically and selectively control the visible light and NIR response. At a low cathodic voltage, the localized surface plasmon resonance (LSPR) of the ITO phase is modulated for the NIR response. When the composite is charged further, the NbO_x phase is reduced to yield a polaronic electrochromic response that modulates visible light transmittance. The dual-band electrochromic smart windows are still in an early stage of development, and are beset with the following issues: (1) complexity of composite preparation; (2) low optical modulations in visible light (400-780nm) and NIR (780-1300nm); (3) a slow switching kinetics.

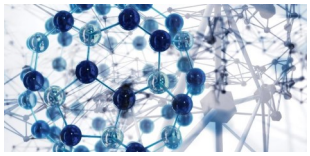
Our project on "Tunable Plasmonic Semiconductor Nanocrystals for Spectrally-Selective Electrochromic Smart Windows" is an attempt at the resolution of these issues. We aim to nano-engineer selected semiconductor nanocrystals (e.g. tungsten oxide, tungsten bronze and doped titanium dioxide) by simple methodologies, and apply them for dual-band electrochromic smart windows to improve their native electrochromic performance. We target the use of single-component materials (instead of composites) for the dynamic and selective modulation of NIR and visible light, by combining LSPR-based NIR electrochromism and polaron-based visible electrochromism in one material.

1. Granqvist, C. G. Electrochromics for smart windows: Oxide-based thin films and devices. *Thin Solid Films* 2014, 564, 1-38.

2. Wang, Y.; Runnerstrom, E. L.; Milliron, D. J. Switchable Materials for Smart Windows. In *Annual Review of Chemical and Biomolecular Engineering, Vol 7*, Prausnitz, J. M., Ed. 2016; Vol. 7, pp 283-304.

3. Runnerstrom, E. L.; Llordés, A.; Lounis, S. D.; Milliron, D. J. Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals. *Chem. Commun.* 2014, 50, 10555-10572.

4. Llordés, A.; Garcia, G.; Gazquez, J.; Milliron, D. J. Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites. *Nature* 2013, 500, 323.



3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

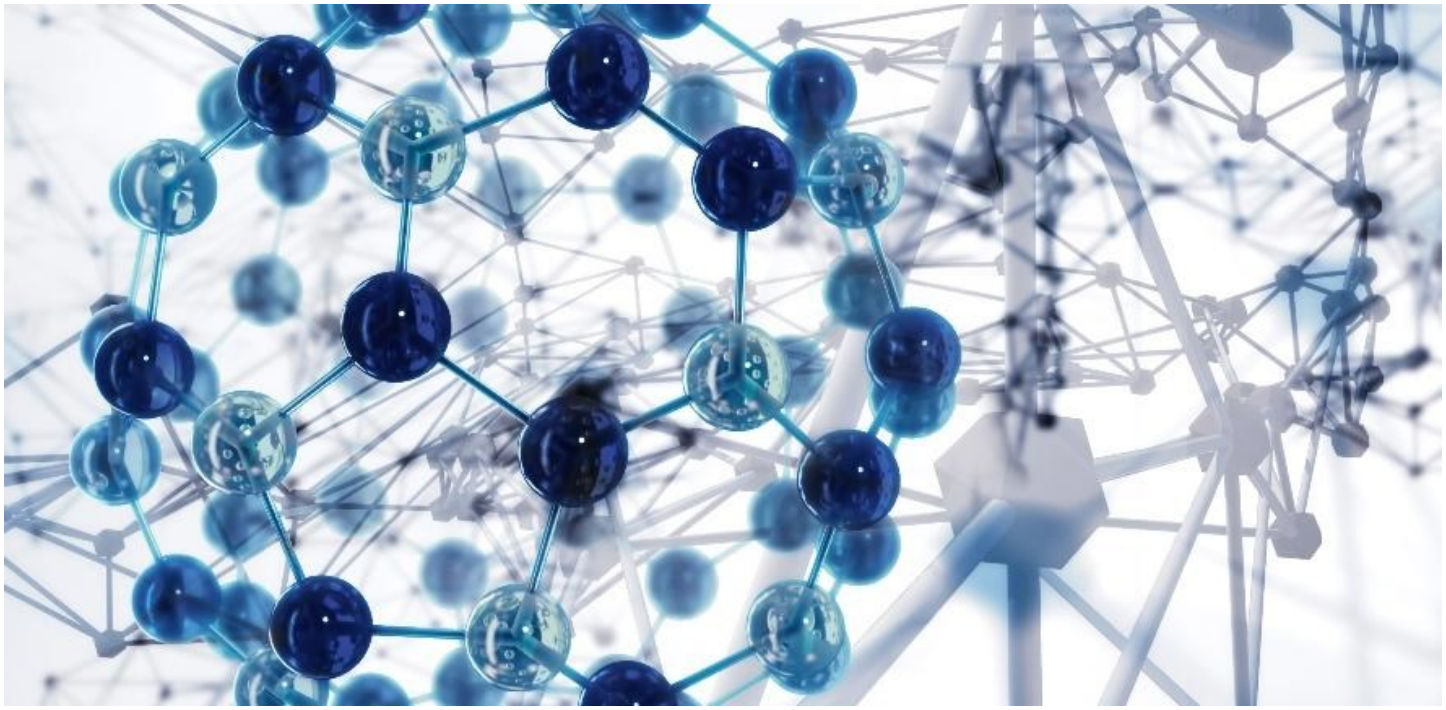
Electrochemical Multi-scale Science, Engineering and Technology

3.3 IRP3 — CAPRICORN

Carbon Abatement in the Petroleum Refining Industry: A Control and Optimisation Research Network

3.4 IRP4 — ICESO

Integrated Chemicals and Electrical Systems Operation



MUSCAT seeks to extend existing expertise in reaction engineering, multi-scale imaging and modelling to reduce the carbon footprint and energy demand of existing chemical processes by making catalytic and separation processes more efficient as well as by introducing enhanced CO_2 capture strategies into existing processes. The aim is to tackle a range of problems relevant to industry in Singapore and to investigate solutions with the potential to have short- and long-term deliverables that improve the economic and environmental performance of both existing and new processes

MUSCAT is led by PIs:

Prof Alexei LAPKIN (Cambridge)

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

Prof. Alexei Lapkin,

University of Cambridge

PI, IRP1

October 2017

3.1.1 IRP1 Research Overview

IRP1 project is working on de-carbonysation of chemical industry through substitution of feedstocks and better energy efficiency of the chemical processes. The project is based on the hypothesis of better control of selectivity of catalytic reactions by nano-structuring of heterogeneous catalysts, and translation of the novel catalysts into energy-efficient advanced processes.

The work-packages currently in progress:

- Chemical looping with advanced oxide carriers
- CO_2 methanation and biomass conversion
- New materials and MOFs
- Multi-scale modelling
- Fundamentals of adsorption and PSA

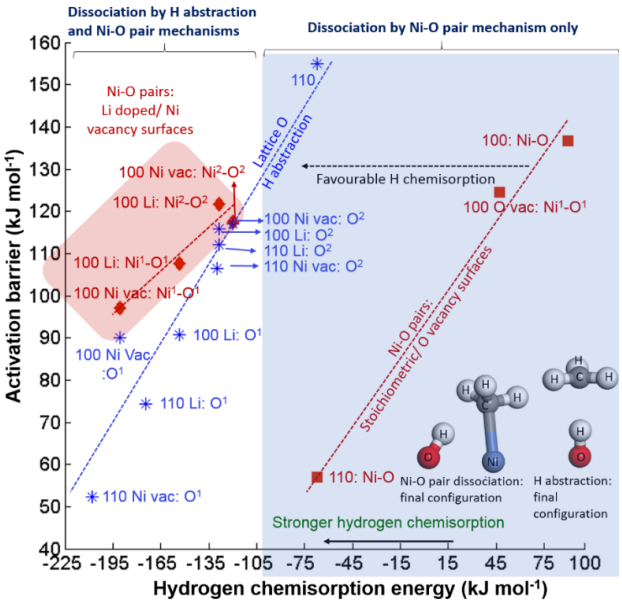
Over the reporting period between May - October 2017 IRP1 reported innovated streamlined shape catalytic nanoparticles, developed in the group of Prof. Hua Chun Zeng (NUS), which offer many new opportunities for developing novel catalytic processes. The group has also reported the methodology for structuring of metal nanoparticle-based catalysts, resulting in multi-functional catalysts, protecting nanoparticles from sintering as well as providing the required reactant's residence time near the catalytic sites. Among other achievements within IRP1 over this period the group in Cambridge has published the methodology for multi-objective optimisation of processes, targeting the economic and environmental optimum sweet-spot for complex processes. The IPR1 group has reported good progress in the integrated project on bio-waste conversion: in this project the experimental programme is guided by results of theoretical predictions of catalysts behaviour at DFT level of theory; the project is entering a new phase when detailed data on interaction of catalysts with solvents will be obtained with the help of magnetic resonance imaging, done in Cambridge in the group of Prof. Gladden. During this period IRP1 held its research seminar day where all researchers have presented their updates and plans for future work. This was an exciting day of scientific exchange and discussion, which IRP1 will repeat early in 2018.

3.1.2 Update on work packages

WP 1.1: Chemical looping with advanced oxide carriers

CAO Li Wei's (RA, NTU, IRP1) work focused on developing a more sustainable society and to reduce carbon dioxide emission therefore the glycerol hydrogenolysis reaction has been investigated in detail. Since glycerol is one of the most important building blocks in the biorefinery feedstock and 1,3-propandiol is a high value-added chemical, the development of an efficient conversion process of glycerol into 1,3-propanediol will make the biodiesel process more profitable. The reaction was conducted under different reaction condition as well as through catalyst with different synthesis method. By collaborating with Dr Jithin VARGHESE (RF, NTU, IRP1), a mechanism study of the reaction was been done based on density functional theory.

Jijiang HUANG (PhD Student, NTU, IRP3) reported that Ni-Fe redox catalysts were developed via a co-precipitation method for the application of chemical looping steam reforming of CH_4. High CH_4 conversion and selectivity to syngas were achieved with binary Ni-Fe catalysts compared with the single Ni- or Fe-based counterparts. It was found that carbon deposition from catalytic CH_4 decomposition on the catalysts during the reduction stage played an important role in the conversion of CH_4. The effects of reaction temperature and O_2 oxidation on the performance were investigated, finding that the production of syngas increased with higher temperature for the binary Ni-Fe redox catalysts and the selectivity to syngas can be further improved in the absence of O_2 oxidation. In addition, co-feeding reforming of CH_4 and steam was performed to compare the performance with looping reforming. It was found that Ni-rich catalysts were reactive and suitable for hydrogen production from co-feeding reforming, while looping reforming was more selective for syngas than co-feeding reforming due to the reduced CO_2 production. This project highlighted the binary Ni-Fe redox catalysts for selective syngas production from chemical looping steam reforming of CH_4 coupled with catalytic decomposition.



Activation barriers for the dissociation of methane on different nickel-oxygen pairs and different oxygen sites on stoichiometric, vacancy defect and Li dopant containing NiO 100) and NiO(110) surfaces as a function of the hydrogen chemisorption strength on the corresponding lattice oxygen sites, showing the linear correlation between these quantities.

Dr Jithin John VARGHESE (RF, NTU, IRP1) reported on his research work on C-H bond activation mechanisms and energetics on vacancy defects and dopant containing nickel oxide (NiO) and a benchmarking study of the Hubbard U parameter to be used for simulating surface phenomena on metal oxides like copper oxide (CuO) and nickel oxide (NiO).

C-H activation on NiO surfaces:

The increase in surface reactivity and surface reducibility due to presence of surface Ni vacancies and low valent do-

pants like Li due to increase in the intrinsic activity of the surface lattice oxygen near the vacancy and dopant are presented and explained. The lower activation barriers for C-H dissociation and the changes in the C-H dissociation mechanism as a function of the chemisorption strength of hydrogen on the NiO surfaces, a descriptor for reactivity of the surfaces, is presented. Doping with low valent metals like Li is proposed as a tool to alter the surface reactivity and reducibility, the extent of which can be ascertained using the hydrogen chemisorption energy.

Benchmarking of Hubbard U parameter for CuO and NiO: Contributed to the combined theoretical and experimental investigation on the appropriate Hubbard U parameter to be used for simulating surface reactions on copper oxide (CuO). It was shown that the commonly used U-value of 7 eV (fitted against CuO bulk properties) overestimates the adsorption enthalpies by 20-40 kJ mol^{-1}. The U-value between 4.5-5.5 eV correctly predicts the adsorption of H_2 on CuO.

A similar investigation of the parameter for Nickel oxide is under progress.

WP 1.2: CO_2 methanation and biomass conversion

Production of terpene-based intermediates from industrial waste feedstocks: integrated environmental assessment and process modelling study

Dr Polina YASENEVA (RF, CAM, IRP1) reported that as a continuation of exploration of potential feedstocks for terpene-based intermediates, two more routes are to be explored: conversion of wood chips to β-pinene and crude sulphated turpentine (CST) to β-pinene. The issue with the production of materials from readily available bio-feedstocks such as wood chips and wood pulp is how to decide upon the optimal process route. A systematic methodology analysing the sustainability of different processes by performing a life-cycle assessment will be able to quantify impacts to help pick the best route.

A process exists whereby paracetamol is produced from transformation of terpenes via intermediates. The purpose of this project is to build a process model and life-cycle assessment for the extraction and separation of different terpenes from wood chips produced by the Norske Skog paper mill.

The principal desired product is β-pinene. A hot water extraction process is used, and the resulting wood extract composition has been provided by Monash University, Australia. A series of decanters and distillation columns has been developed on Aspen Plus.

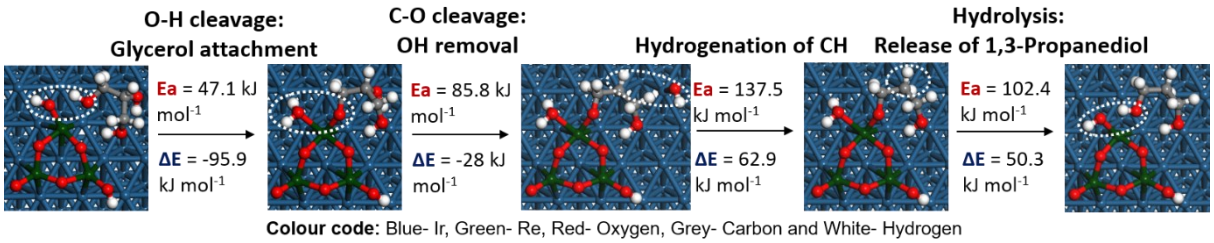
The wood extract is separated into various terpenes; d-limonene, α-pinene and β-pinene. . A Life Cycle Assessment (LCA) model is developed on Umberto. The section developed considers the raw material production of wood up the purification of terpenes.

Dr Jithin John VARGHESE (RF, NTU, IRP1) carried out an investigation of the aqueous phase catalytic hydrogenolysis of glycerol to 1,3-Propane diol (1,3-PDO) using supported Ir/ ReO_x catalyst system.

Glycerol hydrogenolysis to 1,3-Propane diol: Mechanisms for conversion of glycerol to 1,3-PDO and 1,2-PDO have been investigated on clean and ReOx modified Ir(111) surfaces. The preferential attachment of glycerol on the ReOx clusters through its primary hydroxyl groups, the ability of ReOx to facilitate selective C-O cleavage of glycerol (secondary OH), the supply of active hydrogen by the Ir(111) surface, together contributing to the observed higher yield of 1,3-PDO has been demonstrated. Experimental and computational investigations to understand the solvent effect on the conver-

sion and product selectivity are under progress.

Schematic representation of the elementary steps in the transformation of glycerol to 1,3-Propane diol on Re_3O_6



modified Ir(111) catalyst with energetics of each step.

Dr Jithin John VARGHESE (RF, NTU, IRP1) Provided quantitative inputs on the CO_2 elimination/ reduction potential of research projects undertaken by IRP1 in Phase 1 and the CO_2 reduction potential of the research projects proposed by IRP1 in Phase 2 of the C4T program. Provided inputs on the inter-IRP synergies and specific examples of potential collaboration of IRP1 with all the other IRPs during Phase 2 of C4T program.

Dr Yong YAN (RF, NTU, IRP1) reported on his research outcomes. Noble metal based catalyst is more favored for CO_2 metahantion due to the impeccable stability if compared to the Ni-based catalysts with a comparable activity but much lower cost, which is sensitive to metal sintering and coke deposition. Nonetheless, a question on the stability of noble metal catalyst has been raised recently. Dr Yong YAN (RF, NTU, IRP1) and research colleagues observed the disintegration of Ru particles supported on Al_2O_3 as a result of the formation of new Ru-O-Al interface, which was in contrary to the well-established sintering of metal particles that also resulted in deactivation. Unlike the metal sintering which caused the loss of active sites, the disintegration of metal particles led to a drastic change in particle structures as more under-coordinated sites were exposed, which favored the selective formation of CO other than CH_4 for CO_2 hydrogenation at atmospheric pressure. The disintegration of Ru particles was much pronounced on Ru/Al_2O_3 with 1-2 metal loadings, over which a higher concentration of Ru monolayers has been identified, if compared to the exclusive formation of 3D particles over Ru/Al_2O_3 at higher loadings.

Dr YANG Shiliang (RF, NTU, IRP1) reported on his work. The knowledge of the granular segregation phenomenon induced by size or density differences in the ubiquitous polydisperse systems is important for the chemical industry, hence numerous studies have focused on this for the simple yet practical rotating drum. However, in view of the distinctly different characteristics of the two regions (namely, active and passive) for a drum operated in the rolling regime, an understanding of the segregation dynamics in each region is warranted, but remains a gap to date. Accordingly, Dr. Shiliang YANG (RF, NTU, IRP1) has numerically studied the segregation dynamics of the solid phase in a three-dimensional rotating drum consisting of a binary-size mixture via the Discrete Element Method (DEM). The results demonstrate that the total kinetic energy, the angle of repose, the time-averaged streamwise (i.e., parallel to the bed surface) velocity and the position of the active-passive interface are global parameters, which are not influenced by size-segregation and thereby provides a critical basis for comparing different systems of various polydispersities.

In addition, the quick onset of the rapid radial segregation leads to sharp initial changes of the varia-

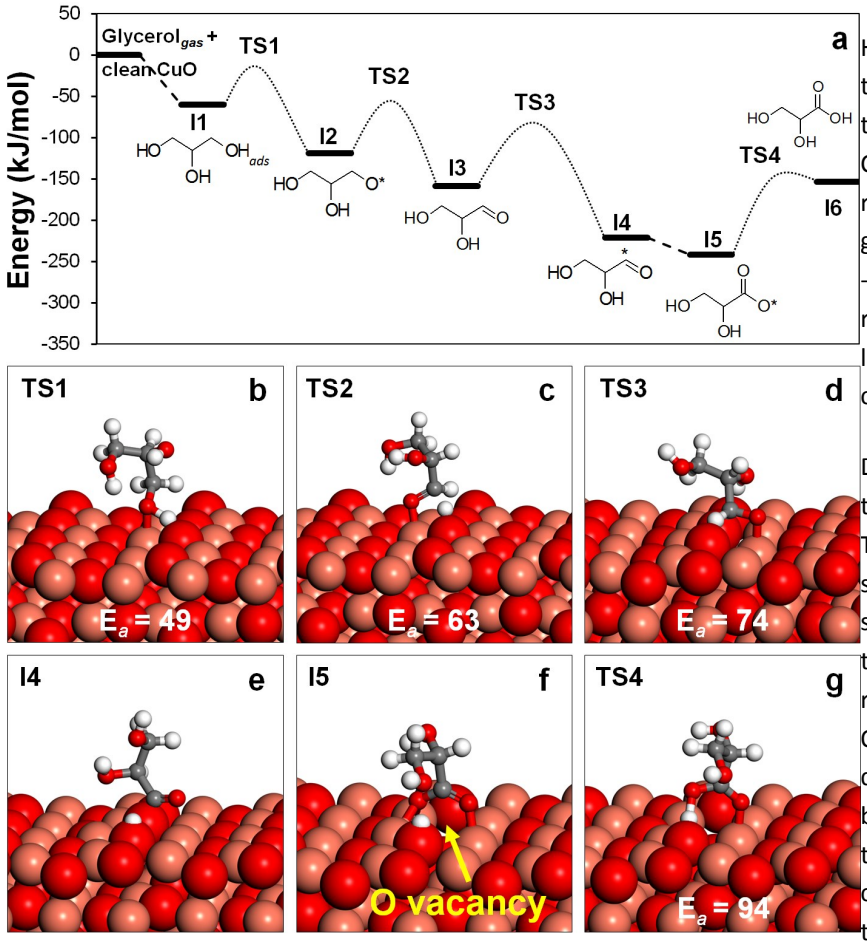
bles associated with the two particle types, after which the slow axial segregation leads to a gradual change of these variables over time. Furthermore, size-segregation leads to the redistribution of the particle number of the two particle types in the active and passive regions. Relative to the monodisperse system, the collision forces exerted on the small and large particles are slightly higher and lower, respectively. The results here provide important insights on the dynamics associated with the inevitable segregation phenomenon, which contributes to better operation and predictive capability of the rotating drum.

Dr YANG Shiliang (RF, NTU, IRP1) highlighted that segregation dynamics of granular mixture was studied via DEM, global parameters independent of size-segregation were also identified, size-segregation redistributes the solid loading in the active and passive regions and slow axial segregation leads to a gradual change of related variables over time.

Chunmiao JIA (PhD Student, NTU, IRP1) reported on the fluidization modelling for CO_2 methanation over NiMgW catalyst was conducted. We did the experiments on the fixed bed to get the kinetics data, and obtained the relations for the reaction rate and partial pressure of feed gas through the nonlinear regression method. Using the two-phase model and the kinetics data, the fluidization modelling gave the concentration of each component in both phases along the fluidized bed.

Dr. Quang Thang TRINH (RF, NTU, IRP1) under the supervision of Prof. Samir H. MUSHRIF (Co-PI, NTU, IRP3) performed Density Functional Theory (DFT) calculations to investigate the mechanistic insight of glycerol activation on CuO nanoleaves morphology and the synergistic role of Hydrogen peroxide in assisting the selective oxidation of glycerol to dicarboxylic acids. Glycerol utilization has been considered a major bottleneck in the sustainable production of bio-diesel as a fuel. Hence, the upgrading and chemical transformation of glycerol to value added chemicals is mandatory not only because it results in a positive economic relief, but also because it serves as a means to mitigate the waste, leading to sustainability.

A number of homogeneous and heterogeneous catalysts have been investigated to convert glycerol to value-added chemicals. Glyceric acids, lactic acid, propanediols, dihydroxyacetone, acrolein, among others are classical examples of potential chemicals to be obtained via glycerol upgrading. However, the conversion of glycerol to dicarboxylic acids, particularly oxalic (OXA) and tartronic acids (TAR), has been less thoroughly investigated despite their numerous applications. Beside their promising utilization in the synthesis of renewable polymers, these two dicarboxylic acids are also employed for the extraction of rare earths from monazite, celluloid production, leather manufacturing and for the synthesis of pharmaceutical intermediates. In our study, the synthesis of copper (II) oxide (CuO) with leaf-like morphology has been achieved under low frequency ultrasound irradiation (19.95 kHz) within less than 30 min, without the use of any template or surfactant. The advantages of the reported synthesis route are: (i) No calcination or post catalyst treatment required. (ii) Fast, green and scalable method (iii) lesser synthesis time (< 30 min). The catalyst morphology was ascertained by SEM and TEM analysis, and further characterized by XPS, XRD and BET. As-synthesized CuO nanoleaves were used in the conversion of glycerol with the presence of H_2O_2 and the yields of oxalic acid and tartronic acid of 56 % and 22 %, respectively were obtained. Density Functional Theory (DFT) calculations were employed to gain insights into the mechanism of glycerol oxidation on the CuO surface. Glycerol is initially activated via the deprotonation of the terminal



Hydroxyl, and subsequently undergoes C-H activation to form glyceraldehyde. These steps are facilitated by the unsaturated surface lattice O_3 site on CuO surface with barriers of 43 and 59 kJ/mol, respectively. The oxidation of glyceraldehyde to glyceric acid requires the activation of the formyl C -H bond with barrier of 74 kJ/mol and the incorporation of the lattice oxygen into glyceric acid, similarly to our reported mechanism of glucose to gluconic acid on CuO.

Due to the symmetric structure of glycerol, both terminal CH_2OH groups could be oxidized to form Tartronic acid, as observed in experimental results. C-C cleavages were also studied and the results revealed that after glyceric acid is formed, the C-C dissociation can occur with activation barrier of 58 kJ/mol, resulting in the precursors for Oxalic acid and C_1 species. However, H atoms produced from O-H and C-H activations are strongly bound on surface lattice O_3 sites, hence block those active sites on CuO. Secondly, Oxygen vacancy generated during the reaction, would result in the reducing CuO to Cu. DFT calculation revealed that H_2O_2 could refill the oxygen vacancies generated during the reaction, resulting into the excellent stability of the catalyst. More interestingly, the surface adsorbed Hydroxyl originating from H_2O_2 can remove H atoms on lattice O_3 site (forming water) and regenerate active sites to increase glycerol conversion. Most importantly, the presence of surface OH opens an alternate reaction pathway with lower activation barriers that does not require the incorporation of lattice Oxygen into the product. The participation of surface OH (from H_2O_2) into the reaction results in excellent glycerol conversion and high catalyst stability. The paper based on those results has been submitted and the abstract of this work has been accepted for oral presentation at the coming 2017 AIChE Annual meeting.

WP 1.3: New materials and MOFs

Flow synthesis and characterization of hydrotalcites materials

Dr Polina YASENEVA (RF, CAM, IRP1) reported that more fundamental characterisation of hydrotalcites materials aged at different temperatures has been done: TGA, in situ Raman and TEM. The results of these characterisations revealed that temperature of treatment greatly influences the morphology and thermal stability of samples under study. These parameters are also greatly affected by the chemical composition of HTs. Thus in general thermal stability of HTs diminishes significantly with the increase of treatment temperature and correlates with particle sizes and porous

structure of the samples under study. As thermal decomposition profile shows how hydrotalcite structure decompose to mixed oxides and consequently to spinel phase it gives us an understanding on the best calcination temperature in order to obtain best basic properties of HT-derived oxides. This work is being finalised for publication and will be submitted by the end of this year.

Nicholas Antonio JOSE (PhD Student, CAM, IRP1) reported on his PhD project which focuses on the development of technologies to improve the design and synthesis of catalysts and adsorbents.

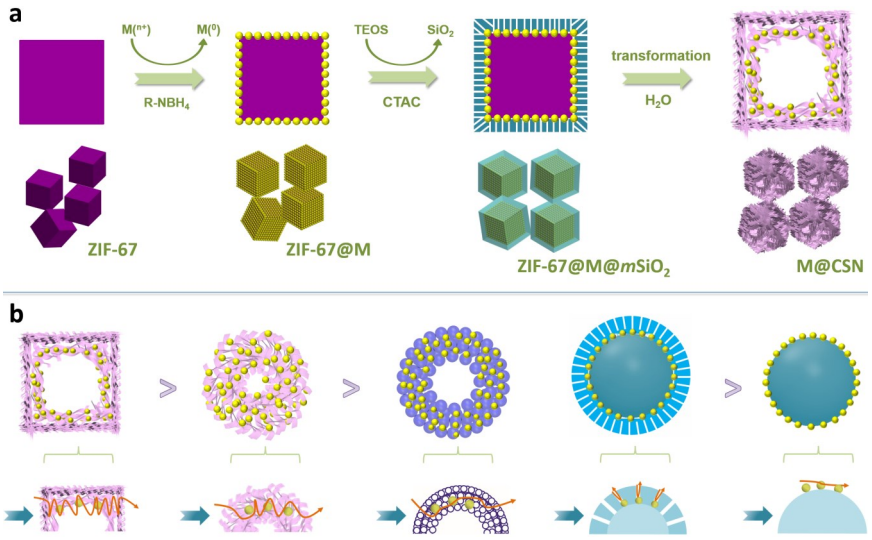
The role of hydrodynamic shear in the coprecipitation of layered double hydroxides (LDH) in a high shear microreactor was studied extensively. Shear forces can be used to tailor the aspect ratio and crystallite size of LDH nanostructures. *In situ* studies of reactor fluid dynamics using high speed confocal microscopy revealed that mixing dynamics were controlled by turbulent flow at the microscale. Liquid TEM studies revealed that LDH particles grow in a nonclassical mechanism called oriented attachment, which can be accelerated by flow. These studies provide much needed insights into how exactly LDH forms during coprecipitation, and will aid the precise and scalable synthesis of nanocatalysts. Future studies involve partnering with others in CARES who utilize LDH-based materials to evaluate the performance enhancement these materials may have. Different material systems, such as metal-organic frameworks, will also be explored.

Prof Hua Chun ZENG's (PI, NUS, IRP1) research group reported on their research activities.

Dr Ping LI (RF, NUS, IRP1) reported on supported Pt-based alloy nanocatalysts for CO_2 hydrogenation. Carbon dioxide (CO_2) is one of the major components of greenhouse gases. To reduce its emission and at the same time to utilize it, the chemical transformation of CO_2 to fuels is particularly attractive. On the other hand, layered double hydroxides (LDH) are a class of economical anionic clay compounds, consisting of positively charged brucite-like host layers, and exchangeable anions situated in the interlayer space to balance the positive charges of host layers. Considering their unique compositional and structural flexibility, LDH can serve as a class of desirable support materials. In this study, by using LDH as the support/precursor, we have developed a variety of nanostructured catalysts for CO_2 hydrogenation to C1 compounds.

- Hierarchically structured MgAl-LDH spheres were firstly fabricated via a one-pot solvothermal method. Then the 2D confined amorphous Prussian-Blue-like cyanide bridged transition metal coordination polymer was generated in the gallery space of LDH through combination of intercalation chemistry and coordination chemistry. After thermal reduction under hydrogen atmosphere, MgAl-LDO supported multimetallic alloy NPs can be obtained. In this project, we have prepared MgAl-LDO supported CoPt alloy NPs and NiPt alloy NPs for CO_2 hydrogenation. Besides, MgAl-LDO supported monometallic Pt NPs was also prepared as a control sample. Regarding their catalytic performance, the MgAl-LDO supported CoPt alloy NPs exhibit excellent activity and outstanding CO product selectivity.
- Hierarchically structured trimetallic CoMgAl-LDH spheres were firstly generated via a simple solvothermal route. Then through facile adsorption of Pt salt followed with hydrogen reduction, MgAl-LDO supported CoPt bimetallic NPs have been obtained. This catalytic nanocomposite displays decent CO_2 conversion and excellent CO product selectivity in the CO_2 hydrogenation.

Dr Guowu ZHAN (RF, NUS, IRP1, NUS) reported on CO_2 hydrogenation to produce useful C1 chemicals (such as CO, CH_4 and CH_3OH) plays a pivotal role in future energy conversion and storage, in which catalysts lie at the heart. However, our fundamental understanding of the correlation between catalyst structures and product selectivity is still limited, due to that in most cases the catalyst structures in nanoscale are not well-defined. Therefore, he reported the design and synthesis of nanoreactors by phase transformations of sandwich-structured ZIF-67@Pt@mSiO_2 nanocubes via a simple water soaking method, where ZIF-67 serves not only as a morphological template but also as a sacrificial cobalt source. The resultant porous maze-like nanoreactors are highly active in gas phase CO_2 hydrogenation, in which the reaction pathway involves (i) dissociation of CO_2 to form CO over Pt site via reverse water-gas shift reaction and then (ii) methanation of CO catalyzed by the nearby cobalt site. It was found that the overall "long retention time" for feed gases on catalysts significantly affected the product distribution. Thereby, the specific activity (in the form of turnover frequency) of the nanoreactors having prolonged diffusion paths was around six times as much as that of other comparative catalysts with shorter diffusion paths.

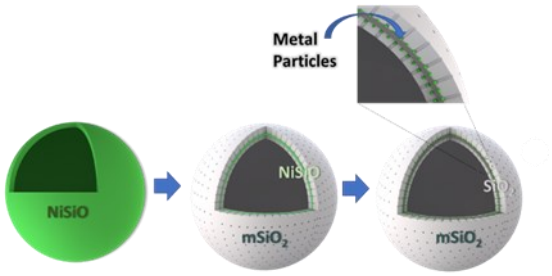


Schematic illustration for the synthesis of nanoreactors and the concept of diffusion pathway. (a) Synthesis of M@CSN nanoreactor starting from ZIF-67 nanocubes. M represents monometallic or bimetallic nanoparticles, mSiO_2 = mesoporous SiO_2, R-NBH_4 = tetrabutylammonium borohydride, CTAC = cetyltrimethylammonium chloride, TEOS = tetraethylorthosilicate. (b) A brief comparison of diffusion pathway in different catalyst structures mentioned in this work (from left to right: Pt@CSN, CoSi@Pt, MnSi@Pt, SiO_2@Pt@mSiO_2, and SiO_2@Pt), showing the influence of retention time of gases over catalysts. The orange colour curves represent gas passing routes through 1D or 3D channels.

Bowen LI (PhD Student, NUS, IRP1) reported on his work: Sandwich like silica supported nickel nanoparticles with high metal dispersion and well controlled morphology have been synthesized through chemical reduction of nickel silicate (NiSiO) with mesoporous silica (mSiO_2) coated on inner and outer surfaces. Formation of nickel nanoparticles was formed at the nickel silicate-silica interface and well confined by the mesoporous coating layers. Utilizing nickel particle surfaces, this catalyst has shown good activity and stability towards dry reforming of methane which converts two well-known greenhouse gases, methane and carbon dioxide, to valuable syn-gas as a product.

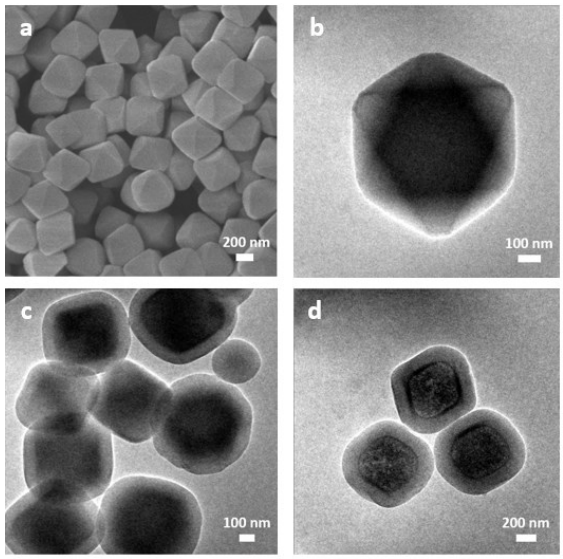
Silica supported NiPt and NiPd bimetallic nanoparticles have also been synthesized with controllable size and noble metal composition. This types of catalysts could be employed to carbon dioxide hy-

drogenation reaction giving methanol as a product.



Process route developed in the present work for the fabrication of nanoreactors with confined metal nanoparticles.

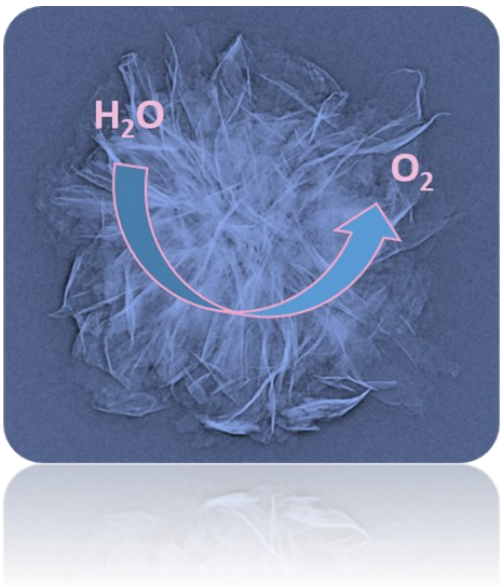
Runze QIN (PhD student, NUS, IRP1) reported on his work. For heterogeneous catalysis by supported metal nanostructures, great efforts have been put on enhancing catalyst performances by downsizing metal particles. However, aggregation of nanosized catalysts has always been a problem for catalyst stability and encapsulation of active nanoparticles is a possible solution for this. In this project, through transformation of UiO-66, a zirconium based metal-organic framework (MOF), mesoporous silica (mSiO$_2$) capped yttrium stabilized zirconia (YSZ) (i.e., TYZ@mSiO$_2$ in Figure below) with rich Lewis and Brønsted acid sites that can work in acid-catalysed reactions was synthesized. Furthermore, it can serve as a stable support for active catalysts and noble metals like Pt could be loaded on. The as-prepared catalyst has potential application for CO_2 hydrogenation. In addition, the resultant YSZ@mSiO$_2$ system can serve as a general platform to catalyse different types of reactions with required active catalysts.



(a) FESEM image of uniform UiO-66 crystals, (b) TEM image of a single UiO-66 particle, (c) TEM image of UiO-66@mSiO$_2$, and (d) TEM image of final YSZ@mSiO$_2$ product.

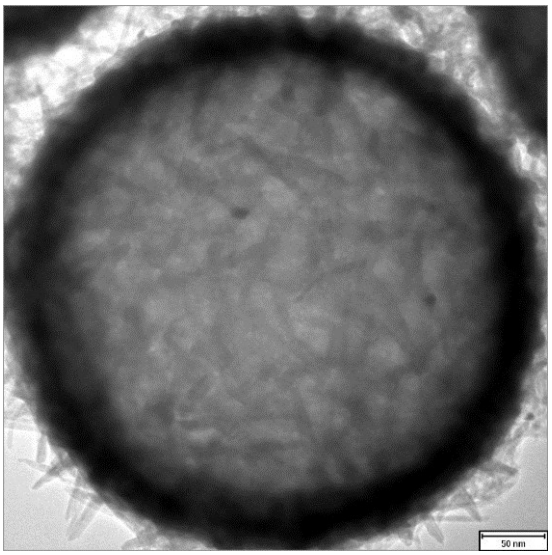
Jingjing WANG (PhD student, NUS, IRP1) reported that Electrochemical splitting of water to produce hydrogen and oxygen is an important process for many energy storage and conversion devices. Developing efficient, durable, low-cost, and earth-abundant electrocatalysts for the oxygen evolution reaction (OER) is of great urgency. In this project, we successfully fabricate two-dimensional ultrathin flakes of cobalt phosphate (CoPi) through a simple conversion from the hexagonal α-Co(OH)$_2$ precursor at room-temperature. The nanoscale CoPi flakes are mainly composed of HPO_4^{2-}, which

have been demonstrated to serve as proton acceptor in proton coupled electron transfer (PCET) process of OER. Due to their ultrathin structure and the compositional merit of HPO_4^{2-}, the CoPi flakes show enhanced OER catalytic activity and good process stability. Through an electrocatalytic mechanism study, the observed excellent performance of OER can be ascribed to enriched active sites and ultrafast electron/proton transport in addition to fast mass transfer.



Schematic representation of the OER process taking place on the surfaces of two -dimensional ultrathin flakes of cobalt phosphate.

Jun Wen YEO (PhD student, NUS, IRP1) reported that spherically structured aluminium oxide within lanthanum oxide shells (Al_2O_3@La_2O_3) integrated nanocatalysts were synthesized in this research. While aluminium oxide is a commonly used catalyst support in bulk catalysts, it is commonly reported that a La_2O_3 supported alumina confers greater stability, especially in the case of Al_2O_3/La_2O_3 supported nickel catalysts for dry reforming of methane (DRM) reaction. The synergy between Al_2O_3 and La_2O_3 as catalyst supports is investigated at the nanoscale in the form of 500 nm spheres. The work in the current stage involves tuning the relative composition within the nanospheres and will extend to functionalization with metal nanoparticles through impregnation in the coming months.



TEM image of alumina encapsulated within a lanthanum oxide shell (i.e., Al_2O_3@La_2O_3).

Prof Cate DUCATI (Co-PI, CAM, IRP1) reported during the reporting period on the work on continuous liquid flow TEM experiments to study the synthesis of nanoparticles for catalysis. With funding provided through Royce Instrument fund a Protochips TEM holder (compatible with FEI microscopes) has been purchased and the first experiments in static and dynamic conditions have been performed.

WP 1.4: Multi-scale modelling

Dr. Liangqi ZHANG (RF, NTU, IRP1), under the supervising of Prof. Jiawei CHEW (Co-PI, NTU, IRP1), is dedicated to the mathematical description of the fluid dynamics with the coupling of the chemical reactions. It is noted that the reactive flow system is governed by the concentration convection-diffusion equation with prescribed boundary conditions. In particular, if surface reaction, such as the absorption-desorption processes, is considered, linear or nonlinear Robin boundary conditions are encountered. Recently, an alternative second-order boundary scheme is proposed under the framework of the convection-diffusion lattice Boltzmann (LB) Method for both straight and curved geometries. With the proposed scheme, boundary implementations are developed for the Dirichlet, Neumann and linear Robin conditions in a consistent way. The advantages of the present boundary implementations over the existing boundary schemes are: (i) no information from neighboring fluid nodes is required; (ii) the three kinds of conditions are realized in a consistent way. Theoretical derivations as well as the numerical validations demonstrate that the present boundary implementations are second-order accurate. The extension of the proposed boundary scheme for nonlinear Robin condition, representing nonlinear surface reactions, is in progress.

WP 1.5: Fundamentals of adsorption and PSA

Dr Mark PURDUE (RF, NUS, IRP1) reported that the CARES pilot plant commissioning work has progressed to complete mechanical construction, electrical communication and rig safety provisions with safety certification provided. Following successful pressure, vacuum and flow path testing of the rig, humidification of feed gas was achieved using: (i) A Nafion membrane with trace heating and chilled deionized water circulating on the tube side (ii) A fast response relative humidity sensor on the feed line that was verified in parallel to an independent humidity sensor using a closed N_2 bubbler. Gas mass flows for He, N_2, CO_2 were validated using mass flow controllers and measured using a low pressure drop Coriolis mass flow sensor. An independent flow measurement technique was integrated using a measured Argon flow ratio using a mass flow controller and a Hiden QGA mass spectrometer. An enhancement of Rockwool insulation was provided for *in-situ* regeneration testing using He, N_2 or compressed air gas purging at high temperature.

All process functionality was incorporated into Labview software to allow adsorption process operation with both dry and wet flue gas, including Dynamic Column Breakthrough (DCB) in any selected column and Vacuum Swing Adsorption (VSA) processes. The VSA process employs a 4 step with light product pressurization (LPP) to compare with simulation work. Both fixed-step (using a time counter) and variable-step (using pressure feedback control) were incorporated into Labview with a pro-

cedure developed to ensure step synchronization during cyclic operation. Programming of proportional solenoid valves was achieved to guide the valve opening for maintenance of a high supply column pressure during the LPP step. Cyclic data logging procedures were tested for all equipment items for pressure, temperature, gas mass flow, gas composition and vacuum pump power consumption. Logging of step time data based upon solenoid valve opening/closing is next required for retrieval of appropriate step power consumption data. A complete CARES pilot plant technical description is also being developed with: (i) Equipment item photos and specifications (ii) Screenshots of data acquisition software for automatic control (iii) Technical process schematics of gas flow scenarios during DCB, VSA and regeneration (iv) A description of required mechanical operations. This reference manual shall facilitate documentation of standard operating procedures and experimental and rig risk assessments.

In an effort to gain physical insight into wet flue gas adsorption on Zeolite-13X (Z13X), molecular simulation data was explored to study adsorption site-exclusion effects using CO_2 and H_2O density plots and radial distribution functions across the full range of relative humidity at 298K and 1atm. The next work activity shall be to record data during DCB, VSA and regeneration demonstration trials, submission of laboratory documentation and incorporate a multicomponent adsorption isotherm model for wet flue gas adsorption on Z13X into process simulation studies. Experimental adsorption process validation shall be tested thereafter.

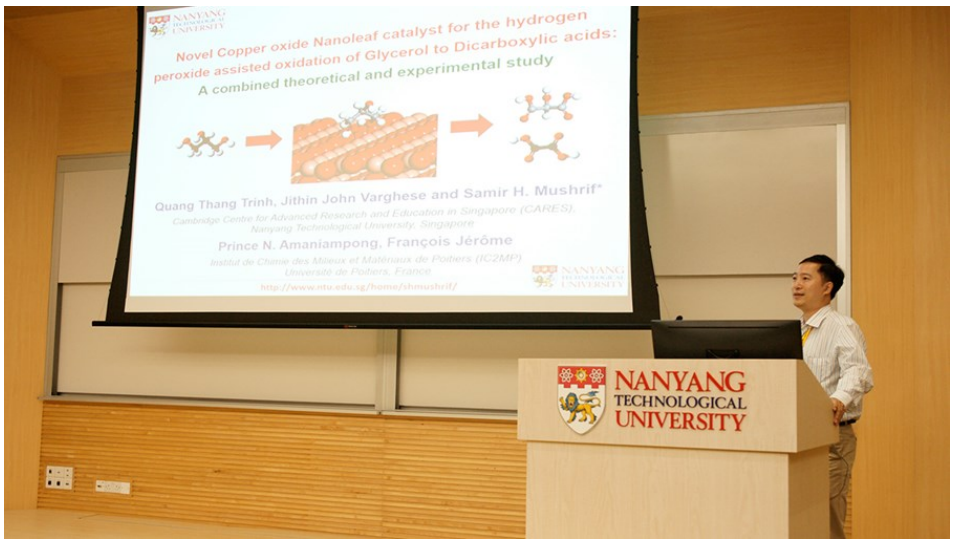
Prerna GOYAL (PhD Student, NUS, IRP1) reported that non-isothermal, non-isobaric adsorption process simulations were performed using MATLAB programming. DCB and a 4 step VSA cycle with and without Light Product Pressurization were simulated to separate dry flue gas containing 15% CO_2 and balance N_2 using Z13X adsorbent. Verification of all process stages was achieved successfully using component mass balance calculations. Multi-objective optimization of VSA processes was used to generate purity-recovery and energy-productivity Paretos. Preliminary work towards a Permit-To-Operate for the CARES pilot plant was performed: (i) Gas supply and automated flow control using Labview (ii) Gas composition analysis using a Hiden QGA Mass Spectrometer (iii) Loading of process columns with adsorbent. The next work activity involves an extension of process simulations to wet flue gas using single and dual column adsorption processes and the performance of DCB experiments using the CARES pilot plant.

Other Activities and Achievements

- Dr Jithin John VARGHESE (RF, NTU, IRP1) Won the Exxon Mobil Poster Award (Consolation Prize) for the poster titled 'The contribution of nickel and oxygen vacancies and of low valent dopants in altering surface reactivity of NiO for C-H activation' at the South-East Asia Catalysis Conference 2017, Singapore, May 22-23, 2017 **.**

- Professor Hua Chun ZENG (PI, NUS, IRP1) received Outstanding Researcher Award from AICHE (Singapore) in July 2017.

- Dr Quang Thang TRINH (RF, NTU, IRP1) was invited to give a talk with the title "Novel Copper Oxide Nanoleaf Catalyst for the Hydrogen Peroxide Assisted Oxidation of Glycerol to Dicarboxylic Acids: A Combined Theoretical and Experimental" at the South East Asia Catalysis Conference (SACC) held on 22 - 23 May, 2017 in Singapore.



3.1.3 Scientific output of IRP1

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP1 during the reporting period. A full list of publications may be found in Appendix A.

Phase interactions in Mg-Ni-Al-O oxygen carriers for chemical looping applications

Jijiang Huang and Wen Liu

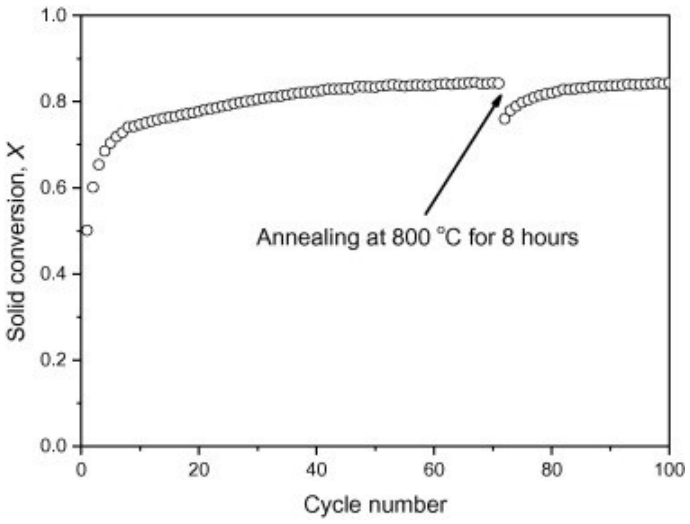
https://doi.org/10.1016/j.cej.2017.05.176

Highlights:

- Ni-Mg-Al-O oxygen carriers with equilibrium phase composition were synthesised by from layered double hydroxides precursors.
- The synthesised oxygen carriers showed excellent performance over 100 redox cycles.
- The phase compositions of the oxygen carriers underwent significant changes over the redox cycles.
- The phase segregation of the NiO-MgO solid solution lead to improved reactivity of the Ni^{2+} during reduction.

Abstract:

Chemical looping combustion offers a solution to achieve carbon capture with minimal energy penalty and significantly reduced NOx formation. The design and synthesis of oxygen carriers play an important role in the advancement of chemical looping combustion. In this investigation, Mg-Ni-Al-O oxygen carriers were synthesised using layered double hydroxides (LDH) as precursors, which facilitate molecular level dispersion of cations in the resulting oxide composites. The behaviour of the synthesised oxygen carriers over 100 chemical looping cycles was studied. The results confirmed the presence of two solid solutions systems: MgO-NiO and MgAl2O4-NiAl2O4, the compositions of which changed over cycles and determined the performance of the oxygen carriers.



NiO conversion versus cycle number for oxygen carrier Ni_2MgAl-OC over 100 cycles at 800 °C. After 70 redox cycles, the sample was calcined in N_2 at 800 °C for 8 h before starting the 71st cycle

Insights into the C-H Bond Activation on NiO Surfaces: The Role of Nickel and Oxygen Vacancies of Low Valent Dopants on the Reactivity and Energetics

Jithin John Varghese, Samir H. Mushrif

DOI: 10.1021/acs.jpcc.7b05226

Abstract:

For the development of nickel oxide (NiO) as an oxidation catalyst, a fundamental understanding of the role of surface morphology and of nickel and oxygen vacancy defects is essential, since they govern the reactivity of the surface. Using density functional theory (DFT) calculations, we investigated the reactivity of two different crystal facets of NiO and reveal the contribution of the coordinatively unsaturated Ni–O pairs, nickel and oxygen vacancies, and low valent dopant Li in determining and altering the reactivity of the surfaces. The most stable surface, NiO(100), is relatively inactive for methane C–H activation with an activation barrier of 136.6 kJ mol–1. However, the relatively less stable NiO(110) surface is extremely active and can dissociate methane with an activation barrier of 57.1 kJ mol–1. The coordinative unsaturation and comparatively low binding strength of the four-coordinated surface lattice oxygen on the NiO(110) surface leads to strong chemisorption of the dissociated H, facilitating extremely low activation barriers for methane dissociation. The presence of a Ni vacancy on the inactive NiO(100) surface brings down the activation barrier for methane dissociation to 90 kJ mol–1. This is a result of weakening of the binding strength of the oxygen, allowing strong chemisorption of the dissociated H. In this work, we predict that an equivalent increase in the surface reactivity can be achieved by doping the inactive NiO(100) surface with low valent metals like Li, which also weakens the binding strength of surface oxygen. The hydrogen chemisorption energy on the oxygen site is identified as a descriptor for estimating the reactivity of surfaces.

Silica nanowires encapsulated Ru nanoparticles as stable nanocatalysts for selective hydrogenation of CO_2 to CO

Dou Jian, Sheng Yuan, Choong Catherine, Chen Luwei, Zeng Hua Chun

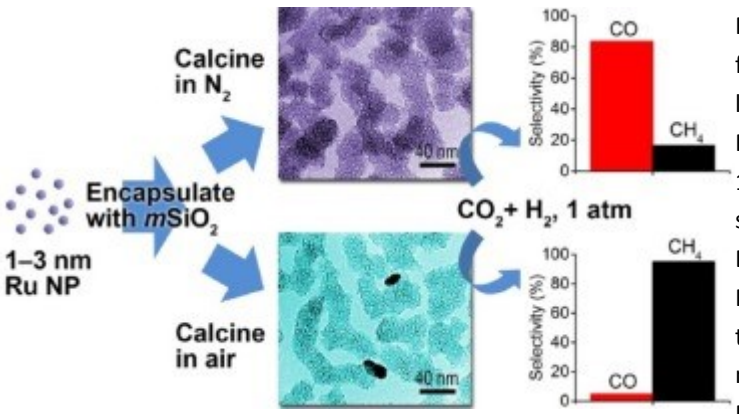
https://doi.org/10.1016/j.apcatb.2017.07.083

Highlights:

- Ru@mSiO_2 has been designed by encapsulating Ru nanoparticles with size of 1–3 nm inside mesoporous channels of silica nanowires.
- Pretreatment of Ru@mSiO_2 catalyst in nitrogen or air leads to generation of 1–3 nm Ru@mSiO_2 and 5–20 nm Ru@mSiO_2 catalyst, respectively.
- Up to 100% selectivity of CO is achieved on 1–3nm Ru@mSiO_2 catalyst, while 95.4% selectivity of CH_4 is achieved on 5–20nm Ru@mSiO_2 catalyst.
- DRIFTS study identifies different reaction intermediates formed: CO-Ru^{n+} on 1–3nm Ru@mSiO_2 and formate on 5–20nm Ru@mSiO_2.
- Stable production of CO with high selectivity has been demonstrated during extended reaction of 50 h.

Abstract:

Hydrogenation of carbon dioxide (CO_2) to produce useful chemicals has been identified as a promising strategy for mitigation of greenhouse gas emission. Ruthenium (Ru) based catalysts have been reported to be the most active catalysts for the hydrogenation of CO_2 to methane (CH4) which unfortunately is also a greenhouse gas and is difficult to activate. Controlling the hydrogenation selectivity to produce carbon monoxide (CO), a direct precursor for enormous important chemicals, thus becomes desirable. However, achieving high CO selectivity with supported Ru catalysts has remained a challenging task. In this work, we report the synthesis of highly selective and stable Ru@mSiO2 nanocatalysts via encapsulation of 1–3 nm Ru nanoparticles within mesoporous silica nanowires for hydrogenation of CO_2 to CO. Calcination of the catalyst in nitrogen prevented sintering of the encapsulated Ru nanoparticles, making high CO selectivity of up to 100% possible, while larger (5–20 nm) Ru particles resulting from calcination in air favored formation of CH4. DRIFTS study of 1–3 nm Ru@mSiO2 and 5–20 nm Ru@mSiO2 catalysts after adsorption of reaction mixture of H2 and CO_2 reveals that different reaction intermediates form on catalyst surface: CO-Run+ on 1–3 nm Ru@mSiO2 and formate species on 5–20 nm Ru@mSiO2, which are responsible for the distinctively different selectivity observed on 1–3 nm Ru@mSiO2 and 5–20 nm Ru@mSiO2 catalysts. Plausible reaction pathways have been proposed for selective hydrogenation of CO_2 on the two types of catalysts, respectively. In addition, high CO selectivity of 1–3 nm Ru@mSiO2 catalyst has been demonstrated to be stable.



Synthesis, Self-Assembly, Transformation, and Functionalization of Nanoscale Artificial Allophane Spherules for Catalytic Applications

Zhou Yao and Zeng Hua Chun

DOI: 10.1021/acs.chemmater.7b01956

Abstract:

Mesoporous materials with large surface area and chemical inertness are of great importance, and currently prevailing synthetic approaches involve usages of micelles as pore-directing agents to create such mesopores. In this work, allophanes, which are hollow aluminosilicate spherules of 3.5–5.5 nm in size, have been synthesized and assembled simultaneously for the first time in a controlled manner to generate mesoporous spherical allophane assemblages (MSAAs) with diameters of 445 ± 40 nm, specific surface area as high as 1032 m2/g, pore volume 1.104 mL/g at P/P0 = 0.975, and average mesopore size at 3.4 nm. Furthermore, the thus-prepared MSAA could be doped with transition metal ions to create a series of isomorphous derivatives; they could also be converted to aluminum-based hierarchical assemblages of layered double hydroxide easily. Different from the conventional channel-like mesopores, the new mesoporosity attained in MSAA is easily accessible be-

cause their mesopores are generated from the interparticle spaces of spherical building units of hollow spherules. Therefore, the mesoporous MSAA provides an excellent platform for construction of integrated nanocatalysts. Highly dispersed noble metal nanoclusters such as Pt, Au, and Pd could be deposited on the surface or in the interior mesopores of the MSAA. Excellent activity and stability of MSAA-based catalysts for Suzuki couplings and electrochemical sensing of H2O2 have been demonstrated using Pd/MSAA and Au/MSAA nanocomposites, respectively.

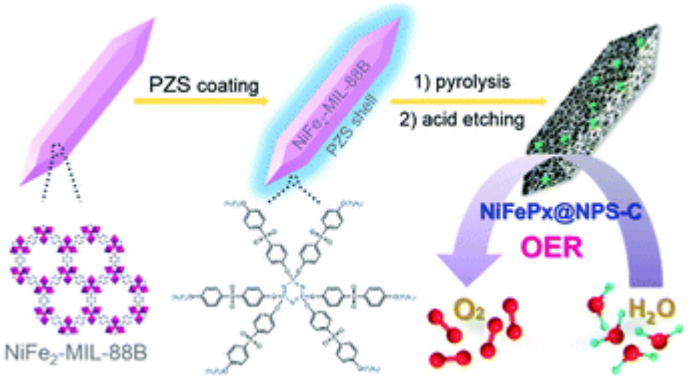
Advanced Oxygen Evolution Catalysis by Bimetallic Ni-Fe Phosphide Nanoparticles Encapsulated in Nitrogen, Phosphorus, and Sulfur Tri-Doped Porous Carbon

Li Ping, Zeng Hua Chun

DOI: 10.1039/C7CC03005C

Abstract:

Through molecular design of a solid precursor, we engineer a novel nanocomposite composed of bimetallic (Ni–Fe) phosphide nanoparticles encapsulated in a N,P,S-tri-doped porous carbon matrix. With tailorable compositional and architectural features, the resultant nanocomposite presents remarkable performance in electrochemical water oxidation.



Sandwich-like Nanocomposite of CoNiOx/Reduced Graphene Oxide for Enhanced Electrocatalytic Water Oxidation

Li Ping, Zeng Hua Chun

DOI: 10.1002/adfm.201606325

Abstract:

The development of cost-effective and high-performance electrocatalysts for oxygen evolution reaction (OER) is essential for sustainable energy storage and conversion processes. This study reports a novel and facile approach to the hierarchical-structured sheet-on-sheet sandwich-like nanocomposite of CoNiO x /reduced graphene oxide as highly active electrocatalysts for water oxidation. Notably, the as-prepared composite can operate smoothly both in 0.1 and 1.0 m KOH alkaline media, displaying extremely low overpotentials, fast kinetics, and strong durability over long-term continuous electrolysis. Impressively, it is found that its catalytic activity can be further promoted by anodic conditioning owing to the in situ generation of electrocatalytic active species (i.e., metal hydroxide/(oxy)hydroxides) and the enriched oxygen deficiencies at the surface. The achieved ultrahigh perfor-

mance is unmatched by most of the transition-metal/nonmetal-based catalysts reported so far, and even better than the state-of-the-art noble-metal catalysts, which can be attributed to its special well-defined physicochemical textural features including hierarchical architecture, large surface area, porous thin nanosheets constructed from CoNiO x nanoparticles (≈5 nm in size), and the incorporation of charge-conducting graphene. This work provides a promising strategy to develop earth-abundant advanced OER electrocatalysts to replace noble metals for a multitude of renewable energy technologies.

The Electrochemical Multi-scale Science, Engineering and Technology, or EMSET, research group targets the development of multi-scale electro-analytical tools for the investigation of catalytic reactions and the adoption of electro-synthesis as a potential source for clean and selective routes for chemical production. In general the research is directed towards mapping chemical demand, usage and transportation, and identifying opportunities for localised chemical production.

EMSET is divided into three work packages:

WP 2.1: Multi-Scale Electrochemical Modelling and Analysis

WP 2.2: Electrode Design and Development

WP 2.3: Electrochemical Reactor Engineering

The EMSET group is led by PIs:

Prof Adrian FISHER (Cam)

Prof Xin WANG (NTU)

Prof Jim Yang LEE (NUS)

Dr. Adrian Fisher,

University of Cambridge

PI, IRP2

October 2017

3.2.1 IRP2 Research Overview

The Electrochemical programme focuses on the development and exploitation of novel technologies and/or processes which offer the potential to lead to a net reduction in CO2 emissions for chemical production either in the area of commodity or speciality chemicals. There are three main trusts to IRP2 first the development of high resolution electrochemical methods using big data approaches which can be be exploited to gain quantitative understanding of the physical and chemical processes which limit efficient electrical conversion, (ii) the investigation and discovery of advanced catalysts, electrode architectures and the wiring of these complex structures to ensure optimal conversion rates and (iii) the development of integrated advanced reactor systems

In the current reporting period significant advances in the core research areas have been achieved. In collaboration with Prof Erik BIRGERSSON (Co-PI, NUS, IRP2) Vishvak KANNAN (PhD Student, NUS, IRP2) has continued their focus on modelling of advanced protocols for electrochemical control and analysis. In their latest activities advanced fluid and electrochemical protocols are under investigation in particular the application of large amplitude periodic input wave functions to explore highly non-linear i/V characteristics have been addressed. These activities have led to further industrial interest from local and international partners and CARES is in the process of negotiating two industrially supported PhD programmes with a provisional start date of October 2018.

In parallel with numerical and theoretical studies, working in collaboration with Prof Xu ZHICHUAN (Co-PI, NTU, IRP2) Dr Chencheng DAI (RF, NTU, IRP2) has recently discovered efficient strategies for the electrochemical production of lactic acid by oxidation of glycerol on AuPt electrode architectures in alkaline environments. In this work, he has reported a method to explore the production of lactic acid via direct electrochemical oxidation of glycerol, yielding a high selectivity, low energy pathway for production of this valuable substrate. Advanced studies have been carried out to evaluate the surface catalysis characteristics of the reaction and explore the highest selectivity routes. It has been found that a 72.9% yield was achieved using AuPt nanoparticles with 13% surface Pt. The glycerol conversion rate was found to be 28.9% over a 12 hour period and these promising results suggest an efficient, cheap and environmentally friendly method for lactic acid production.

The development of the IRP2 international outreach programme has also continued within the current reporting period. June 2017 saw the launch of an advanced electrochemical techniques masterclass in Singapore, in collaboration with the ISE Singapore section. This 2 day activity brought together local experts from industry and IRP2 to highlight advances made in the electrochemical monitoring aspects from WP1 and applications in chemical analysis and catalysis. The course comprised keynote lectures from IRP2 PI Adrian Fisher and ‘hands on’ training in the use of state of the art analysis techniques. The programme, sponsored by our long-term collaborator, Methrohm, was attended by 24delegates, including, UK and Singapore University postdocs/Students and local consultancy firms.. Preparations are underway for 3 further IRP2 outreach activities in the UK in October 2017, Melbourne December 2017 and Singapore March 2018.

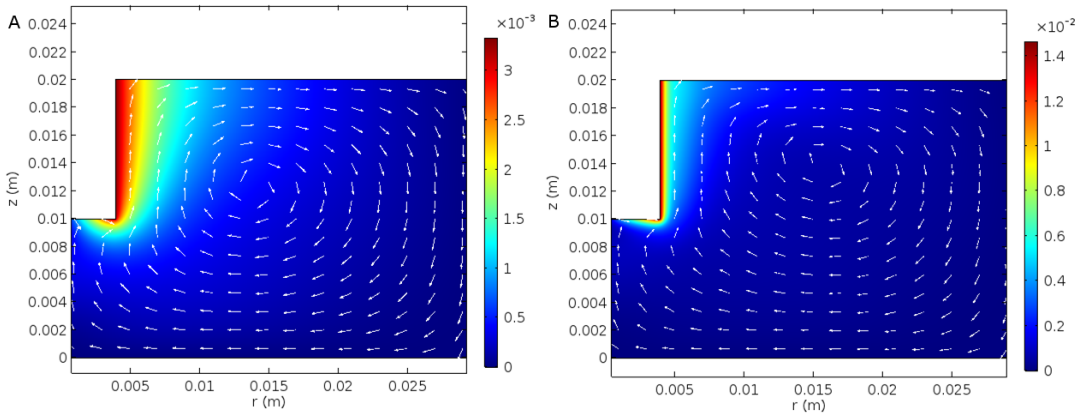
IRP2 industrial collaboration links continue to strengthen. IRP2 PI Adrian Fisher has recently been appointed co-director of Stemnovate a drug discovery company that seeks to use advanced analysis approaches to streamline and accelerate the identification of candidate drugs for personal medicine applications. The company a prospective partner to IRP2 in the phase 2 programme has recently been awarded a £1m innovate UK grant to develop next generation organ-on-a-chip technologies which employ advanced sensor strategies.

3.2.2 Update on work packages

WP 2.1: Numerical multi-scale electrochemical modelling and analysis

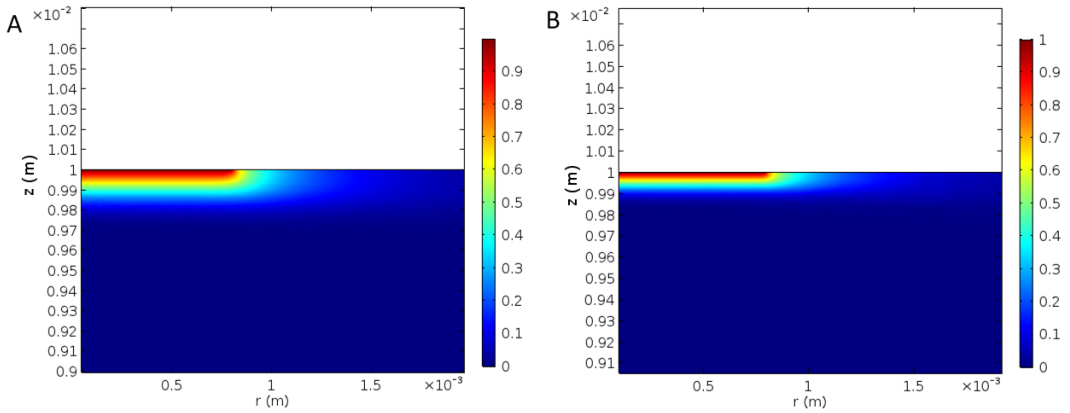
Vishvak KANNAN (PhD Student, NUS, IRP2) reported that the Rocking disk electrode (RoDE) is a recently developed, novel hydrodynamic tool used for electrochemical applications. The experimental setup and the construction of this tool have been discussed in the earlier reports. We set-up a 2 dimensional axially symmetrical numerical model for the momentum and mass transport around a rotating disk electrode (RDE) and the RoDE, in COMSOL Multiphysics®. Vishvak KANNAN (PhD Student, NUS, IRP2) investigated the velocity (figure below) and concentration (figure 2 below) profiles around the RDE and the RoDE, for the same input angular frequency.

Velocity profiles around the RDE (A) and the RoDE (B)



A more uniform hydrodynamic boundary layer around the RoDE was obtained when compared to the RDE, as observed in the above figure. The maximum velocity transferred to the electrolyte for the same input angular frequency is of an order of magnitude bigger for the RoDE was also observed.

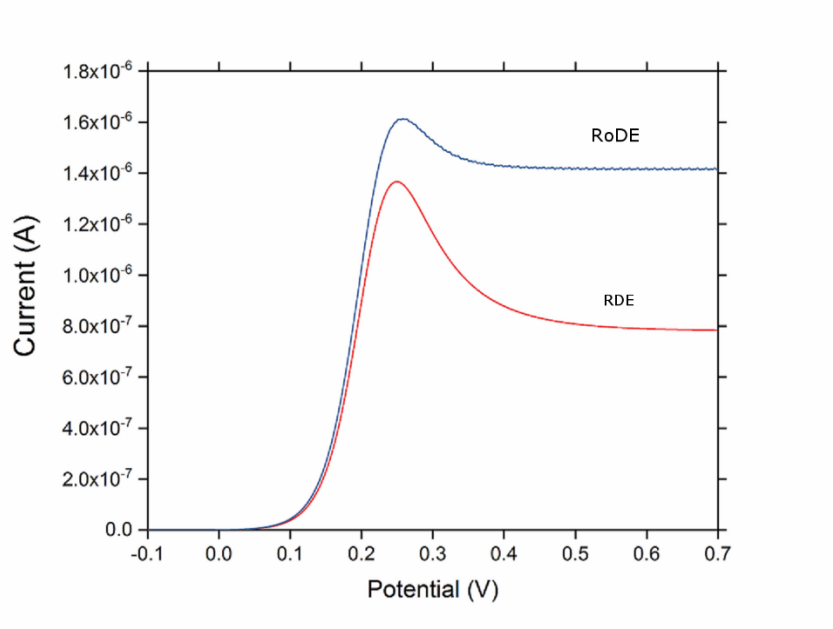
Concentration profiles around the RDE (A) and the RoDE (B)



The above figure shows the concentration profile around the surface of the RDE and the RoDE. This illustrates the diffusion layer and its thickness near the electrode surface. The thickness of the diffusion layer for the RDE is 200 (μ m) whereas it is 100 (μ m) for the RoDE, for the same input angular frequency. A thinner diffusion layer for the RoDE wsa achieved, which means we have smaller currents due to capacitive effects, whence more accurate limiting current measurements. The uniform hydrodynamic layer protects the diffusion layer, which increases the stability of the polarization curve. Mass transport limitations reduce as the thickness of the diffusion layer decreases. This

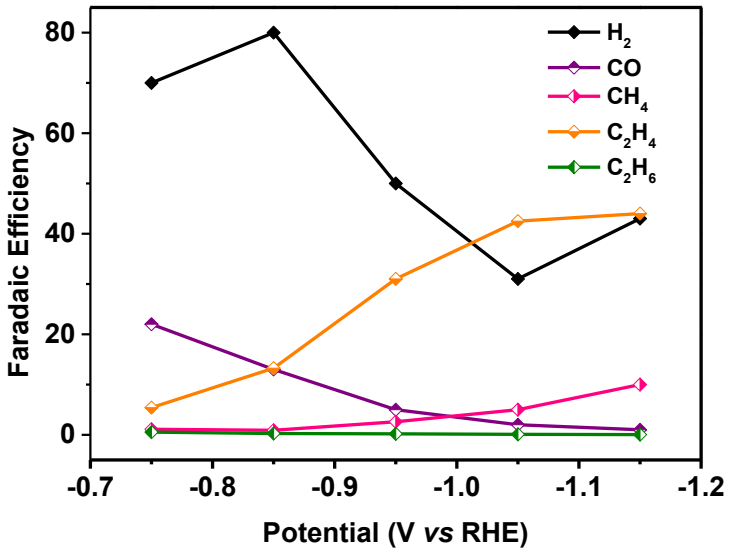
means that the reaction will move towards electron transfer limitation rather than by diffusion limitations, as the thickness of the diffusion layer reduces.

From the measured concentrations around the electrode surface, Vishvak KANNAN (PhD Student, NUS, IRP2) calculated and analysed the current at the electrode surface. A higher limiting current as shown in the figure below at the surface of the RoDE was achieved and a periodic behaviour for the current at the surface of the RoDE corresponding to the motion of the electrode was noticed.



Current at the surface of the RDE (red) and the RoDE (blue)

Dr Libo SUN (RF, NTU, IRP2) reported on the highly selective production of ethylene with mesoporous silica-templated copper In this work, the mesoporous silica, like classical SBA-15, was employed as template to fabricate copper catalyst. The copper catalyst was introduced to the mesopore by dissolving copper salt in well dispersed SBA-15 slurry and the following heat treatment under reducing atmosphere. After removal of the silica skeleton, copper catalyst obtained can be used for electrochemical CO_2 reduction. The reducing products were well analysed with on-line gas chromatography (GC) and high performance liquid chromatography (HPLC) quantitively. The highest selectivity of ethylene could reach around 42%, using such catalysts at an applied potential of -1.05 V vs. reversible hydrogen electrode (RHE), with also higher selectivity when compared to other hydrocarbon materials. This technique provides an opportunity for the efficient and highly selective production of C2 hydrocarbons with a relatively easily and facile catalyst preparation method. Such method can also be available to other mesoporous silica materials.



WP 2.2: Electrode Development and Testing

Prof Richard WEBSTER (Co-PI) reported that a detailed study of the polycyclic aromatic hydrocarbon (PAH) composition of particles ≤ 10 micron in size that exist in the atmosphere in Singapore has been conducted. These particles are produced by local industries as well as through transboundary burning activities such as the annual biomass burning in Indonesia. The particles are thought to be particularly toxic to human health, therefore, it is important to understand their composition in as much detail as possible.

Dr Bahareh KHERZI (RF, NTU, IRP2) studied the electrochemical reduction of CO_2 using Cu based catalysts and catalysts decorated with Cu in collaboration with Prof Zdenek Sofer from UCT, Prague. The target producs are CH_4, C_2H_4, formic acid and alcohols. In this stage the materials have been synthesized, characterized and the catalytic performance (activity, faradic efficiency and current density) in CO_2 saturated aqueous solution investigated. The product of CO_2 conversion will be detected with GC, HPLC and NMR.

In addition, in collaboration with Dr Kamal ELOUARZAKI (RF, NTU, IRP2), Dr Bahareh KHERZI (RF, NTU, IRP2) reported that a literature survey in Electrochemical CO_2 Reduction through molecular catalyst, new trends, benchmark and challenges has been planned.

Guo Xiong THAM (PhD Student, NTU, IRP2) reported that experimental work has been dedicated to use an optimum ratio of vitamin compounds that were to be drop casted onto the glassy carbon macroelectrodes in order to attain a desirable current peak height ratios close to unity. In order to achieve results whose pH measurements behave accurately and realistically as per any commercial pH meter, my research is focusing on the optimizing the electrochemical behaviour of the vitamin compounds which are drop casted onto a chemically modified screen printed carbon electrode (SPCE). Currently, various chemically modified methods are explored which include the use of carbon nanotubes as well. Suitable characterization techniques such as scanning electron microscopy are employed to characterize the morphology of the electrode surfaces of various chemically modified screen printed carbon electrodes.

Nur Farhanah Bte ROSLI (PhD Student, NTU, IRP2) reported on her project on the cytotoxicity studies of Pt dichalcogenides, a class of nanomaterials which has been reported to have promising electrocatalytic properties in hydrogen evolution reaction (HER). The toxicity of Pt dichalcogenides was compared with the toxicity of Pt on carbon (Pt-C), the best performing electrocatalyst for HER. This study is important as toxic implications of new materials which can potentially be used in large scale for clean energy applications, such as HER, requires deeper understanding so as to ensure potential health hazards are avoided.

Dr ZHANG Wenyu (RF, NTU, IRP2) reported that silicene is becoming increasingly popular due to its unique properties. However, the synthesis of silicene remains challenging and limits its wide applications. In this work, a top-down lithiation and delithiation process is developed to prepare few layer silicene nanosheets. Ball milled silicon nanopowders are employed as the starting ma-

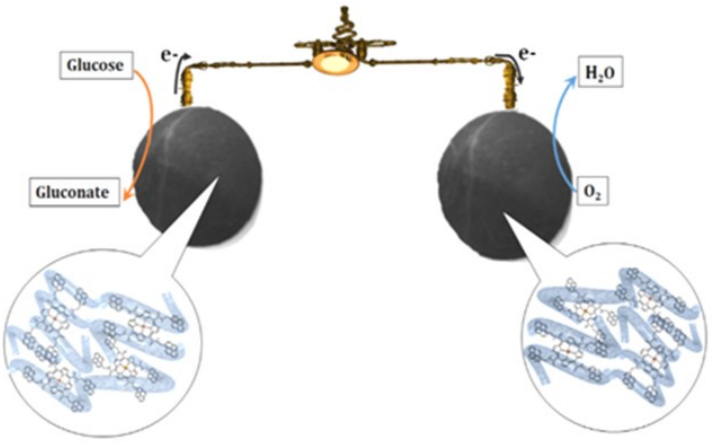
terials, followed by lithiation in Li-ion coin cells and delithiation in isopropyl alcohol. This process renders two dimensional (2D) silicene products with 30-100 nm in length and ~2.4 nm in thickness. The electrochemical characterization analysis suggests that the sample product shows high performance for rechargeable Li-O_2 batteries with 73% energy efficiency and high stability. The top-down synthesis strategy proposed in this work not only provides a new solution to the challenging preparation issue of silicene but also proves to be applicable to produce 2D materials from non-layered starting structures.

Dr ELOUARZAKI Kamal (RF, IRP2, NTU) reported on the new promising field of exploiting natural systems for designing bio-electronic setups. Enzymes, which allow energy conversion and electron transfer in many biological processes are good candidates for such biomaterials. During this period, original and efficient advanced approach based on the association of two key functions, in which one function contributed to enzymes orientation and the second one to enzymatic electron transfer can be designed via chemical covalent linking between two functional sites. Electrochemical tests demonstrate an efficient electron transfer mechanism within the engineered compound and between the oriented biocatalysts and the conductive electrode. This strategy was successfully applied to the construction of a fuel cell with enhanced performance. This new approach will enable the engineering of a large variety of redox mediators, of tunable compositions and structures according to needs. For example, the proposed structure can easily be replaced with other redox mediators to tune the potential to mediate other enzyme reactions or to be applied to the CO_2 fuel cell or biosensors. The structure modulation and the method flexibility might open up enormous possibilities for the development of CO_2 bioelectronics.

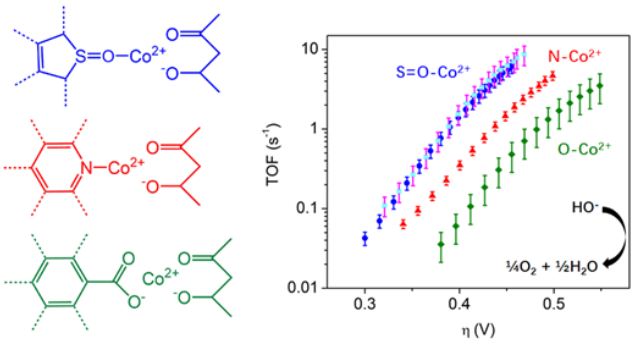
Naziah Binte MOHAMAD LATIFF (PhD student, IRP2, NTU) studied the toxicity aspects of various layered materials that have shown potential in energy applications such as the electrochemical conversion of water to hydrogen and other useful products. She is currently studying layered metal phosphorus chalcogenide materials with a general formula MPX_Y where M is a transition metal element, X is a chalcogen (i.e. S or Se) and Y is either 3 or 4. In addition, Naziah Binte MOHAMAD LATIFF, is also investigating the cytotoxicity of different allotropes of phosphorus (i.e. black, red, violet). These studies are necessary to be informed of the possible health hazards posed by such materials in view of their possible commercialization in the future.

WP 2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

Dr ELOUARZAKI Kamal (RF, IRP2, NTU) reported that an unprecedented simple, scalable and especially facile strategy has been developed for fabricating non-enzymatic and precious-metal free fuel cell using buckupaper based molecular catalysts. The buckupapers show individually enhanced electrocatalytic properties towards glucose oxidation reaction and oxygen reduction reaction with a high stability. The as-designed fuel cell using the anodic and cathodic molecular catalyst buckupaper electrodes significantly outperformed the metallic and enzymatic fuel cell in the output power density. This innovative approach might boost further studies to explore buckupaper-based molecular catalysts for the CO_2 reduction.



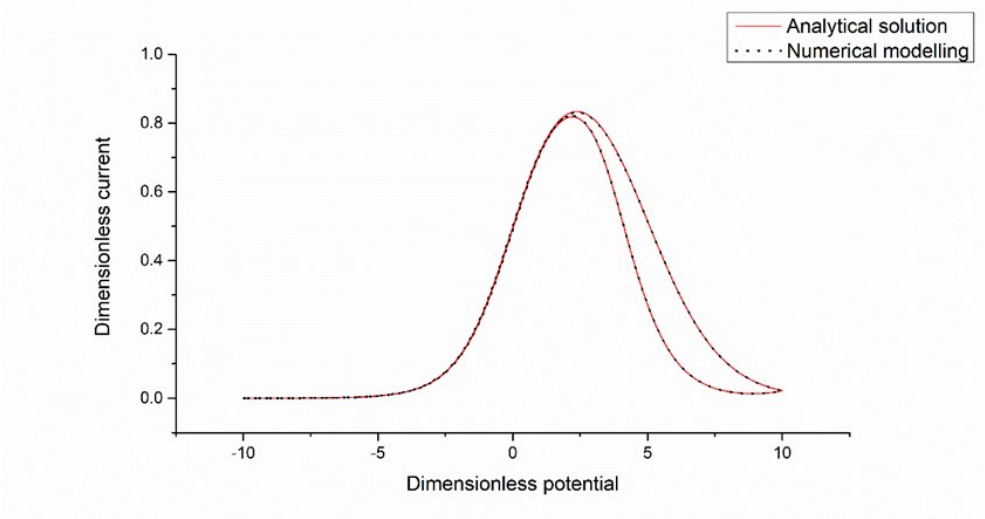
Dr WANG Jiong demonstrated that Co^{2+} ions were heterogenized by various heteroatom-doped graphene-based solid matrices and served as the center of OER active sites. The heteroatoms (S, N, and O atoms) of graphene directly functioned as the binding sites to anchor Co^{2+} ions. A C–S=O configuration was demonstrated to substantially increase the turnover frequencies (TOFs) of Co sites, resulting in a TOF greater than that of an IrO_2 catalyst. Unlike conventional Co_3O_4, where dual Co sites are regarded as the active sites, the OER was found to be catalyzed by single Co ions with terminal oxo ligands formed after a sequential conversion of $Co^{2+} \rightarrow Co^{3+} \rightarrow Co^{4+}$ coupled with HO^- (H^+) transfer. We proposed that a side-on hydroperoxo ligand on the Co^{4+} active sites enabled formation of dioxygen.



Dr Tianran ZHANG (RF, NUS, IRP2) reported his work on nanoporous manganese oxide nanosheets (np-MnO_2-ns) as an ORR electrocatalyst. Manganese oxides have drawn significant interest as a low-cost ORR catalyst. However, their activities are inferior to the platinum-metal catalysts because of their poor electronic conductivity and the low intrinsic activity of the MnO_6

units. One possible solution to elevate the activity of manganese oxides is to design structures with a high surface area and a large number of active centers. Porous two-dimensional (2D) manganese oxides would provide such a structure, however, it is still a great challenge to prepare such structure since manganese oxides are easily transformed and there was no known layered precursor to decompose from. To solve this issue, Dr. Zhang has developed a sulfurization method to produce np-MnO_2-ns. The as-prepared np-MnO_2-ns with pore size of 7 nm displayed excellent ORR activities, superior to those of the pristine MnO_2 nanosheets (MnO_2-ns). The half-wave potential of np-MnO_2-ns was 0.73 V and only ~90 mV negative to that of commercial Pt/C. Besides, the np-MnO_2-ns also showed considerable OER activity, making them a good bifunctional oxygen electrocatalyst for rechargeable Zn-air batteries. The discharge performance of Zn-air batteries with the np-MnO_2-ns catalyst was similar to that of batteries using a commercial Pt/C catalyst with an even lower charge voltage than the Pt/C cell. The full cell could run for more than 60 h of continuous operation.

WANG Yian (PhD Student, NTU, IRP2) reported that a twisted reverse cyclic voltammetric behaviour is first observed in a fully molecular based catalytic oxidation mechanism (shown in the figure below), which has previously been observed for catalysis by immobilised redox enzymes. In order to investigate the kinetic characteristics and potential applications of this fully molecular electrocatalytic system, we thus propose a procedure for the simulation of twisted reverse cyclic voltammetric responses of molecular catalysis-based glucose fuel cell at higher pH value. Fore-



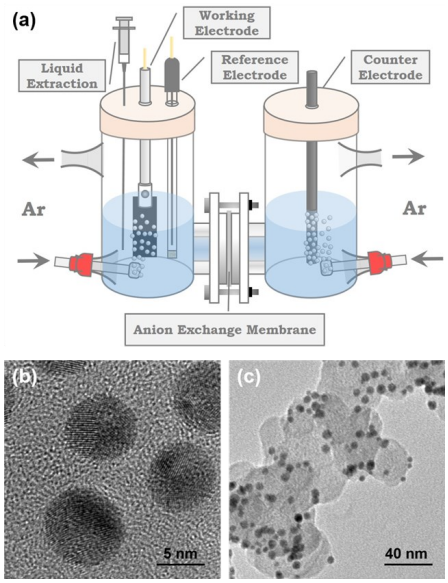
Chemical inactivation -redox reactivation mechanism. Dimensionless current-potential responses in analytical solution and numerical modelling result, respectively. The relative error is less than 0.1%.

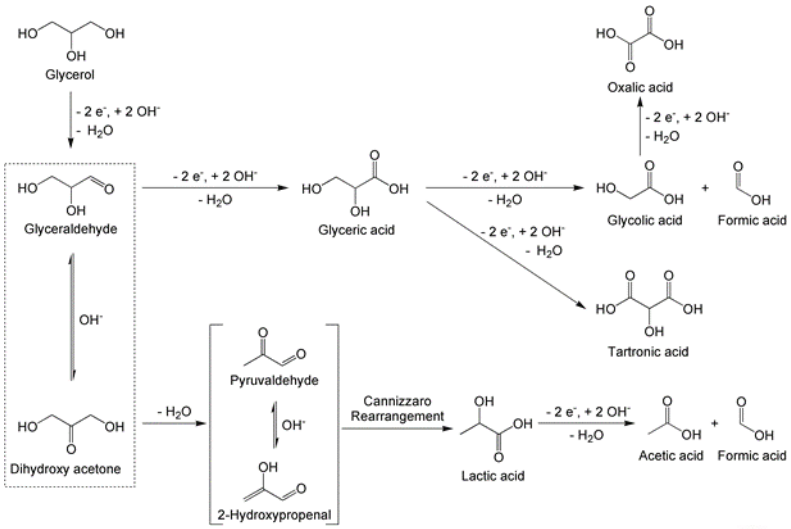
cast of the voltammetric responses of the deactivation and reactivation given by the theory and simulation procedures, can estimate the kinetic parameters and derivate the dynamic characteristics in the reactions. This information will help to optimise the current experiments and further to design new devices. Linear diffusion associated with planar electrodes is assumed as the simplest case used in the simulation. The electrochemical reactions at the electrode strictly follows the empirical Butler-Volmer (BV) kinetical law, which is regarded as the most widely used model in electrochemistry for a long-time period. All numerical simulations are performed with the ba-

sis of a software (MATLAB MathWorks) to illustrate the actual data.

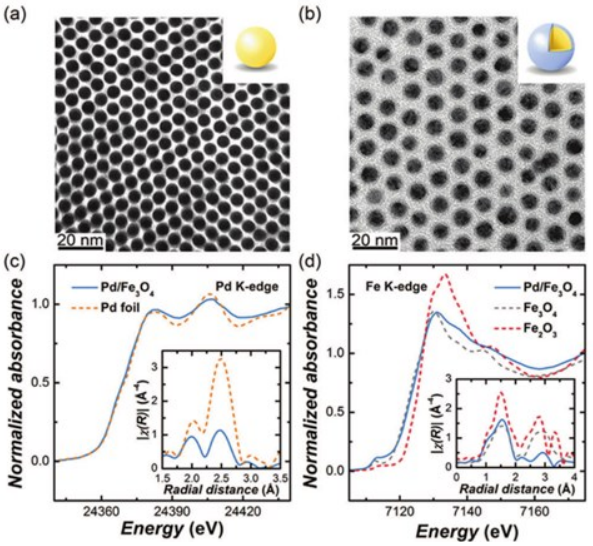
Dr Chencheng DAI (RF, NTU, IRP2) reported on the production of lactic acid by the electro-oxidation of glycerol. In this work, lactic acid was prepared by the one-pot electrochemical oxidation of glycerol catalyzed by AuPt nanoparticles in alkaline solution at room temperature and pressure. AuPt nanoparticles with different surface compositions were prepared by heat treatment, and characterized by cyclic voltammetry, transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and inductively coupled plasma mass spectrometry (ICP-MS), etc.. The performance of the AuPt catalysts were optimized by tuning parameters, including AuPt surface composition, applied potential, electrolyte pH and glycerol concentration. The oxidation products were analyzed by nuclear magnetic resonance (NMR) and high performance liquid chromatography (HPLC) qualitatively and quantitively. The highest selectivity reaches 73%, using an Au rich surface at an applied potential of 0.45 V vs. reversible hydrogen electrode (RHE). This technique provides an opportunity for the efficient, energy-saving, environmental-friendly and commercial production of lactic acid. In addition, metal nanoparticles embedded with metal organic framework (MOF) or mesoporous carbon also have been investigated for glycerol electro-oxidation. This work is related to WP 2.2 electrode design and development and WP 2.3 electrochemical reactor engineering.

Dr Chencheng DAI (RF, NTU, IRP2) reported on an a multisite strategy for enhancing the hydrogen evolution reaction on nano-Pd surface in alkaline media. The hydrogen evolution reaction (HER) on a noble metal surface in alkaline media is more sluggish than that in acidic media due to the limited proton supply. To promote the reaction, it is necessary to transform the alkaline HER mechanism via a multisite catalyst, which has additional water dissociation sites to improve the proton supply to an optimal level. Here, this study reports a top-down strategy to create a multisite HER catalyst on a nano-Pd surface and how to further fine-tune the areal ratio of the water dissociation component to the noble metal surface in core/shell-structured nanoparticles (NPs). Starting with Pd/Fe_3O_4 core/shell NPs, electrochemical cycling is used to tune the coverage of iron (oxy)hydroxide on a Pd surface. The alkaline HER activity of the core/sell $Pd/FeO_x(OH)_{2-2x}$ NPs exhibits a volcano-shaped correlation with the surface Fe species coverage. This indicates an optimum coverage level where the rates of both the water dissociation step and the hydrogen formation step are balanced to achieve the highest efficiency. This multisite strategy assigns multiple reaction steps to different catalytic sites, and should also be extendable to other core/shell NPs to optimize their HER activity in alkaline media. This work is related to WP 2.2 electrode design and development.

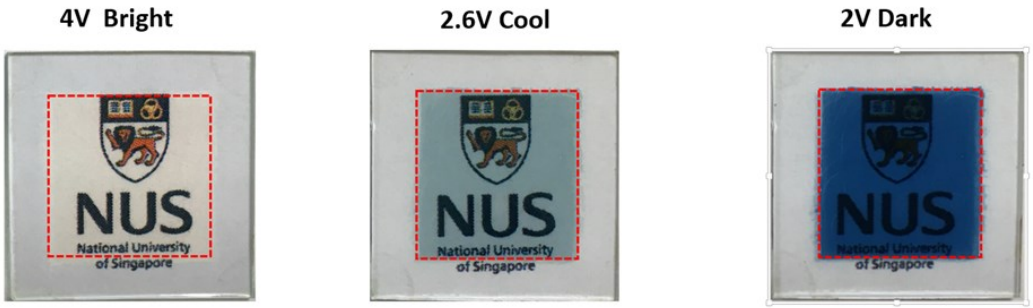




In addition, Dr Chencheng DAI (RF, NTU, IRP2) , reported on cations in Octahedral Sites: A Descriptor for Oxygen Electrocatalysis on Transition-Metal Spinels. Exploring efficient and low-cost electrocatalysts for the oxygen-reduction reaction (ORR) and oxygen-evolution reaction (OER) is critical for developing renewable energy technologies such as fuel cells, metal–air batteries, and water electrolyzers. A rational design of a catalyst can be guided by identifying descriptors that determine its activity. Here, a descriptor study on the ORR/OER of spinel oxides is presented. With a series of $MnCo_2O_4$, the Mn in octahedral sites is identified as an active site. This finding is then applied to successfully explain the ORR/OER activities of other transition-metal spinels, including $Mn_xCo_{3-x}O_4$ (x = 2, 2.5, 3), $Li_xMn_2O_4$ (x = 0.7, 1), XCo_2O_4 (X = Co, Ni, Zn), and XFe_2O_4 (X = Mn, Co, Ni). A general principle is concluded that the e_g occupancy of the active cation in the octahedral site is the activity descriptor for the ORR/OER of spinels, consolidating the role of electron orbital filling in metal oxide catalysis. This work is related to WP 2.2 electrode design and development.



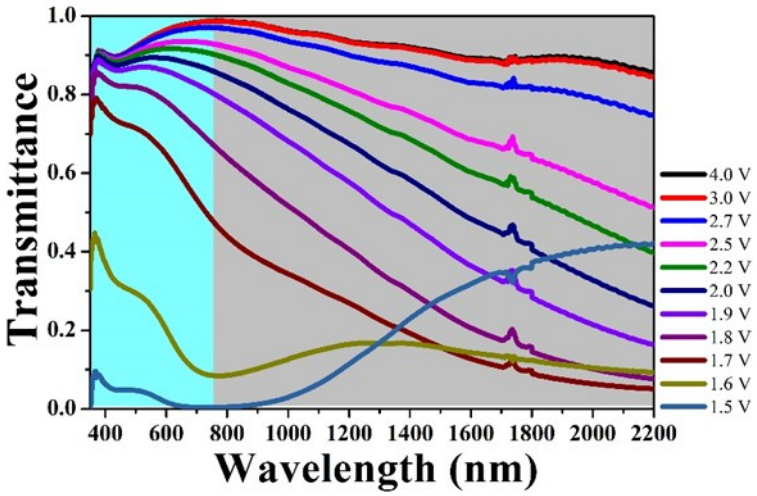
Shengliang ZHANG (PhD Student, NUS, IRP2) reported on his project "Tunable Plasmonic Semiconductor Nanocrystals for Spectrally-Selective Electrochromic Smart Windows". For the reporting period he synthesized tungsten oxide nanowires which exhibit strong absorption in the entire NIR range (780-2500nm). They are expected to deliver the desired electrochromic performance when applied as smart windows. More importantly, the visible light and IR spectral response can be dynamically and independently tuned by an externally applied potential. In the 4V-2.6V range, Li^+ would adsorb on the WO_3 surface, tuning the NIR response based on LSPR absorption to operate in the cool mode. In the 2.6V-2V range, Li^+ would intercalate into the WO_3 matrix, tuning the visible light based on intraband transition to operate in the dark mode. In the cool mode (2.6V), the WO_3 film could block ~ 93.8% of NIR radiation (780-2200nm) while maintaining a high (60%) transmittance of the visible light (400-780nm). In the dark mode (2V), the film blocks 83.1% of visible light and almost all of the NIR (99.7%). The tungsten oxide nanowires also exhibit a high optical modulation of greater than 90% at 633, 800, 1200 and 1600nm, and a high durability of more than 1000 cycles. The excellent electrochromic performance of WO_3 is attributed to its nanowire structure which tunes the material NIR response dynamically based on LSPR absorption under an applied potential; without sacrificing the visible light response. In addition, the nanowire structure can also facilitate intercalation of Li^+ to achieve a high optical modulation.



Spectrally-Selective Electrochromic Smart Windows under different applied potentials

Dr CAO Sheng (RF, NUS, IRP2) reported on his study on doped titanium dioxide (TiO_2) for use in smart windows. TiO_2 is an abundant nontoxic material with interesting physical and chemical properties and high thermal and chemical stability. It is one of the most widely used compounds in UV sunscreens, water splitting, and sensors. Incorporating dopants ions into TiO_2 nanoparticles can be a versatile means to tailor the electronic properties of TiO_2 and its localized surface plasmon resonance (LSPR) in the near infrared region (NIR). The doped TiO_2 nanoparticles can also be used electrochemically

activated to form dual-band electrochromic (EC) devices that which can dynamically and selectively modulate the NIR and visible light based on the LSPR and the intervalence change transfer mechanisms respectively. Dr CAO Sheng (RF, NUS, IRP2) has developed a generic one-pot strategy for the synthesis of doped TiO2 nanocrystal inks with strong LSPR properties. In addition, he has also successfully fabricated a dual band EC device based on the doped TiO2 nanocrystal inks. The preliminary EC device can provide three model responses: (1) bright model (transparent to the entire solar spectrum); (2) cool model (visible light transparent and NIR blocking); (3) dark model (both visible light and NIR blocking). His ongoing work will focus on the fabrication of transparent flexible EC devices and the characterization of their optical performance.



Transmittance of doped TiO_2 nanoparticle films at different bias voltages. The green and grey backgrounds are used to indicate the visible and near infrared spectral regions respectively.

Dr CAO Sheng (RF, NUS, IRP2) reported that he and research members successfully fabricated a dual band EC device based on the doped TiO_2 nanoparticles. As shown in Figure 1, the EC device provides two complementary spectroelectrochemical responses, which can be independently controlled through an externally applied potential: A large variation of the optical transmittance in the near-infrared region (by the intensification of localized surface plasmon scattering) was achieved in the 4-1.8V voltage window, attaining values greater than 68% in the 780 to 2200 nm spectral range. Visible light absorption could also be tuned by further lowering of the potential (from 1.8 to 1.5V), where the Li+ intercalation into the TiO_2 anatase lattice almost blocked the entire visible light region (97.3%).

Other Activities and Achievements

- Nur Farhanah Bte ROSLI (PhD Student, NTU, IRP2) and Naziah Binte MOHAMAD LATIFF (PhD student, IRP2, NTU) attended an annual research conference of the Department of Chemical Engineering and Biotechnology (CEB), University of Cambridge which was held on 26 to 27 June 2017. We both presented posters of our recent projects titled “Cytotoxicity of exfoliated layered Vanadium dichalcogenides” and “In vitro cytotoxicity of exfoliated Thiobarbituric Acid-modified Molybdenum Disulphide”.
- Prof Martin PUMERA (Co-PI, NTU., IRP2) and Prof Jim Yang LEE (PI, NUS, IRP2) were named “Highly Cited Researcher 2017” by Clarivate Analytics (owner of Web of Science). Selection for this award is based solely on the excellence in research and published works.
- With the prof. Donald Martin’s team at CNRS-University of Grenoble Alpes. A first important outcome was the submission of a Singapore-France joint grant between the French PI (Donald Martin, UJF), Singaporean PI (LEE Jong-Min, NTU), Cambridge PI (Adrian FISHER, University of Cambridge), and CARES PI (Kamal ELOUARZAKI, CARES) which was selected for the final evaluation.

- With the Dr. Abdelkader Zebda's team at INSERM-University of Grenoble Alpes. A second important outcome was the submission of a Singapore-France Merlion grant between the French PI (Abdelkader Zebda, UJF), Singaporean PI (LEE Jong-Min, NTU), and CARES PI (Kamal ELOUARZAKI, , CARES).
- With the Assoc. Prof. Yong Ken Tye School of Electrical and Electronic Engineering (NTU) and Prof. LI Yin Institute of Microbiology, Chinese Academy of Sciences (IMCAS). A third important outcome was the submission of a Singapore-Chinese joint grant between the Chinese PI (Prof. LI Yin, Chinese Academy of Sciences), Singaporean PI (Prof. Yong Ken Tye, NTU), and CARES PI (Adrian FISHER, CARES) which was selected for the final review.

3.2.3 Scientific output of IRP2

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP2 during the reporting period. A full list of publications during the period may be found in Appendix A.

Regional transport, source apportionment and health impact of PM10 bound polycyclic aromatic hydrocarbons in Singapore's atmosphere

Dejan Urbančok, Anthony J.R. Payne, Richard D. Webster

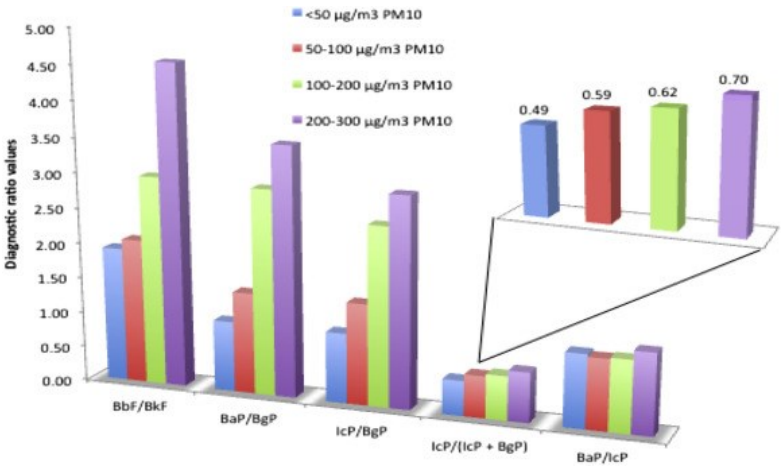
https://doi.org/10.1016/j.envpol.2017.07.086

Highlights:

- PM_{10} adsorbed PAHs were quantified during high haze (AQI>100) and normal days (AQI<100).
- PAH concentrations doubled during high haze periods with maximum (total) of 6 ng m^{-3}.
- No notable seasonal variation of PAHs except for higher values during high haze events.
- Health risk assessment indicated PAHs were slightly above allowed threshold during haze.
- Incremental life-time cancer risk was calculated to be low during high and low haze

Abstract:

A study of 16 United States Environmental Protection Agency (USEPA) priority listed PAHs associated with particulate matter ≤ 10 μm (PM10) was conducted in Singapore during the period 29th May 2015 to 28th May 2016. The sampling period coincided with an extensive, regional smoke haze episode (5th September to 25th October) that occurred as a result of forest and peat fires in neighboring Indonesia. Throughout this study, 54 atmospheric PM10 samples were collected in 24 h periods using a high volume sampler (HVS) and quarts fiber filters (QFF) as the collection medium. Hysplit software for computing 3-D backward air mass trajectories, diagnostic ratio analysis and ring number distribution calculations were used to examine the sources of PAHs in the atmosphere in Singapore. Under normal conditions the total PAH concentrations were in a range from 0.68 ng m−3 to 3.07 ng m−3, while for the high haze period the results showed approximately double the concentrations with a maximum value of 5.97 ng m−3. Diagnostic ratio (DR) and principal component analysis (PCA) were conducted and indicated the contribution of the traffic as a dominant pyrogenic source of PAHs during normal periods, while results from the haze dataset showed relatively strong influence of smoke from peat and forest fires in Indonesia. Environmental and health risk from PAHs were assessed for both regular and hazy days.

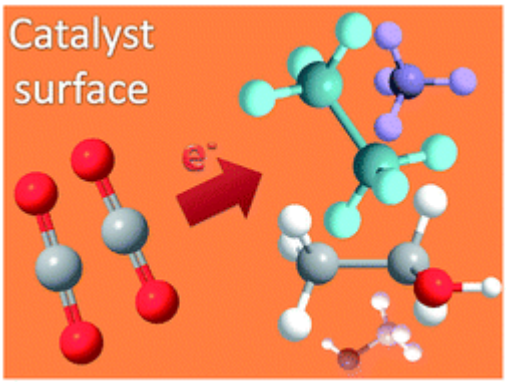


Diagnostic ratio values of PAH congeners during the haze period computed for different levels of haze intensity.

CO_2 reduction: the quest for electrocatalytic materials

Bahareh Khezri, Adrian C. Fisher, Martin Pumera

Rising levels of carbon dioxide (CO_2) are of significant concern in modern society, as they lead to global warming and consequential environmental and societal changes. It is of importance to develop industries with a zero or negative CO_2 footprint. Electrochemistry, where one of the reagents is electrons, is an environmentally clean technology that is capable of addressing the conversion of CO_2 to value-added products. The key factor in the process is the use of catalytic electrode materials that lead to the desired reaction and product. Significant progress in this field has been achieved in the past two years. This review discusses the progress in the development of electrocatalysts for CO_2 reduction achieved during this time period.



Cations in Octahedral Sites: A Descriptor for Oxygen Electrocatalysis on Transition -Metal Spinels

Chao Wei, Zhenxing Feng, Günther G. Scherer, James Barber, Yang Shao-Horn, Zhichuan J. Xu

DOI: 10.1002/adma.201606800

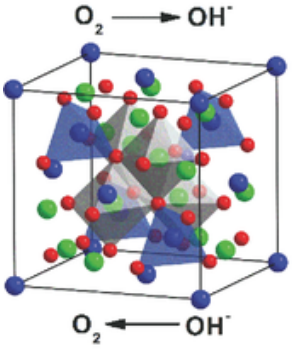
Highlights:

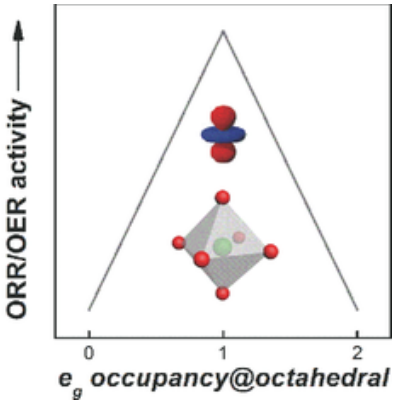
- The eg occupancy of the active cation in octahedral sites is identified as the descriptor that governs the activity of the oxygen-reduction reaction and the oxygen-evolution reaction on transition-metal spinel oxides;
- With a series of MnCo2O4, the Mn in octahedral sites is identified as an active site;
- This finding is then applied to successfully explain the ORR/OER activities of other transition-metal spinels, including MnxCo3−xO4 (x = 2, 2.5, 3), LixMn2O4 (x = 0.7, 1), XCo2O4 (X = Co, Ni, Zn), and XFe2O4 (X = Mn, Co, Ni).

Abstract:

Exploring efficient and low-cost electrocatalysts for the oxygen-reduction reaction (ORR) and oxygen -evolution reaction (OER) is critical for developing renewable energy technologies such as fuel cells, metal–air batteries, and water electrolyzers. A rational design of a catalyst can be guided by identifying descriptors that determine its activity. Here, a descriptor study on the ORR/OER of spinel oxides is presented. With a series of $MnCo_2O_4$, the Mn in octahedral sites is identified as an active site. This finding is then applied to successfully explain the ORR/OER activities of other transition-metal spinels, including $Mn_xCo_{3-x}O_4$ (x = 2, 2.5, 3), $Li_xMn_2O_4$ (x = 0.7, 1), XCo_2O_4 (X = Co, Ni, Zn), and XFe_2O_4

(X = Mn, Co, Ni). A general principle is concluded that the e_g occupancy of the active cation in the octahedral site is the activity descriptor for the ORR/OER of spinels, consolidating the role of electron orbital filling in metal oxide





A Multisite Strategy for Enhancing the Hydrogen Evolution Reaction on a Nano-Pd Surface in Alkaline Media

Hanbin Liao, Chao Wei, Jingxian Wang, Adrian Fisher, Thirumany Sritharan, Zhenxing Feng, Zhichuan J. Xu

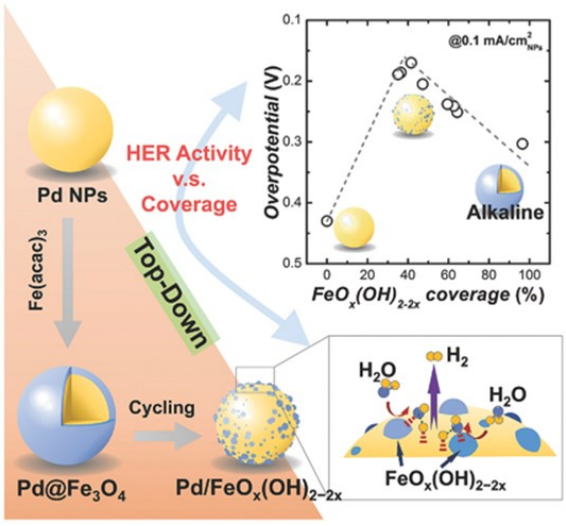
DOI 10.1002/aenm.201701129

Highlights:

- Enhanced hydrogen evolution reaction (HER) on noble metal (nano-Pd) surface in alkaline media to overcome the lack of proton supply in alkaline media;
- To promote the reaction, a multisite catalyst, which has additional water dissociation sites to improve the proton supply to an optimal level, has been synthesized using a top-down strategy;
- Starting with Pd/Fe_3O_4 core/shell NPs, electrochemical cycling is used to tune the coverage of iron (oxy)hydroxide on a Pd surface;
- The alkaline HER activity of the core/sell $Pd/FeO_x(OH)_{2-2x}$ NPs exhibits a volcano-shaped correlation with the surface Fe species coverage.

Abstract:

The hydrogen evolution reaction (HER) on a noble metal surface in alkaline media is more sluggish than that in acidic media due to the limited proton supply. To promote the reaction, it is necessary to transform the alkaline HER mechanism via a multisite catalyst, which has additional water dissociation sites to improve the proton supply to an optimal level. Here, this study reports a top-down strategy to create a multisite HER catalyst on a nano-Pd surface and how to further fine-tune the areal ratio of the water dissociation component to the noble metal surface in core/shell-structured nanoparticles (NPs). Starting with Pd/Fe_3O_4 core/shell NPs, electrochemical cycling is used to tune the coverage of iron (oxy)hydroxide on a Pd surface. The alkaline HER activity of the core/sell $Pd/FeO_x(OH)_{2-2x}$ NPs exhibits a volcano-shaped



correlation with the surface Fe species coverage. This indicates an optimum coverage level where the rates of both the water dissociation step and the hydrogen formation step are balanced to achieve the highest efficiency. This multisite strategy assigns multiple reaction steps to different catalytic sites, and should also be extendable to other core/shell NPs to optimize their HER activity in alkaline media.

Microwave irradiated N- and B,Cl-doped graphene: Oxidation method has strong influence on capacitive behaviour

Naziah Mohamad Latiff, Carmen C. Mayorga-Martinez, Lu Wang, ZdeněkSofer, Adrian C Fisher, Martin Pumera

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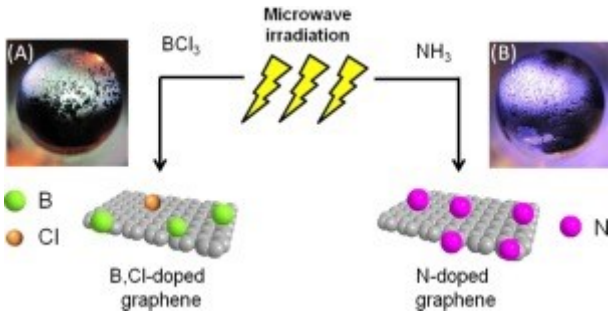
Highlights:

- Graphene oxides were doped, exfoliated, and reduced *via* microwave irradiation.
- Microwave irradiation under BCl_3 and NH_3 atmospheres gave B,Cl- and N-doped graphene
- Graphite oxidation methods (Staudenmaier, Hummers, Hoffman) influences doping levels.
- Capacitance result correlates well with the amount of doping achieved.
- Doped graphene prepared *via* Hummers and Hoffman routes performed better.

Abstract:

Graphene and its derivatives show promising potential in future capacitor systems due to their excellent conductivity and large surface area. Here, we study the effect of different graphite oxidation methods (*i.e.*, Staudenmaier, Hummers, and Hoffman methods) on the capacitive behavior of heteroatom-doped graphene. After graphite oxidation, the graphene materials were simultaneously doped, exfoliated, and reduced using microwave irradiation in BCl_3 and NH_3 atmospheres to produce B,Cl- and N-doped graphene. Our findings show that the graphite oxidation method employed plays a strong influence on their doping levels, which in turn affects their capacitive behavior. The capacitance result correlates well with the amount of doping achieved. The heteroatom-doped graphene prepared here *via* Hummers and Hoffman oxidation routes prove superior compared to the Staudenmaier method.



Carbon Abatement in the Petroleum Refining Industry: A Control and Optimisation Research Network, or, CAPRICORN, aims at answering the question of how to minimise CO_2 emissions while optimally running a modern industrial park including complex refinery operations to produce downstream fuel blends. The research uniquely combines and advances the state-of-the-art in low carbon research encompassing fields of surrogate fuel modelling, fuel blending using nonlinear correlations, fuel-engine mapping for emissions regulation compliance, inorganic and organic nanoparticle flame synthesis. Uncertainty propagation, Bayesian parameter estimation, dynamic optimisation of refinery operations and associated energy loads, and model predictive control are methods used to develop sustainable low-carbon refinery operations.

CAPRICORN is split into five interacting work packages:

WP 3.1: Industrial network model of Jurong Island – Process Flow Sheets: energy and material

WP 3.2: Link of refinery products with engine operations – surrogate fuels: model and experiments

WP 3.3: Nanoparticle/film flame synthesis – kinetics and application

WP 3.4: Modelling and optimisation of unit operations

WP 3.5: Automated model development and experimental design/decision support

The CAPRICORN group is led by PIs:

Prof Markus KRAFT (Cam)

Prof Raymond Wai Man LAU (NTU)

Prof Iftekhar KARIMI (NUS)

Prof. Markus Kraft,

University of Cambridge

PI, IRP3

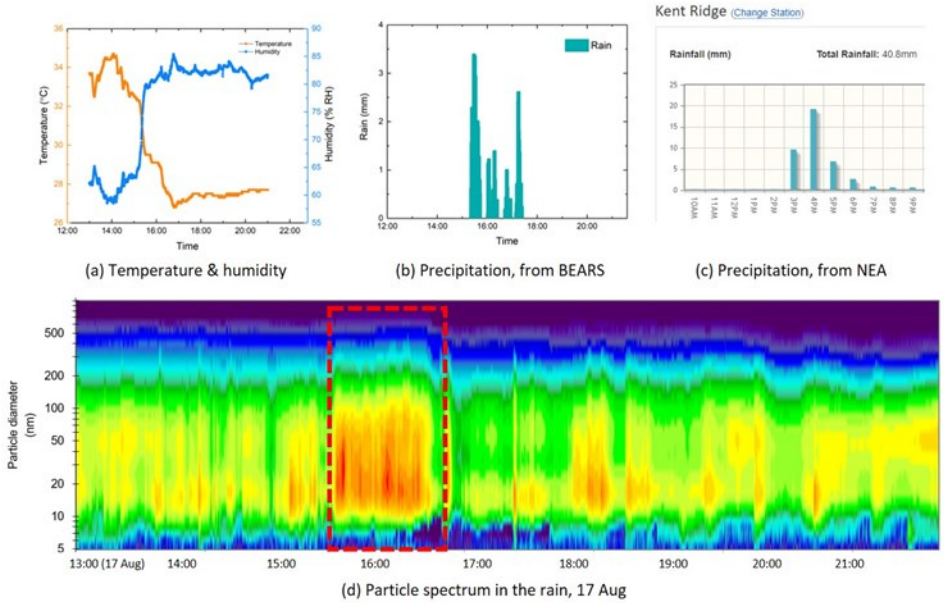
October 2017

3.3.1 IRP3 Research Overview

In this reporting period, we have managed to further extend the capabilities of the J-Park Simulator (JPS) – our virtual simulation platform to exploit synergies within Jurong Island eco-industrial park. In particular, we have been able to quantify CO_2-emissions on Jurong Island as well as potential contributions the JPS can make towards reducing them. This process also demonstrated the value an ontological approach can add to intelligent decision-making. In a similar vein, we have added a feature which allows users to make simple queries formulated in natural language. Both these examples reflect that we are beginning to take advantage of the fact that we use ontologies as underlying structures to represent data and knowledge formalised through models, thus making use of the unique possibilities offered by this which would not be available if we had employed conventional database concepts. In addition, we have continued to expand our collection of applications which involve acquisition of measurement data, such as urban particulate matter concentrations (see figure below), and Building Management System (BMS) data. This data is represented in ontological form within the JPS, thereby ensuring real-world information is being fed in useful form into the JPS in real time.

With our state-of-the-art laboratory facilities in Singapore as well as Cambridge now up and running, progress has continued apace with our ability to flame-synthesise and characterise various nanomaterials. This includes the measurement and characterisation of soot in a number of flame configurations, as well as a variety of inorganic nanostructured materials with promising catalytic properties for applications such as hydrogen-generation.

We have furthermore continued to complement our experimental activities by accompanying modelling work. Our population balance models describing nanoparticle formation in flames, which are the most detailed models available, have now begun to reach a level of detail where we can include properties that are critical to the functionality of the particles, such as the crystal phase in titania.



Particulate matter (PM) spectrum recorded at CREATE Tower on 17th August 2017. Increased levels of nanoparticle concentrations are observed during a rain episode (Dr ZONG Yi-chen, RF, NUS, IRP3).

3.3.2 Update on work packages

WP3.1 Industrial network model of Jurong Island – Process Flow Sheets: energy and material

ZHANG Chuan's (PhD student, NTU, IRP3) research interests include energy system environmental assessment, urban energy system design and optimisation, sustainable heating and cooling, fossil fuel power plant decarbonisation, demand side response, and waste heat recovery. He has been mainly working on the CO_2-emission accounting functionality of the J-Park Simulator (JPS), and the design and optimisation of energy and material networks on Jurong Island. He has submitted a paper on the knowledge management within an Eco-Industrial Park (EIP) for efficient energy utilisation, in which an intelligent energy management system for EIPs based on an explicit domain ontology is proposed. By applying the JPS to solve a waste heat utilisation problem, it is shown that an ontology-based approach can facilitate intelligent decision-making, increase knowledge interoperability within an EIP, and can allow self-optimisation without human intervention within the Internet of Things (IoT).

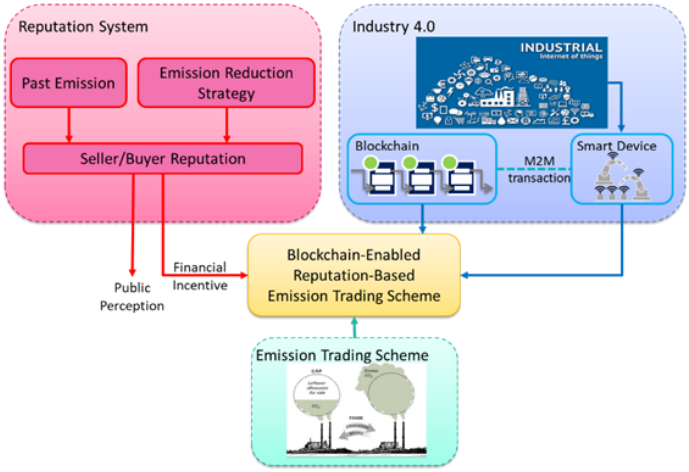
Related to this, LIM Mei Qi (Project Officer, NTU, IRP3) has been working on developing simulation models and ontologies for the J-Park Simulator. Her main research interest is in process modelling. She has produced quantitative estimates of CO_2-emissions from Jurong Island using the Carnegie Mellon (US 2002 Producer Price) Model and information available in the public domain. She then used this, as well as literature data, to quantify the CO_2-reduction potential of the J-Park Simulator.

ZHOU Li's (RF, NUS, IRP3) main research interest lies in the study of chemical process modelling and optimisation. Recently, she has been focusing on developing an ontology for Eco-Industrial Parks and J-Park Simulator (JPS) development. She has documented the eco-industrial park ontology, the underlying principles and the development steps in the JPS manual, for the guidance of future ontology development. She has submitted a paper on an ontology framework for information modelling and management, which presents a skeletal ontology for eco-industrial parks. A decentralised information management system is constructed for Jurong Island by applying the developed ontology. Jointly with Harshjyot SINGH and ZHOU Xiaochi, she has started building functionality which, based on the created ontological knowledge base, allows carrying out natural language information queries in the J-Park Simulator. At present, the JPS can answer simple questions such as "Which chemical plants produce benzene?

Overview of the J-Park Simulator (Leonardus Kevin ADITYA, Project Officer, NTU, IRP3).

Leonardus Kevin ADITYA's (Project Officer, NTU, IRP3) research interests include energy topics, especially environmentally friendly renewable energy and how to reduce CO_2-emissions produced by non-renewable fossil fuel energy. His current focus is on ontology and J-Park Simulator development. For the domain of electricity networks, the ontology was extended so that it can be used for

the electrical network on Semakau Island. It contains individual Web Ontology Language (OWL) files for every network component available, which are photovoltaic cells, batteries, diesel generators, load points, marine generators, transmission lines, and wind turbine. In addition, other parts of Semakau such as buildings are also represented in the individual OWL files, which can be seen connected to the Semakau Island nodes in the graphical visualisation. The relationship between the photovoltaics knowledge base and the real-time source data of solar irradiation is made to dynamically simulate the model in J-Park Simulator using PowerWorld – a commercial piece of software used in IRP4 to simulate power grids. In addition, the ontology has been extended to incorporate a Building Management System (BMS), specifically related to the CARES laboratory. Samples for every type of sensor knowledge base files were created to be the files which store the real-time data obtained from the sensors attached to equipment in the CARES lab. Ontology and knowledge base files were also created for the HVAC system of the CARES lab, which is connected to the process control system for the fume hood and other lab equipment. A poster giving a general overview of the J-Park Simulator was presented during the British High Commission event 'Science is Great' on 13 June 2017.



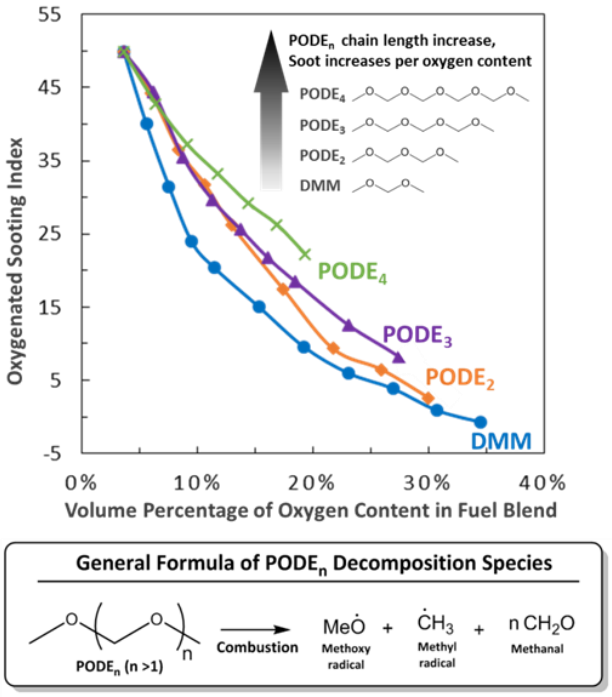
The concept of a blockchain-enabled emission trading scheme (Khamila Nurul KHAQQI, PhD student, NTU, IRP3).

Khamila Nurul KHAQQI's (PhD student, NTU, IRP3) research is focussed on blockchain applications with relevance to the chemical process industry. She has continued her investigation into blockchain -enabled emission trading and how the addition of a reputation system to the application and its utilisation to distribute trading benefits can provide added incentive for the participants to invest more in research and adoption of clean technology (see Fig. 3.3). Several of the research findings have been presented at international conferences, and a journal paper on incorporating a seller/buyer reputation system into a blockchain platform for emission trading has been submitted to Applied Energy. The next step is to connect the blockchain application to the J-Park Simulator so that the application is seamlessly integrated into the virtual eco-industrial park simulation platform. This connection is accomplished through a task ontology currently being developed. The task ontology will act as the logic and decision maker to execute trades in blockchain environment in an automated fashion.

WP3.2: Link of refinery products with engine operations – surrogate fuels: model and experiments

In order to complement the study of soot emission from fuels, Dr Maria BOTERO (RF, NUS, IRP3) has worked on the characterisation of soot particles from 'the Yale flame' – a reference co-flow diffusion flame defined in the combustion community, with nitrogen-diluted ethylene as fuel. She is particularly interested in the morphology and nanostructure evolution along the flame and between the centreline and wings. A thermophoretic sampling technique has been used to obtain soot samples in the flame, and transmission electron microscopy to image the particles. She further developed a fringe analysis algorithm that allows the study of the soot nanostructure with respect to the particle radius, with the aim to understand the carbonisation and oxidation processes that happen inside the flame. The experimental conditions were selected to allow the direct comparison with flame simulations performed by Dr Edward YAPP (Project officer, NTU, IRP3). They are comparing the experimental and simulation results to further improve the soot models and to gain insight of the chemical and physical phenomena involved in the formation of soot, the growth of the primary particles and aggregates and their oxidation. Simultaneously with Dr Jochen DREYER (RF, UCAM, IRP3), they built a system that allows the evaporation of liquid fuels into these ethylene flames. This evaporation system will enable a more controlled, systematic and fundamental study of soot formation from liquid fuels, such as commercial automotive and marine fuels and additives.

Drs TAN Yong Ren and Maria BOTERO (both RF, NUS, IRP3) have been working on the characterisation of the pollutant suppression ability of a promising oxygenated additive, poly oxy-methylene dimethyl ether (PODE), using the ASTM D1322 smoke point lamp (Fig. 3.4). Of particular interest is the chain length effect of the PODE series in soot suppression ability. Measuring the smoke point of the PODE series as well as other oxygenated additives has been completed to investigate the chain length effect and make a comparison of how PODE fare as compared to other selected oxygenated additives. Further characterisation of the PODE series such as through particle size distribution, Laser-Induced Incandescence (LII), and Laser-Induced Fluorescence (LIF) measurements will also be conducted so as to shed light on the sooting mechanism and species in the PODE flames. An increase in chain length in the PODE series, and thus an increase in oxygen content, does not improve the soot reduction ability possibly because the additional oxygen molecules do not produce radical species that could assist in soot reduction. Oxygen content is not the sole consideration in defining the sooting propensity, but decomposition pathways and molecular structure need to be taken into account in predicting sooting propensity of oxygenated hydrocarbons.



Soot suppression ability of the Poly Oxy methylene Dimethyl Ethers (PODE) series (Drs TAN Yong Ren and Maria BOTERO, both RF, NUS, IRP3).

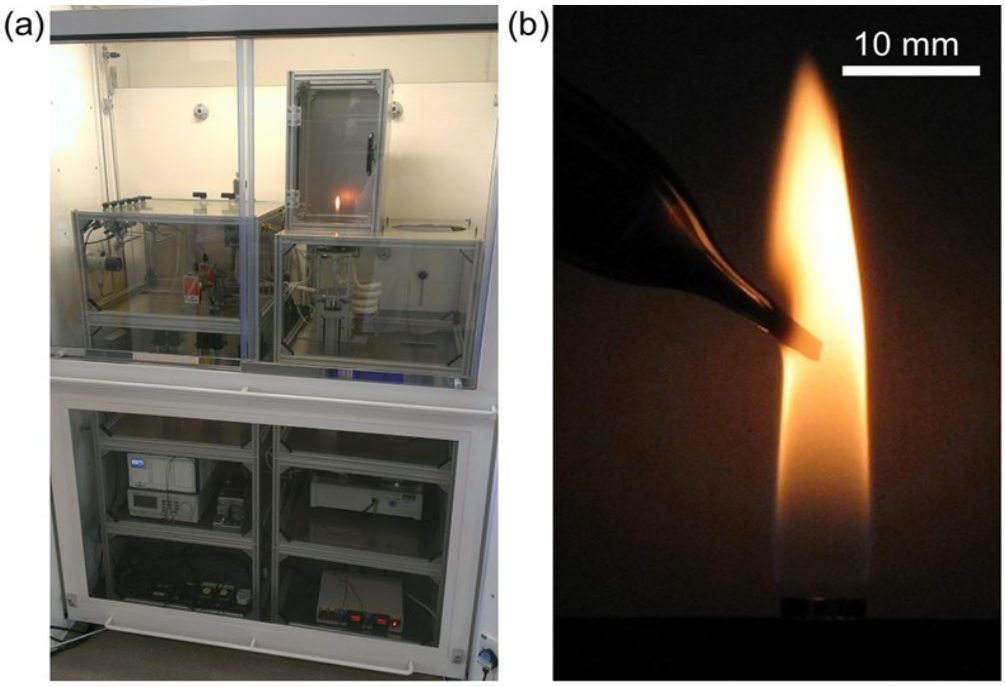
Drs ZONG Yichen and Maria BOTERO (both RF, NUS, IRP3) have jointly been working on measuring particle size distributions of PM2.5 and PM1.0 in Singapore, and apportioning possible sources. A particulate matter (PM) measurement station has been built at the terrace of the CREATE Tower, directly facing the busy AYE toll road. PM size distribution, temperature and humidity are automatically recorded at a frequency of 1Hz. A measurement campaign has been conducted, collecting about 180 hours of PM emission data and basic weather information. Current results reveal the impact of both traffic and weather condition on PM concentration and distribution (see Fig. 3.1). PM induced by traffic reaches a peak at about 8-9am in the morning and 7-8pm in the evening. The weather condition has been found to also play an important role in the nucleation and growth of ambient PM, and an interesting example is the precipitation. Large amounts of small particles (< 50 nm) are observed during and after each precipitation event. Currently, the second phase of the measurement campaign is ongoing, which aims to understand the nucleation and growth of PM induced by the typical tropical environment in Singapore. Secondly, Drs Zong and Botero have started preparing a campaign to measure PM size distributions from ships (harbour) and chemical industry emissions. This project, in conjunction with the J-Park Simulator, will lead to important information on the impact of marine engine and chemical technology emissions on the air quality in Singapore.

Furthermore, Drs ZONG and BOTERO have been constructing our brand-new laser lab at CARES for optical diagnostics of nanoparticles in combustion. The laser lab is aimed to study flame-made nanoparticles – soot and metal oxides – via state-of-the-art laser techniques. After several months of market survey and negotiation, we have finally ordered the LaVision FlameMaster system with Quantel pump and dye laser. The system can be used for LIF, LII, extinction/absorption and online temperature measurements. Once the laser system arrives in October we aim to conduct *in situ* investigations of the evolution of soot, from PAH reactions to particle nucleation.

The flame rig recently developed by Dr Jochen DREYER (RF, UCAM, IRP3) was moved to the new facilities of the Department of Chemical Engineering and Biotechnology (CEB), University of Cambridge, and the experimental work on soot formation during hydrocarbon combustion has started (Fig. 3.5a). Ongoing work aims at elucidating the influence of the fuel structure on the soot nucleation and growth mechanism. For instance, Maximilian POLI, a visiting Master student from the Technical University of Munich, has been using n-heptane/toluene mixtures for the vapour-fed diffusion flame and takes soot samples from within the flame at different stages of soot formation (Fig. 3.5b). This approach enables us to monitor the complete evolution of soot formation, starting from primary particle nucleation, particle growth, aggregation and agglomeration, to oxidation (Fig. 3.6). Comparing the soot number density, particle size distribution, and their time/temperature history to the utilised fuel gives insight into the combustion chemistry and soot generation mechanisms. The experimental results are compared to numerical simulations to improve state-of-the-art models of flames and soot formation and in the future facilitate predictions about the sooting tendency of different fuels and combustion systems.

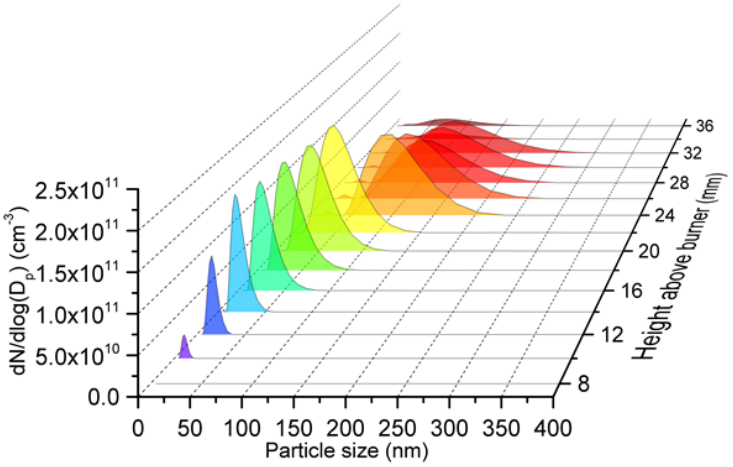
In another project, jointly with Angiras MENON (PhD student, UCAM, IRP3), IRP3 researchers have developed new techniques to characterise flame properties and physiochemical features of soot. Here, state-of-the-art Density Functional Theory (DFT) methods were applied to predicting the electronic structure of polycyclic aromatic hydrocarbons (PAHs), the main constituent of soot. The simulations were compared to experimental UV-Vis absorption and photoluminescence measurements of commercial PAHs. The work is expected to be submitted for publication this year and future ex-

periments will include more complex PAH mixtures and soot.



(a) Recently completed flame rig for soot and inorganic nanoparticle research inside a fume cupboard in the new CEB laboratory facilities. (b) A quartz sampling tube inside a vapour-fed diffusion flame. Samples are taken from within the flame at different stages of soot formation and the particle size and number density is measured (Dr Jochen DREYER, UCAM, IRP3).

In parallel to the ongoing experimental work, a new premixed stagnation flame is currently being implemented into the flame rig to extend the flexibility and versatility of the current setup. The stagnation surface hereby represents a well-defined boundary condition for comparison with numerical simulations while pre-mixing of the fuel and oxidiser allows us to compare the experimental data to 1-D combustion models. The addition of another burner for synthesising metal oxides in flames is scheduled for the end of the year.



Particle size distributions of soot taken at different heights above the burner along the centreline of a co-flow diffusion flame fed with a 20% toluene/n-heptane mixture (Dr Jochen DREYER, UCAM, IRP3).

WU Shaohua (PhD student, NUS, IRP3) is studying fundamentals of soot formation in combustion, with the primary goal being to develop a mathematical model to describe the soot formation and oxidation processes accurately. He is using population balance equations to describe the soot particle dynamics and the method of moments to solve these equations. The developed model is adopted in simulations of combustion in diesel engines as well as flames (both premixed and opposed-flow diffusion flames). Most recently, he has been working on the implementation of a moment projection method (MPM) to simulate the combustion process inside diesel engines. A new scaling method has been developed to treat the soot moments in the code so that higher computational efficiency can be achieved. The model has been tested in simulations of constant volume reactors, homogeneous charge compression ignition

engines, and direct injection diesel engines. For the diesel engine simulations, 18 test cases covering a wide range of engine operating conditions were considered to validate the applicability of the model. The model is able to complete all these simulations at a small computational cost. Furthermore, this model has been used to simulate a 'Great Wall' diesel engine and compared with experimental data. One paper based on this has accepted for the 9th International Conference of Applied Energy (ICAE). Besides engine simulations, flames have also been investigated. An in-house flame code has been successfully coupled with the MPM-based soot model. In order to overcome convergence difficulties related to the flame code, a post-processing method to solve the soot model separately has been developed and the results have been used as the initial condition for soot moments in the flame code. Results suggest that this post-processing method can significantly help achieve convergence for the flame code. Work is in progress to integrate the flame code with the post-processing code.

Jacob MARTIN (PhD student, UCAM, IRP3) is currently studying the formation of soot using molecular dynamics and quantum chemistry to look at gas-soot interactions and self-assembly processes within carbon materials. He is continuing to explore the impact of curved structures on the formation of soot. A poster was presented at the Carbon 2017 conference detailing the importance of using atom-centred dipoles to describe the flexoelectric dipole moment in these molecules. The impact of curved fragments on why some materials such as soot, charcoal or carbon fibres do not convert into graphite at high temperature is a topic of interest due to our recent work on understanding the degree of carbonisation in soot particles. On this topic, jointly with visiting student Laura PASCAZIO, we are currently simulating the hardness of different crosslinked materials using reactive molecular dynamics with the goal of correlating various crosslinked structures with the hardness of soot determined using nanoindentation studies. We have recently published a paper on the carbonisation of fullerene soot in the journal Carbon. Fullerene soot contains closed curved fragments (fullerenes) – similar structures have been found in Euro-VI soot. We found that coalescence of carbon cages led to the formation of giant fullerenes which can be produced up to C_{300}. This has important implications for the reactivity of soot as it is carbonised during combustion. Coalescence of small curved fragments into larger fragments decreases their reactivity.

WP 3.3: Nanoparticle/film flame synthesise—kinetics and application

SHENG Yuan's (PhD student, NTU, IRP3) research has been focused on Co_3O_4 and $Fe_xCo_{3-x}O_4$ nanoparticles and films synthesised in premixed stagnation flames. Built on the basis of earlier work on the optimisation of the burner set-up, the synthesis and electrochemical (oxygen evolution reaction, OER) performance of the Co/Fe oxides were studied in detail using a lean $C_2H_4/O_2/Ar$ flame. By accurately controlling the temperature of an in-house precursor vaporiser, tuning of the average size of Co_3O_4 and $Fe_xCo_{3-x}O_4$ nanoparticles between 3.5-5.5 nm was achieved. The particles can now be prepared with good reproducibility at production rates of up to 1 mg/min. When supported on Ni foam electrodes, the nanoparticle catalysts showed stable OER overpotentials of 295 mV at 10 mA/cm^2 and Tafel slopes of 39 mV/dec at the best, comparable to the performance of state-of-the-art (Fe-doped) Co_3O_4 catalysts synthesised by wet chemical methods. It was discovered that the environment inside the flame promoted formation of surface defect sites on the nanoparticles, which contributed to their high activity. Moreover, morphological control of nanostructured thin-films of the same materials were also carried out successfully on graphite substrates. Granular and columnar films can now be selectively prepared, with an intermediate film morphology found to be most beneficial to OER performance. To prepare for further studies on performance enhancement of the

Co/Fe oxide catalysts and on synthesis of other mixed transition metal oxide nanoparticles such as Cu_2O/ZnO and $NiCo_2O_4$, a two-stage precursor vaporiser with separate temperature control was designed and assembled. It will allow free tuning of chemical composition of binary metal oxides.

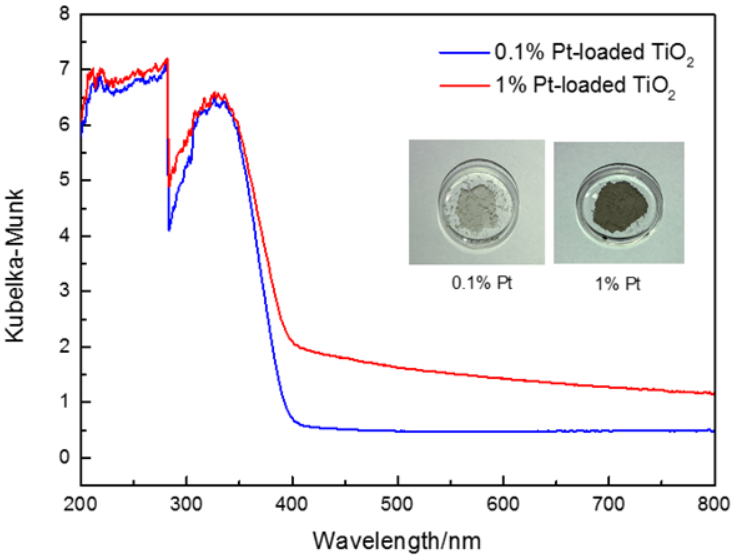
As preliminary research for laser diagnostics of flame-made nanoparticles, Dr ZONG Yichen (RF, NUS, IRP3) has theoretically investigated the laser-nanoparticle interaction and the laser-induced emissions are simulated in the model. For both soot and metal oxide particles (like TiO_2 in flame synthesis), the laser-nanoparticle interaction can be divided into three stages, namely the absorption of photons, the excitation of atoms, electrons, and ions, and the heating and evaporation of surface material. In the calculation, the particle volume fraction is proportional to the signal intensity and the size information can be inferred from the incandescence decay with the proper heat transfer model of nanoparticles.

WU Shuyang (PhD student, NTU, IRP3) has been focussing on flame-synthesised metal oxides for the application in photocatalytic hydrogen-generation and CO_2-reduction. The goal and significance of this work is to seek a sustainable way to produce green energy to substitute traditional fossil fuels and thus further address the global energy challenge, and mitigate greenhouse effects. This recent work can be divided into two parts. The first part is to complete previous characterisation work of flame-made TiO_2 for photocatalytic H_2-generation in the UV-Vis light region. The catalytic performance is superior to most of the results reported in the literature. The highest hydrogen-generation rate we have achieved so far is 21.9 mmol/g/h. The second part is concerned with using flame-made blue TiO_2 for H_2-generation in the visible light region. The precursor for synthesising TiO_2 is different from the first part of the work. We have shown that using $TiCl_4$ as precursor and controlling the reaction time within 15 min can produce Ti^{3+}-doped blue TiO_2. The Ti^{3+} and oxygen vacancies in the catalyst have a significant impact on the final application and it can improve the utilisation of the visible light for photocatalytic reaction. We have combined C_3N_4 and Ti^{3+}-doped TiO_2 to form a composite for the application of H_2 generation under visible light. According to zeta-potential data, TiO_2 has negative charges and C_3N_4 has positive charges. They can combine with each other to form heterojunctions by electrostatic attraction. The highest H_2-generation rate achieved is 2.1 mmol/g/h. The composite has a better performance than TiO_2 on its own (0.16 mmol/g/h) or C_3N_4 on its own (0.36 mmol/g/h).

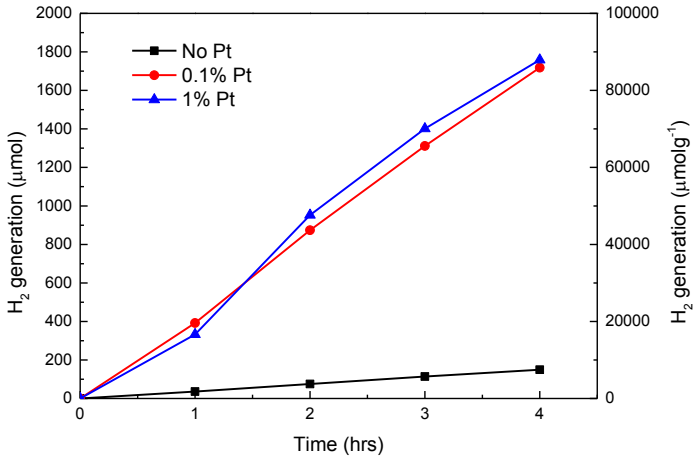
Energy shortage and environmental deterioration have been increasingly urgent and severe over the past decades. The limited non-renewable fossil fuels can hardly meet the growing energy demand. Thus, the exploitation of new green energy resources has become a global concern in recent years. Sunlight and water are abundant natural resources, which can be utilised to produce renewable energy in the form of hydrogen through water splitting. Thus, our work has been focused on this promising area. Our flame-made TiO_2 has many advantages over the traditional TiO_2 which is made by wet chemistry. The small particle size (10-15nm), the large specific surface area (150 m^2/g), the simple procedure and mass production can improve the hydrogen-generation rate significantly compared to other catalysts. Besides, the excellent durability and environmental-friendly property can make our TiO_2 nanoparticles a promising substitute for toxic heavy metal catalysts like CdS, CdO, and MoP.

The first part of our work shows that our flame-made TiO_2 can produce H_2 at a very high rate under UV-Vis light using very small amounts of Pt as co-catalyst. Although the catalytic performance in the UV-Vis region is excellent, the UV radiation in the solar light is limited and the activity may reduce significantly when using solar light. Thus, in the second part of work, we seek a new way to utilise

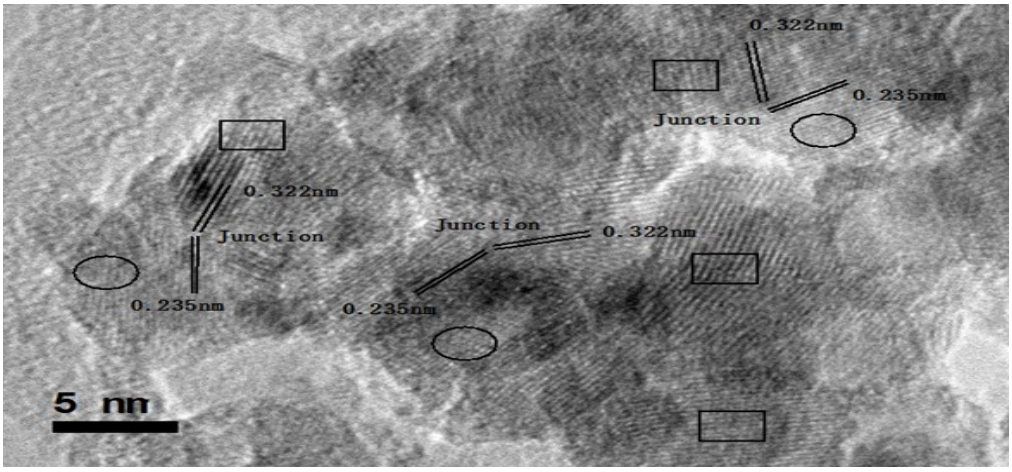
visible light for H_2-generation and other energy applications. We changed our precursor to $TiCl_4$ and produce the Ti^{3+} doped blue TiO_2. The Ti^{3+} and generated oxygen vacancies can promote efficient charge separations and enhance the utilization of photo induced electron to reduce H^+ to H_2. The goal of this work is to determine if there is a synergetic effect when combining blue TiO_2 and g-C_3N_4 for H_2 generation under visible light. As we know, TiO_2 is a good, stable, environmentally friendly catalyst for photocatalytic reaction, but the limited absorption of visible light inhibits its application. Graphite-like carbon nitride (g-C_3N_4) has been reported to be a non-toxic, stable and facile metal-free visible light photocatalyst. The band-gap of g-C_3N_4 is about 2.7 eV, indicating a strong absorption in the visible light region. g-C_3N_4 has displayed excellent properties in photodegradation of organic contaminant and H_2 evolution. However, the key issue with the high recombination of photoinduced electron-hole pairs is still limited the photocatalytic applications of g-C_3N_4. To resolve this problem, coupling g-C3N4 with other semiconductors has attracted much attention,



UV spectra of TiO_2 (ER=2.3) loaded with 0.1% and 1% Pt. When observing the colour of the samples after reaction, we can find the colour of 0.1% Pt loaded is almost white and 1% Pt loaded is deep grey. The deep colour is due to more Pt deposited on the catalyst. Deep colour will block the light TiO_2 could absorb and utilise. Thus, it may have a negative effect on the photocatalytic reaction. From the UV spectrum, we can also see 1% Pt has a large absorption compared to 0.1% Pt (WU Shuyang, PhD student, NTU, IRP3).



Photocatalytic H_2-generation with different Pt loads. The photocatalytic performance is almost the same for 0.1% and 1% Pt, but it increased substantially compared to no Pt added (WU Shuyang, PhD student, NTU, IRP3).

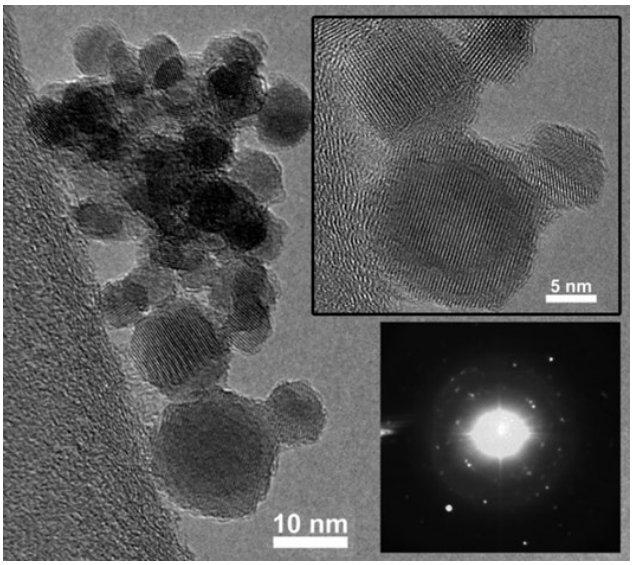


HRTEM image of TiO_2 with heterojunctions. The selected areas indicate heterojunctions with rutile (110) facets (boxes) and anatase (001) facets (ellipses). (WU Shuyang, PhD student, NTU).

which inhibits the recombination of photoinduced electron-hole pairs and thus improves catalytic performance.

Astrid BOJE's (PhD student, UCAM, IRP3) interests are in applying stochastic population balance methods and models to industrial process design and optimisation. Her research project is focussed on modelling industrial titania synthesis. She is currently developing a reactor network model for this which includes a detailed description of the particle population. This has been developed in close collaboration with our industrial co-sponsors Huntsman (previously Huntsman Pigments and Additives, now Huntsman Venator), and a paper has just been published. Most recently, an energy balance has been incorporated into the coupled gas-phase chemistry and particle model. This introduced additional numerical challenges, which are currently being addressed *e.g.* through weighted schemes to address high numerical rates, and the use of multithreading to improve efficiency.

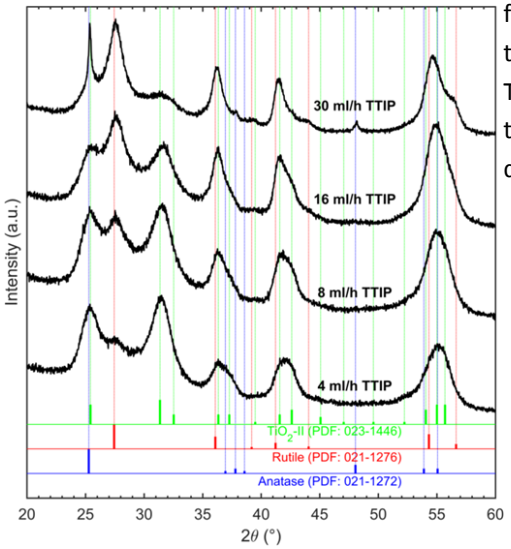
Casper LINDBERG's (PhD student, UCAM, IRP3) research is focused on investigating the flame synthesis of titanium dioxide nanoparticles using detailed population balance models, and in particular on developing a particle model that captures detailed morphological information and the crystal phase of particles. Such a model can be used to study the relationship between the reactor conditions under which nanoparticles form and their performance in the post-synthesis milling process. He is developing a detailed population balance model for titanium dioxide and improving the way in which particles are represented and evolve under surface growth and sintering processes. This allows tracking morphological properties such as the particle free surface area, neck size, and primary diameter. The detailed morphological data can be used to relate reaction conditions during particle synthesis to the milling properties of the particles. The model is currently being used to investigate TiO_2 synthesis from titanium tetraisopropoxide (TTIP) in a stagnation flame. Several simulated quantities can be directly compared with experiment, such as the numbers and size distributions of primary particles. A key next step will be to extend the model to the crystal phase of titanium dioxide particles.



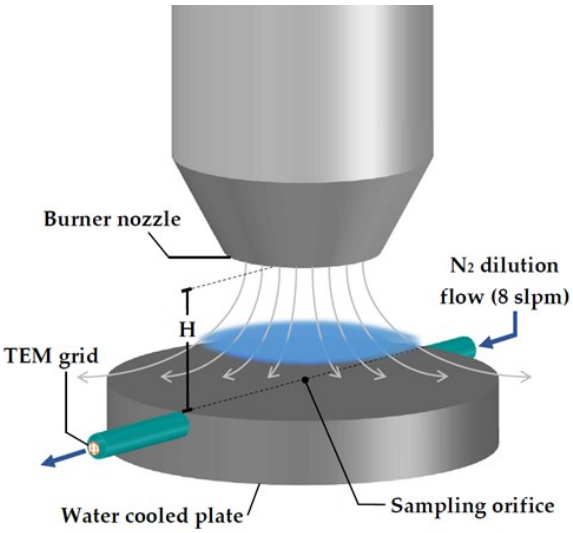
A high resolution TEM image of flame-synthesised TiO_2 particles with single-crystalline spherical primaries of 5-10 nm in diameter. The insets are a zoomed-in area showing lattice fringes (top) and a selected area electron diffraction pattern (SAED, bottom) (Manoel MANUPUTTY, PhD student, UCAM, IRP3).

Manoel MANUPUTTY's (PhD student, UCAM, IRP3) research project aims to investigate the formation and dynamics of TiO_2 (titania) nanoparticles in flames using both computational modelling and experimental tools, and more broadly nanoparticle formation and characterisation. Recent progress was achieved in developing and benchmarking experimental methods for nanoparticle sampling and measurements including with differential mobility spectrometer (DMS) and TEM sampling. The measured particle sizes and distributions were obtained for different experimental conditions which are then used to construct a model to describe the particle formation from gas phase precursor. The modelling effort builds upon previous successes where a one-dimensional stagnation flow model with a simple moment-based particle model was developed. The output from the moment-based model is then fed into a detailed particle code

through post-processing to resolve for particle properties which are directly comparable to experimental results. More recently, there has been growing interest to further understand phase transformations of titania nanoparticles in flames due to their importance in different catalytic applications. The current focus is an experimental investigation of these phase transformations, accompanied by model development.



Powder X-ray diffraction (PXRD) spectra of TiO_2 particles collected from laminar flame experiments stabilised on a rotating plate with varying precursor loading. The spectra show the presence of a mixture of mainly rutile and TiO_2-II phases as a function of the precursor loading. Anatase is observed only at a very high loading (Manoel MANUPUTTY, PhD student, UCAM, IRP3).



A schematic showing the experimental setup of a laminar flame stabilised on a stagnation plate with a built-in sampling line. The particles are sampled through an orifice, quenched with a nitrogen dilution flow, and deposited on a TEM grid for quantitative analysis (Manoel MANUPUTTY, PhD student, UCAM, IRP3).

WP 3.4: Modelling and optimisation of unit operations

Aravind DEVANAND (PhD student, NUS, IRP3) has been working on the creation of knowledge bases for power plants located all over the world. As a first step, he created an ontology for power plants which is capable of holding all the targeted information. It is also compatible with, and extends, the Eco-Industrial Park ontology developed by the J-Park Simulator group. Based on the power plant ontology, he developed code to take information for specific power plants from the Global Energy Observatory database and converted it into a set of knowledge bases built for the power plants. This knowledge base will be utilised for many other applications like optimisation, modelling, *etc.*

VO Chi Hung's (PhD Student, NUS, IRP3) research focuses on the construction of a metabolic model for the methanogen *M. maripaludis S2*, an organism capable of capturing CO_2 and producing useful chemical products such as methane. A refined setup of the experiment has been achieved, which required tackling successfully several challenging aspects of the setup. This included ensuring an anaerobic environment for the growth of the organism, and guaranteeing safe operation since flammable gases are involved. The setup of the experiment was finalised after consulting with several other professors and visiting a few other microbiology laboratories. Feedstock purchases and risk assessments have been completed and first experiments will be conducted once the risk assessments have been approved. Knowledge gained from investigating the metabolic reactions of this organism will allow genetic modification to enhance its CO_2 capture. The long-term goal is to demonstrate the feasibility of a bioreactor which can convert CO_2 into useful fuel or other organic products.

Pulkit CHHABRA (PhD student, NTU, IRP3) has continued his work on developing a generalized kinetic model for transesterification and saponification – key reactions involved in the process of bio-

diesel production. The model can account for any biodiesel feedstock composed of a specific set of fatty acids. The work involves the following three aspects: 1) modelling the reaction kinetics of biodiesel production, 2) optimising reactor operating parameters affecting the biodiesel production process, and 3) building an ontological framework for modelling and optimisation of biodiesel production process. He has recently completed a paper about the first part – the reaction kinetics for biodiesel production, which is due to be presented at the AIChE Annual Meeting 2017 in Minneapolis, Minnesota. In addition, a Bayesian estimation technique for estimation of the most sensitive parameters and their associated uncertainties has been applied. The next steps are reactor optimisation and the development of an ontology for the kinetic model to be incorporated into the J-Park Simulator.

WP 3.5: Automated model development and experimental design/decision support

Sushant GARUD's (PhD student, NUS) research focuses on the design and analysis of computer experiments for the parameterisation of complex systems. This involves (a) modelling and simulating complex chemical processes using custom-made process simulators, (b) studying various sampling techniques for designing computer experiments and developing adaptive intelligent sampling techniques for surrogate approximation, (c) analysing computer simulations with the help of parameterisation, and (d) studying the parameterisation on different levels in complex systems. Our review paper on the design of computer experiments published previously has received a positive response from the research community. He furthermore contributed to the development of the J-Park Simulator (JPS). He mainly worked on developing an agent related to a Building Management System (BMS) for the JPS. This agent uses data from the BMS to quantify the energy usage and chilled water requirement of the MAU in the CARES lab and visualises it on the JPS website. He currently investigates a guidance and evaluation scheme for selecting surrogate models (GENESIIS).

Other Activities and Achievements

- Prof. XU Rong (Co-PI, NTU, IRP3) gave an invited Keynote Speech at the 8th International Conference on Hydrogen Production in Brisbane, Australia, 29-31 July 2017. In addition, her paper, Tu *et al.*, "Investigating the Role of Tuneable Nitrogen Vacancies in Graphitic Carbon Nitride Nanosheets for Efficient Visible-Light-Driven H_2 evolution and CO_2 reduction" (DOI: 10.1021/acssuschemeng.7b01477) was selected as cover page for ACS Sus. Chem. Eng. and ACS Editors' Choice Article.
- Several IRP3 staff have been involved in presenting the J-Park Simulator to a number of stakeholders, including the Singapore Energy Market Authority, the National Research Foundation, the British High Commission, and the Prime Minister's Office Strategy Group.
- Dr Maria BOTERO (RF, NUS, IRP3), Manoel MANUPUTTY (PhD student, UCAM, IRP3), and Sushant GARUD (PhD student, NUS, IRP3) were selected as delegates and presented research posters at the Commonwealth Science Conference held in Singapore on 13-16 June 2017.
- Manoel MANUPUTTY (PhD student, UCAM, IRP3) gave an invited oral presentation on flame

synthesis of TiO_2 nanoparticles at the CEB Research Conference, 26-27 June 2017, at University of Cambridge. Manoel MANUPUTTY, Dr ZONG Yichen (RF, NUS, IRP3), and Astrid BOJE (PhD student, UCAM, IRP3) also presented posters at the same event.

- Astrid BOJE and Manoel MANUPUTTY (both PhD students, UCAM, IRP3) presented posters at the Cambridge Particle Meeting on 23 June 2017 in Cambridge.
- Dr ZHOU Li (RF, NUS, IRP3), Janusz SIKORSKI (PhD student, UCAM, IRP3), WU Shaohua (PhD student, NUS, IRP3), ZHANG Chuan (PhD student, NTU, IRP3), and Khamila Nurul KHAQQI (PhD student, NTU, IRP3) each presented a paper at the 9th International Conference on Applied Energy in Cardiff, UK, 21-24 August 2017.
- Dr ZHOU Li (RF, NUS, IRP3), Leonardus Kevin ADITYA (Project Officer, NTU, IRP3), ZHANG Chuan (PhD student, NTU, IRP3), and WU Shaohua (PhD student, NUS, IRP3) each spent several weeks as visiting researchers at Cambridge University.
- Jacob MARTIN (PhD student, UCAM, IRP3) presented a poster on the dipole moment in curved aromatic molecules at the Carbon 2017 conference in Melbourne, Australia entitled “Impact of fullerene-like structures in carbon materials: Describing the electrostatics of curved polycyclic aromatic hydrocarbons”.

3.3.3 Scientific output of IRP3

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP3 during the reporting period. A full list of publications during the period may be found in Appendix A.

Compartmental residence time estimation in batch granulators using a colourimetric image analysis algorithm and Discrete Element Modelling

McGuire, Andrew, Lee, Kok Foong, Dosta, Maksym, Mosbach, Sebastian, Rosenboom, Jan-Georg, Heinrich, Stefan, Kraft, Markus

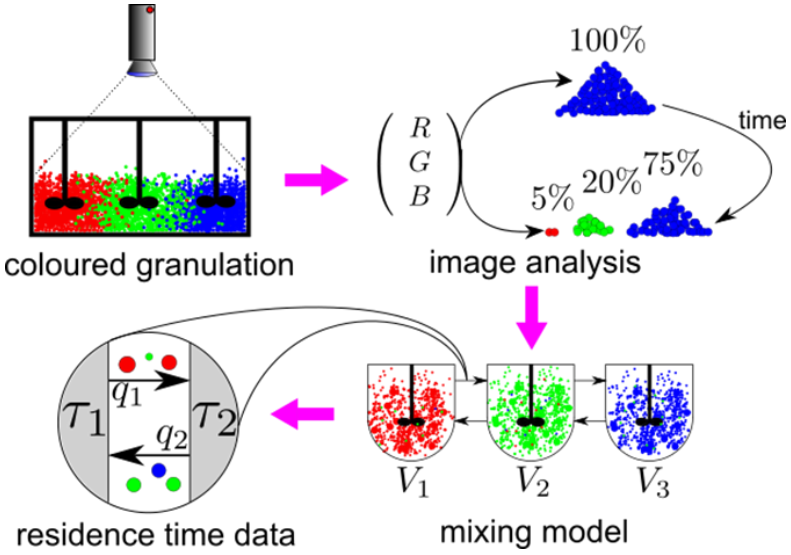
doi.org/10.1016/j.apt.2017.06.005

Highlights:

- An experimental method/colourimetric algorithm for the estimation of coloured particle volume fractions in regions of a batch granulator is presented.
- The algorithm is coupled with a mixing model to obtain residence times within key regions of system.
- The performance of the combined algorithm/model is assessed using three distinct granular test cases.

Abstract:

In this paper we present an experimental technique and a novel colourimetric image analysis algorithm to economically evaluate particle residence times within regions of batch granulators for use in compartmental population balance models. Residence times are extracted using a simple mixing model in conjunction with colourimetric data. The technique is applied to the mixing of wet coloured granules (binary and ternary systems) in a laboratory scale mixer. The resulting particle concentration evolutions were in qualitative agreement with those from the mixing model. It was seen that the algorithm was most stable in the case of the binary colour experiments. Lastly, simulations using the Discrete Element Method (DEM) were also performed to further validate the assumptions made in the analysis of the experimental results. Particle concentrations from the simulations showed the same trends as the experiment and highlighted the importance of particle size distributions on the DEM residence times.



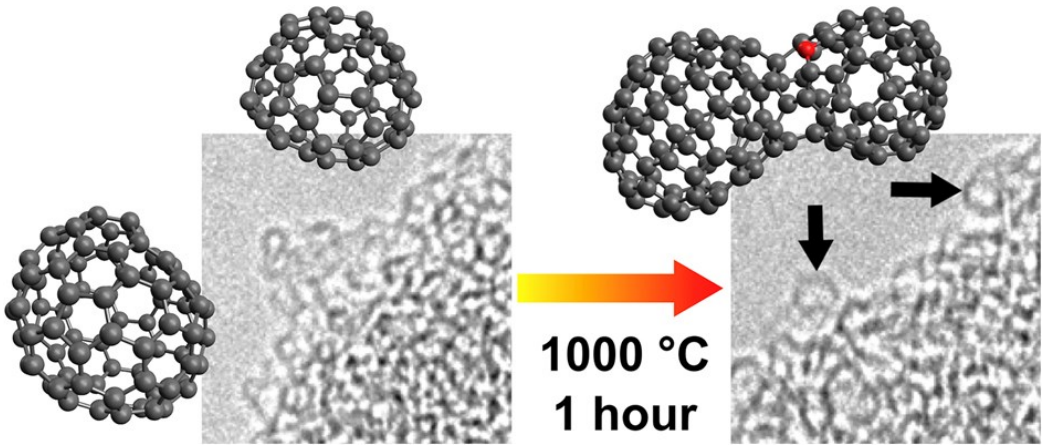
Giant fullerene formation through thermal treatment of fullerene soot

Martin, Jacob , McIntosh, Grant, Arul, Rakesh, Oosterbeek, Reece, Kraft, Markus, Soehnel, Tilo

doi.org/10.1016/j.carbon.2017.09.045

Abstract:

Coalescence of fullerenes into giant fullerenes (C_n n > 100) has been observed in the gas phase and inside carbon nanotubes. In this work, we demonstrate the formation of giant fullerenes by heating fullerene soot. Extracting the majority of the magic number fullerenes (C_{60} and C_{70}) allowed the underlying distribution of fullerenes in the solid state to be measured. Upon heating at 800–1000 °C for 30–60 min under vacuum the mass distribution of fullerenes was found to shift toward larger masses. High resolution electron microscopy was used to compare formation of giant fullerenes by



thermal heating and electron beam irradiation, showing the former produced more isolated giant fullerene fragments >1 nm in size. The driving force for coalescence and growth by thermal heating was suggested to be vertex strain at pentagonal sites, providing a route towards the synthesis of fullerenes up to C_{300}.

Theoretical study of the Ti-Cl bond cleavage reaction in TiCl4

Nurkowski, Daniel, Jasper, Ahren, Akroyd, Jethro, Kraft, Markus

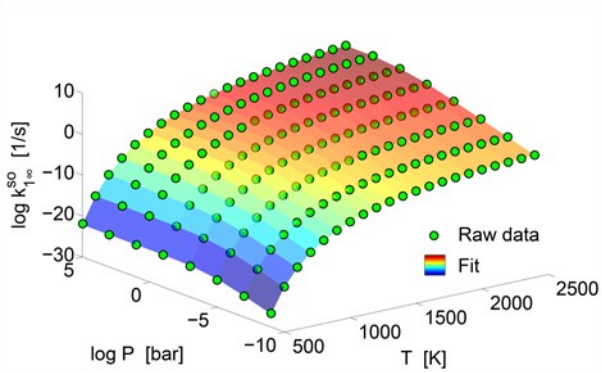
doi.org/10.1515/zpch-2016-0866

Highlights:

- A detailed theoretical study of the rate of the TiCl3 + Cl reaction is presented.
- Variable-reaction coordinate transition-state theory is combined with the master equation to estimate the rate coefficients at various pressures and temperatures.
- Multireference CASPT2(6e,4o)/cc-pVDZ level of theory is employed to dynamically build the reactive surface.
- Collisional energy transfer parameters for TiCl4-Ar system are estimated using a "one-dimensional minimisation" and classical trajectories methods.

Abstract:

In this work the kinetics of the TiCl4 <=> TiCl3 + Cl reaction is studied theoretically. A variable-



reaction coordinate transition-state theory (VRC-TST) is used to calculate the high-pressure limit rate coefficients. The interaction energy surface for the VRC-TST step is sampled directly at the CASPT2(6e,4o)/cc-pVDZ level of theory including an approximate treatment of the spin-orbit coupling. The pressure-dependence of the reaction in an argon bath gas is explored using the master equation in conjunction with the optimised VRC-TST transition-state number of states. The collisional energy transfer parameters for the TiCl4-Ar system are estimated via a "one-dimensional minimisation" method and classical trajectories. The Ti-Cl bond dissociation energy is computed using a complete basis set extrapolation technique with cc-pVQZ and cc-pV5Z basis sets. Good quantitative agreement between the estimated rate constants and available literature data is observed. However, the fall-off behaviour of the model results is not seen in the current experimental data. Sensitivity analysis shows that the fall-off effect is insensitive to the choice of model parameters and methods. More experimental work and development of higher-level theoretical methods are needed to further investigate this discrepancy.

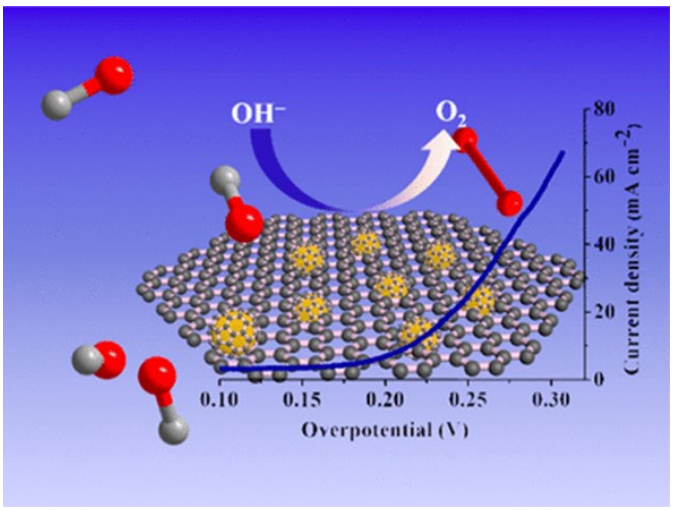
Phosphonate-Based Metal–Organic Framework Derived Co–P–C Hybrid as an Efficient Electrocatalyst for Oxygen Evolution Reaction

Tianhua Zhou, Yonghua Du, Danping Wang, Shengming Yin, Wenguang Tu, Zhong Chen, Armando Borgna, and Rong Xu

DOI: 10.1021/acscatal.7b00937

Abstract:

Cobalt phosphate is considered to be one of the most active catalysts for the oxygen evolution reaction (OER) in neutral or near-neutral pH media, but only a few transition-metal phosphates are investigated in alkaline media, probably due to their poor intrinsic electrical conductivity and/or tendency to aggregate. Herein, in situ-formed cobalt phosphate decorated with N-doped graphitic carbon was prepared using phosphonate-based metal–organic frameworks (MOFs) as the precursor. It can serve as a highly active OER catalyst in alkaline media, affording a current density of 10 mA cm–2 at a small overpotential of 215 mV on the Ni foam. A combination of X-ray absorption spectroscopy and high-resolution XPS elucidates the origin of the high activity. Our observations unveil that cobalt diphosphate having the distorted metal coordination geometry with long Co–O and Co–Co distances is mainly responsible for the high OER activity.



These results not only demonstrate the potential of a low-cost OER catalyst derived from phosphonate-based MOF but also open a promising avenue into the exploration of highly active and stable catalysts toward replacing noble metals as oxygen evolution electrocatalysts.

Combustion modeling in RCCI engines with a hybrid characteristic time combustion and closed reactor model

Dezhi, Zhou, Wenming, Yang, Jing, Li, Kun Lin, Tay, Markus, Kraft

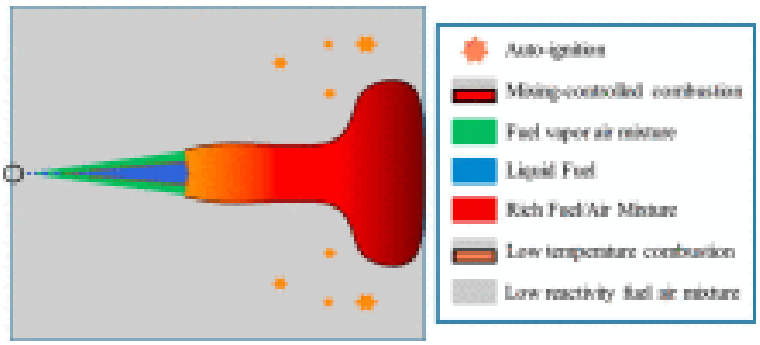
Doi: 10.1016/j.apenergy.2017.08.137

Highlights:

- A hybrid model based on the classical CTC model and CHEMKIN model was proposed
- The proposed hybrid model is able to model RCCI combustion with detailed chemistry
- The hybrid model is robust and efficient for RCCI combustion simulations

Abstract:

This study proposed a hybrid model consisting of a characteristic time combustion (CTC) model and a closed reactor model for the combustion modelling with detailed chemistry in RCCI engines. In the light of the basic idea of the CTC model of achieving chemical equilibrium in high temperature, this hybrid model uses the CTC model to solve the species conversion and heat release in the diffusion flame. Except for the diffusion flame, the auto-ignition in RCCI combustion is computed by a closed reactor model with the CHEMKIN library by assuming that the computational cells are closed reactors. The border of the transition between the CTC model and closed reactor model is determined by two criteria, a critical temperature and a critical Damköhler number. On the formulation of this hybrid model, emphasis is placed on coupling detailed chemistry into this hybrid model. A CEQ solver for species equilibrium calculations at certain temperature, pressure was embedded with CTC for detailed chemistry calculation. Then this combustion model was integrated with the CFD framework KIVA4 and the chemical library CHEMKIN-II and validated in a RCCI engine. The predicted in-cylinder pressure and heat release rate (HRR) show a good consistency with the data from the experiment and better accuracy than that computed from the sole closed reactor model. More importantly, it is observed that this model could save computational time compared with closed reactor model due to less stiff ordinary differential equations (ODEs) computation. A sensitivity analysis of the critical temperature and critical Damköhler number was conducted to demonstrate the effect of these two parameters in the current model.



Developing breakage models relating morphological data to the milling behaviour of flame synthesised titania particles

Lindberg, Casper, Akroyd, Jethro, Kraft, Markus

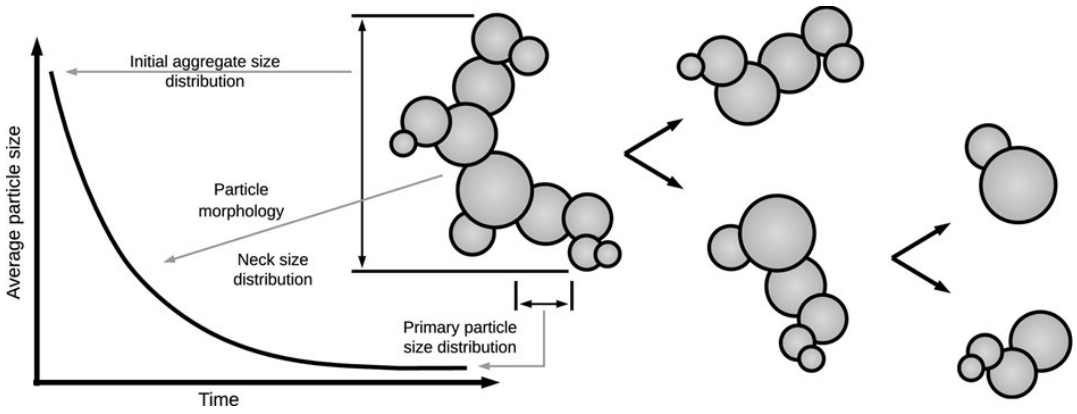
Doi:10.1016/j.ces.2017.03.016

Highlights:

- A hot wall titania reactor is simulated using a detailed population balance model.
- Breakage models are developed utilising morphological data from the particle model.
- Models are used to relate reactor conditions to the milling behaviour of particles.

Abstract:

A detailed population balance model is used to relate the reactor conditions of flame synthesised titanium dioxide particles to their milling behaviour. Breakage models are developed that utilise morphological data captured by a detailed particle model to relate the structure of aggregate particles to their size-reduction behaviour in the post-synthesis milling process. Simulations of a laboratory-scale hot wall reactor are consistent with experimental data and milling curves predicted by the breakage models exhibit features consistent with experimental observations. The selected breakage model considers the overall fractal structure of the aggregate particles as well as the neck size between neighbouring primary particles. Application of the model to particles produced under different reactor residence times and temperatures demonstrates that the model can be used to relate reactor conditions to the milling performance of titanium dioxide particles.



Impact of Various Factors on the Performance and Emissions of Diesel Engine Fueled by Kerosene and Its Blend with Diesel

Wenming, Yang, Kun Lin, Tay, Kah Wai, Kong

Highlights:

- A compact but robust skeletal chemical reaction mechanism for the combined combustion of diesel and kerosene is developed in this work
- An extensive numerical investigation on the combustion and emission formation of a diesel engine fueled by kerosene and its blend with diesel has been presented
- The impact of major factors such as the fuel blend ratio, fuel injection timing, fuel injection

duration and fuel injection angle on the performance of the engine was examined.

Abstract:

As a response to the single fuel concept introduced by the North Atlantic Treaty Organization (NATO) as well as increasing cases of adulteration of diesel fuel with kerosene, it is important for us to have a better understanding on the performance of diesel engine fueled by kerosene and its blend with diesel. An extensive numerical investigation on the combustion and emission formation of a diesel engine fueled by kerosene and its blend with diesel is presented in this paper. The impact of various factors such as the fuel blend ratio and the fuel injection angle on the performance of the engine was examined. The results indicated that the fuel with a higher percentage of kerosene tend to give higher maximum power output, lower carbon monoxide emission. It is also found that for each fuel, there is an optimum fuel injection angle that gives the highest maximum power output and relatively low emissions.

The Integrated Chemicals and Electrical Systems Operation , or ICESO (pronounced I-say-so), group focuses on the Jurong Island electrical sub-network to optimise coordination of energy generation and consumption within the electrical/chemical system. ICESO seeks to discover how a tighter integration of electrical supply network and chemical supply plant load can reduce the carbon footprint of the chemical industry, given the trend towards smart grids.

The research programme is divided into six work packages:

WP 4.1: Fast numerical algorithms for solving large MPC problems for networked systems

WP 4.2: Extension of Multiplexed MPC to non-Gaussian noise, nonlinear and hybrid models

WP 4.3: Modelling and Control of heterogeneous power generation networks with chemical process loads

WP 4.4: Modelling of chemical process load and local generator-based electrical network akin to Jurong Island

WP 4.5: Model building, integration and maintenance

WP 4.6: Demonstration of proposed algorithms on pilot scale

The ICESO group is led by PIs:

Prof Gehan AMARATUNGA (Cam);

Prof Jan MACIEJOWSKI (Cam);

Prof Keck Voon LING (NTU);

Prof Sanjib Kumar PANDA (NUS)

Prof. Gehan Amaratunga *and* ***Prof. Jan Maciejowski,***

University of Cambridge

PIs, IRP4

October 2017

3.4.1 IRP4 Research Overview

ICESO aims to exploit synergies in the generation and consumption of electrical and thermal energy, in the context of industrial consumers, especially in the chemical industries, in order to reduce the amount of energy that needs to be generated, and hence to reduce the associated carbon emissions. The expertise in the ICESO team is concentrated in control systems and in electrical power distribution. Research Fellows have been recruited with expertise in multi-agent power system control, artificial intelligence methods for smart grid configuration, communication strategies for power system data acquisition and for real time control, model predictive control, in non-convex optimization, and in power network analysis. Resources available to IRP4 include two lab-scale microgrids (one at NTU, one at NUS), which include real and simulated renewable and traditional generators, and we have acquired a powerful real-time power system simulator.

IRP4 is addressing questions related to coordination of electrical and thermal power generation, distribution and consumption. The possibility and impact of introducing renewable generation, in addition to traditional generators, are being investigated. Also heterogeneous structure of the power system, including the incorporation of microgrids as subsystems, is being studied. This is particularly suitable for including the chemical plant electrical network and its loads, together with any co-generation sources, as an extension of the distribution system. With IRP3, directly linking the electrical loads (e.g. pumps, motors) to chemical process parameters in a simulation environment is being explored. The impact of such loads on the larger network, for example in terms of power factor and harmonic generation, is a key consideration in terms of modelling. At present, various problems are being addressed, both standard power system problems and new ones which arise as a result of these various possibilities. Major questions which have been identified are: (1) Is it appropriate to maintain the traditional time-scale hierarchy for controlling power systems, when the range of time constants of equipment is being reduced, and computational algorithms are getting more powerful? (2) One strategy which has been proposed, for coping with renewable generation, is to configure interface inverters such that all generators behave like traditional synchronous generators – so-called ‘virtual power plants’; is this really the best way to proceed? (It seems unlikely.) A range of problems is being considered, from automatic voltage control to optimal despatch problems, with both centralized and decentralized control structures being investigated.

The research vision is to work towards a new architecture of control, estimation, and optimization for a `smart future grid' that facilitates the optimal dynamic operation of power systems at intervals of a few minutes. This dynamic operation contrasts with the usual `quasi-static' operational regime of the currently operated power systems that look for an update at every half an hour or a longer time interval.

3.4.2 Update on work packages

WP 4.1: Fast numerical algorithms for solving large MPC problems for networked systems

Prof Jan Maciejowski (PI, CAM, IRP4) reported that a journal paper has been written, with Dr Anthony Tran and Prof. Keck Voon Ling, setting out the theory of the Generalised Dissipativity Constraint. It will be submitted for publication once a good example has been finalised.

DANG V. Thuy (PhD Student, NTU, IRP4) reported that he submitted a journal paper about control algorithm for networked/embedded systems measurement dropouts and time-varying computing power. The paper is currently under review. In the middle weeks of July-2017, DANG V. Thuy (PhD Student, NTU, IRP4) presented a paper at the 20th World Congress of the International Federation of Automatic Control in Toulouse, France and attended the TEMPO Workshop on embedded optimisation in Bratislava, Slovakia. The collaboration project with A. Eberle, a German company, has started in the beginning of June-2016. This project is being led from the CARES side, by Prof. LING Keck Voon (PI, NTU, IRP4) and Prof. Jan MACIEJOWSKI (PI, CAM, IRP4). DANG V. Thuy (PhD Student, NTU, IRP4) reported that the company has sent their hardware device to Singapore, and that he is working on implementing Model Predictive Control on the device using his optimisation algorithm. The first application is automatic voltage regulation. Once the implementation and simulation in CARES Singapore have been completed, DANG V. Thuy (PhD Student, NTU, IRP4) will visit the company to test the algorithm with a real power system.

WP 4.2: Extension of Multiplexed MPC to non-Gaussian noise, nonlinear and hybrid models

There has been no work on this WP in this period.

WP 4.3: Modelling and Control of heterogeneous power generation networks with chemical process loads

Ashok KRISHNAN (PhD student, IRP4, NTU) has been working on multi-energy scheduling of generators as a part of an energy management system (EMS) suitable for large industrial parks like Jurong Island. The complexities in this problem arise from the significant coupling which exists between various system components. Most industries require electricity, steam and cooling for their processes. Combined cycle power plants generate most of the electricity on Jurong Island. They can also be used to service the demand for thermal energy and cooling when operated in combined heat and power (CHP) or combined cooling heat and power mode (CCHP). Modern power generation networks are also heterogeneous in nature comprising renewable energy sources (RESs), battery energy storage systems (BESSs) and conventional fossil-fuel based generators.

Ashok KRISHNAN (PhD student, IRP4, NTU) has also been working on developing a comprehensive modelling framework to accommodate these diverse system elements. The model has provisions for

incorporating load management strategies which account for unique load characteristics in different industries. The model integrates the supply of heat and electricity through detailed models of CHP plants and boilers. The model is developed using the mixed logical dynamical (MLD) framework with scheduling problems solved using a model predictive control scheme. Ashok KRISHNAN (PhD student, IRP4, NTU) is currently working on integrating the optimal power flow (OPF) problem in the EMS. The OPF problem is used to minimize power losses in the network and to verify the feasibility of results obtained from the scheduling module in the EMS. Power sharing between neighbouring industrial parks is also examined through the formulation of a multi-microgrid EMS problem.

Xuebing CHEN (PhD Student, NTU, IRP4) and Dr Yuaho SUN (SRF, NTU, IRP4), under supervision of Associated Prof RUSLI (Co-I, NTU, IRP4) and Prof Gehan AMARANTUNGA, (PI, CAM, IRP4) reported on the development of a data management system for µPMU project to achieve data acquisition and centralization for grid networks. The system is essential to implementation of real-time data processing and data analysis. The data acquisition software is developed based on an open source software OPEN PDC. It is capable of receiving multiple µPMU data in real-time.

The data analysis software has been developed to efficiently convert the coded data in real time stream from machine to readable database files. The files are then stored in the local database. An interface between the database and Matlab is set up for µPMU data analysis.

In addition, Xuebing CHEN (PhD Student, NTU, IRP4) and Dr Yuaho SUN (SRF, NTU, IRP4) designed the software to link up the µPMU sensors to our server on a cloud. It provides an easy access platform/ interface to allow follow up layers to process the data to evaluate and forecast based on the received properties from the present condition.

Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported on her studies that popular tools used for electrical simulations have been found to be disassociated with the economic computations and the CO2e estimations required for attaining the objectives of C4T. A toolbox/block-set is hence being

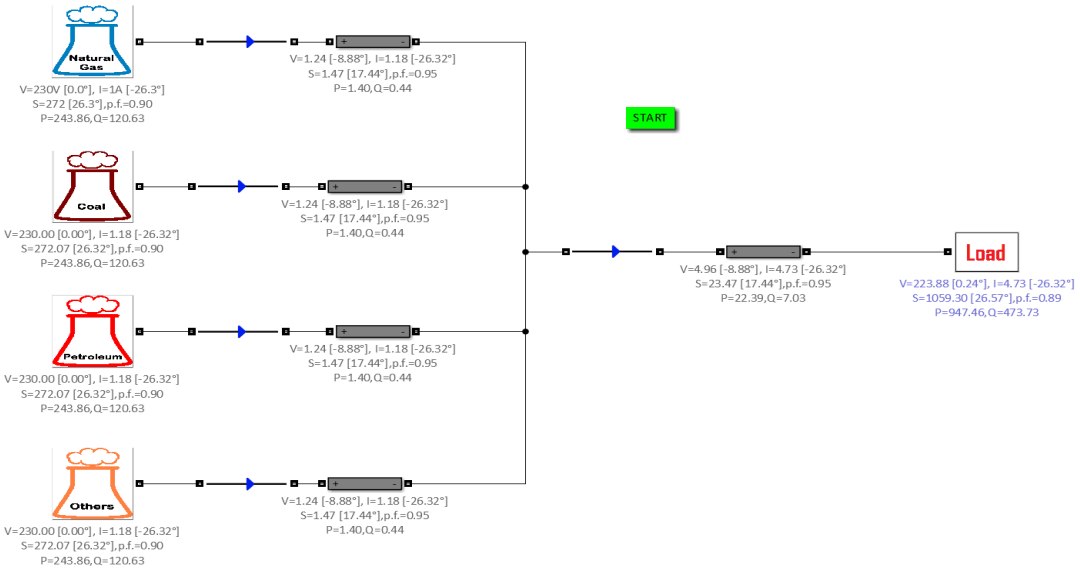


Figure: A sample simulation that automatically displays the corresponding steady-state electrical parameters for heterogeneous power generation is shown. The block-set would later include automated display of cost incurred for energy and carbon-dioxide equivalent emissions.

developed that automatically computes the electrical parameters as well as the associated economic and CO2e information, with due consideration to the heterogeneous fuel-type used in different generation units. Even though this task's planning and execution are very challenging, an initial ver-

sion has been tested with electrical parameters alone and a sample display is shown in the Figure above.

Prof Jan MACIEJOWSKI (PI, CAM, IRP4) reported that work has continued on the development of a decentralized control scheme for Automatic Generation Control of a multi-area power generation and distribution system, using model predictive control enhanced by the General Dissipativity Constraint. This work has been mainly done by Dr Anthony TRAN (RF, NTU, IRP4).

A novel scheme has been demonstrated for controlling a multi-generator power network using nonlinear model predictive control with global optimization based on Bernstein polynomials. A paper entitled *Optimal nonlinear model predictive control based on Bernstein polynomial approach* has been accepted for the IEEE Conference on Decision and Control to be held in Melbourne, Australia, in December 2017. This work has been led by Dr Bhagyesh PATIL (RF, NTU, IRP4).

Partha Pratim BISWAS (PhD student, NTU, IRP4) reported that state-of-the-art variants of differential evolution algorithms for single objective optimization and evolutionary algorithms for multi-objective optimization have been applied to various problems in power system. Advanced constraint handling (CH) techniques of evolutionary algorithms have been integrated with variants of DE to handle operational and security constraints in power system. A proper CH method has been found to be more effective in optimizing constrained, non-linear power system problems. Optimal power flow problem has been formulated with stochastic wind and solar power, active and reactive power losses have been minimized in radial distribution network, complex problems on windfarm layouts have been solved using evolutionary algorithms. All these results and findings have been published in reputed journals.

In addition, Partha Pratim BISWAS (PhD student, NTU, IRP4) reported that future work on problems such as economic-environmental dispatch will be formulated and solved incorporating renewable sources. CH techniques will be integrated with multi-objective evolutionary algorithms (MOEA) and will be tested on constrained power system problems with multiple objectives. Problems such as unit commitment, phasor measuring unit placement will also be investigated.

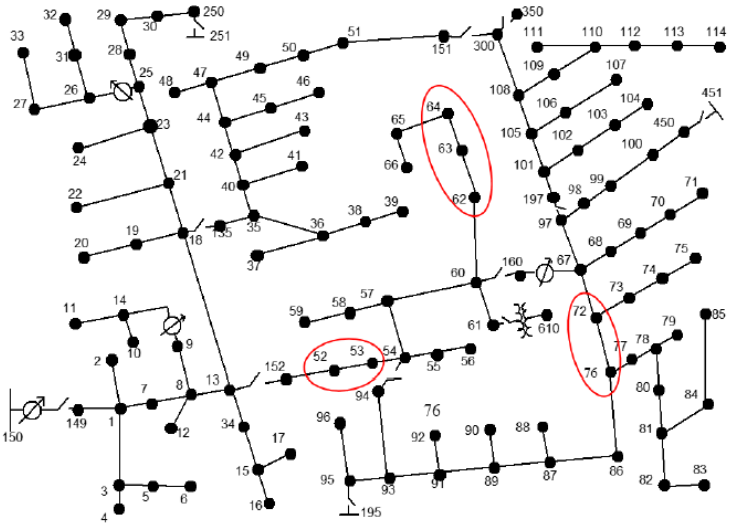
CHEN TengPeng (PhD student, IRP4, NTU) reported on his PhD thesis, ``Robust and distributed state estimation for power systems" examined and accepted by the school of EEE. Power system state estimation (PSSE) plays an important role in power system operation. In this thesis, an analytical

Real-time power system state estimation: a simulation using RT-LAB

equation is derived using the Influence Function (IF), a tool from robust statistics, to calculate approximately the variances of the estimates of these robust estimators such as Quadratic-Constant

(QC), Quadratic-Linear (QL), Square-Root (SR), Multiple-Segment (MS) and Schweppe-Huber Generalized-M (SHGM). This variance formula has many advantages: (i) It can be used to express the variance of state estimate as a function of measurement variances thus enabling the selection of sensors for specified estimator precision; (ii) It can be used to design an optimal estimator; (iii) Although numerical methods can also be used to find variance, the derived equation as a mathematical function is more insightful and requires less computational effort. In addition, this thesis proposes a robust estimator based on the maximum likelihood criterion, and a noise model with t-distribution probability density function (pdf). The thick tail property of t-distribution down weighs outliers so that the proposed estimator is robust to outliers. Instead of solving the optimization problem numerically, the IF is employed to give an approximate solution to reduce computational load. Moreover, a robust estimator based on the moving horizon estimation (MHE) technique is proposed for PSSE in this thesis. This robust estimator is called re-weighted MHE. The proposed estimator reduces its sensitivity to the outliers by updating their error co-variances in real time and then uses these re-weighted error co-variances for robust PSSE. Compared with other robust state estimators such as MS and Least Absolute Value (LAV) estimator, one advantage of the proposed estimator is that it can directly incorporate constraints on the states to mitigate the outliers. Finally, the centralized estimator is not applicable when the size of power system becomes very large. Two distributed versions of the proposed robust estimator based on MHE are considered: distributed MHE (DMHE) and partitioned MHE (PMHE). For DMHE, each local area will obtain the states of the whole system. It is suitable for the advanced applications such as wide-area monitoring systems (WAMSs) that require the system-wide state to be available to all the regional transmission organizations (RTOs). For PMHE, each local area only uses its local measurements and the states of border buses exchanged from its neighbourhoods. It solves a smaller optimization problem to obtain the states of local states. Therefore, the communication load and computational load are reduced.

Finding exhaustive solutions for Optimal PML Placement: A intermediate step where the nodes in the network are categorized following specific rules.



Lu SUN (PhD student, NUS, IRP4) worked, under supervision of Prof Jan MACIEJOWSKI (PI, CAM, IRP4) on the paper “Robust State Estimation with t-Distribution Noise: Influence Function Approach’. A robust and efficient estimator is proposed in the paper that can be used for robust state estimation in general systems, including power systems. He also worked with Dr SUN Yuhao (SRF, NTU, IRP4) and Prof Gehan AMARATUNGA (PI, CAM, IRP4) on the paper “Robust State Estimation with PMU Packet Loss in Smart Grids”. The paper studies the state estimation algorithm that can handle missing packets during the real-time observation of the power network.

Xueheng QUI (PhD Student, NTU, IRP4) reported on his project “Forecasting Algorithms with Applications in Power Systems”. Its primary objective is to reduce the probability of faults occurring with

the help of accurate fault prediction methods. Currently, his research field is mainly focused on deep learning methods and ensemble algorithms. In his study, various kinds of time series forecasting algorithms have been reviewed, including Artificial Neural Network (ANN), Support Vector Regression (SVR), Random Forest (RF), Kernel Ridge Regression (KRR), Deep Belief Network (DBN), Long Short Term Memory (LSTM) and ensemble methods. A decision tree ensemble method called least square estimation based oblique RF has been proposed for time series forecasting, which has been published in the journal Information Sciences recently.

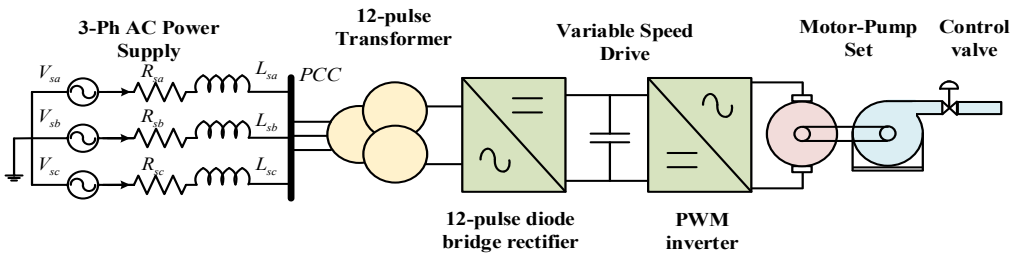
Xueheng QUI (PhD Student, NTU, IRP4) investigated a randomized version of neural network, which is called Random Vector Functional Link Network (RVFL), and proposed a both effective and efficient learning model for short term electricity load demand forecasting by combining Discrete wavelet transform (DWT), EMD and RVFL with incremental learning. This work has been submitted to Knowledge-Based Systems.

Moreover, he reported that several conference papers have also been published. An Empirical Mode Decomposition based ensemble kernel machine is proposed for electricity price forecasting, which has been published in International Conference on Computational Science (ICCS2017). An ensemble method for wind power forecasting, ramp rate forecasting and ramp classification has been accepted by SSCI 2017.

WP 4.4: Modelling of chemical process load and local generator-based electrical network akin to Jurong Island

Srinivasarao Rao KAMALA (PhD Student, NUS, IRP4) reported that variable speed drives (VSD) operations in petrochemical plants on the Jurong Island in Singapore causes power quality issues in the distribution system. Passive harmonic mitigation techniques, 12-pulse/24-pulse transformers are being used to minimize the voltage/current harmonics because of their lower cost, but these methods are less efficient. A possible potential solution for this problem is to use the active power filters (APFs). However, power electronic drives with motor loads which have negative impedance characteristics make the system susceptible to oscillations and thus creates small signal stability problem in the distribution system. In the latest report, power quality improvement with the APFs and the preliminary results of impedance estimation of the three phase voltage source inverter (VSI) are given.

The power quality improvement in the petrochemical plants obtained by using the APFs are verified through a down scale experimental laboratory setup of 9.0 kW motor drive system. The schematic of the power system architecture of the petrochemical plant for the pumping operations is shown in the figure below. The load is supplied from the three phase AC supply system with 415V, 50Hz



Schematic of power system architecture for pumping operations in petrochemical plant

through a 12-pulse rectifier to the motor drive system. The experiment has been conducted for the

following three different scenarios viz: drive system with 12-pulse rectifier, harmonic mitigation of 6 -pulse drive system with the SAF, harmonic mitigation of drive system with the AFE.

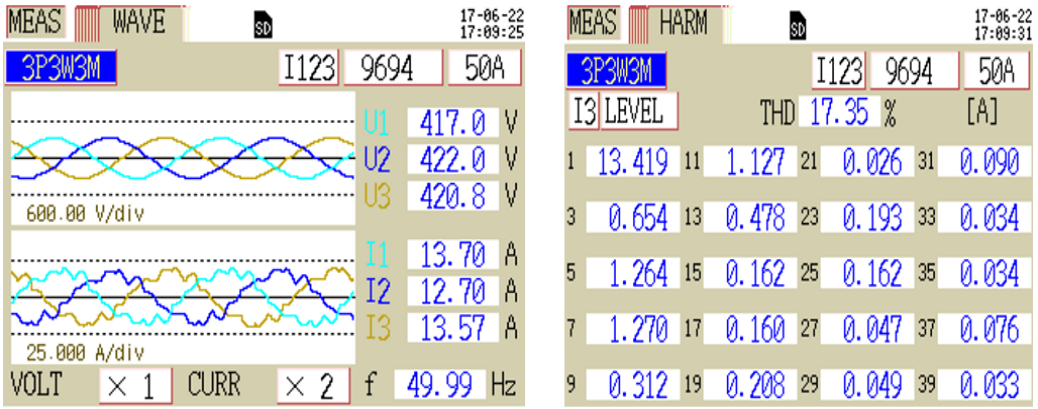


Fig. a) Three phase source voltage and current waveforms feeding 12-pulse rectifier drive system with SAF (b) Total harmonic distortion (THD) analysis of source current waveform.

The three phase source voltage and current waveforms, THD content in source current and the supply apparent values of the conventional 12-pulse drive system with 9.0 kW load applied to the motor-generator set are shown in the figure below (a) and (b). The THD value in the source current is 17.35% in the conventional system and the % THD is not within the limits of IEEE guide lines.

The three phase supply waveforms, %THD content in source current and the supply power values

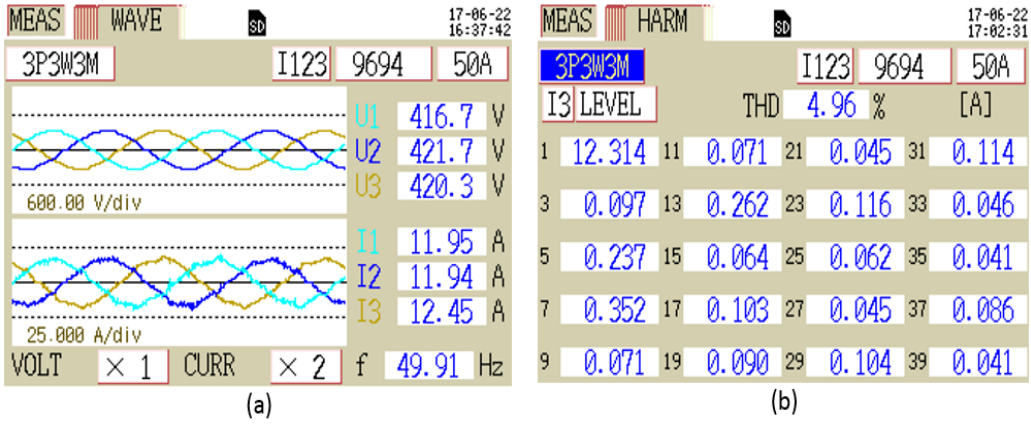


Fig. (a) Three phase source voltage and current waveforms feeding 6-pulse rectifier drive system with SAF (b) Total harmonic distortion (THD) analysis of source current waveform.

are showed in the Fig. below (a) and (b) with the Shunt Active Power Filter (SAF) connected to 6-pulse drive system. The THD in the source current has been reduced from 17.35% to 4.96%, improved by 28% by removing bulky 12-pulse transformer and by installing SAF.

The three phase supply waveforms, %THD content in source current and the supply power values are showed in the figure. below (a) and (b) with the Active Frontend Converter (AFE) connected to the drive system. The THD in the source current has been reduced from 17.35% to 8.64%, improved by 51% by removing 12-pulse transformer and by installing the AFE.

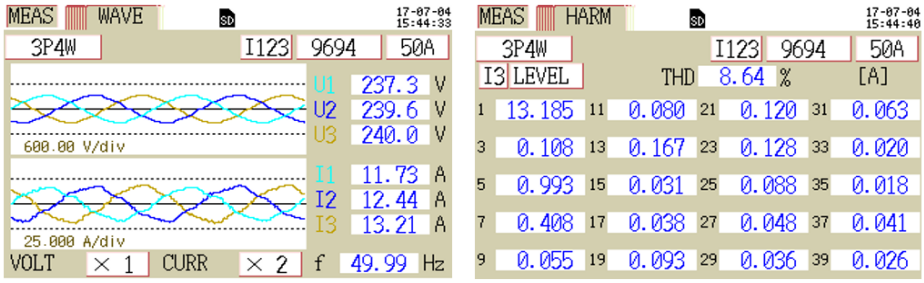


Fig. (a) Three phase source voltage and current waveforms feeding drive system with AFE (b) Total harmonic distortion (THD) analysis of source current waveform.

Small-signal stability is a great concern for distributed power systems with a large number of regulated power converters. These power converters exhibit a negative incremental input resistance characteristics within the output voltage regulation bandwidth. Impedance estimation is an important task to address the small signal stability of the three phase distribution system.

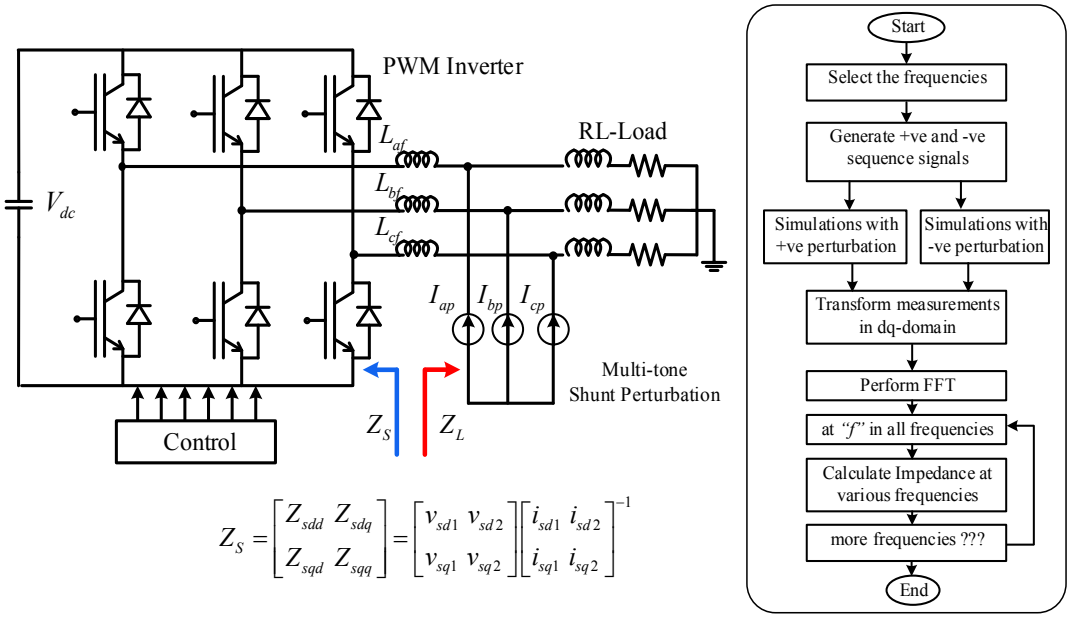
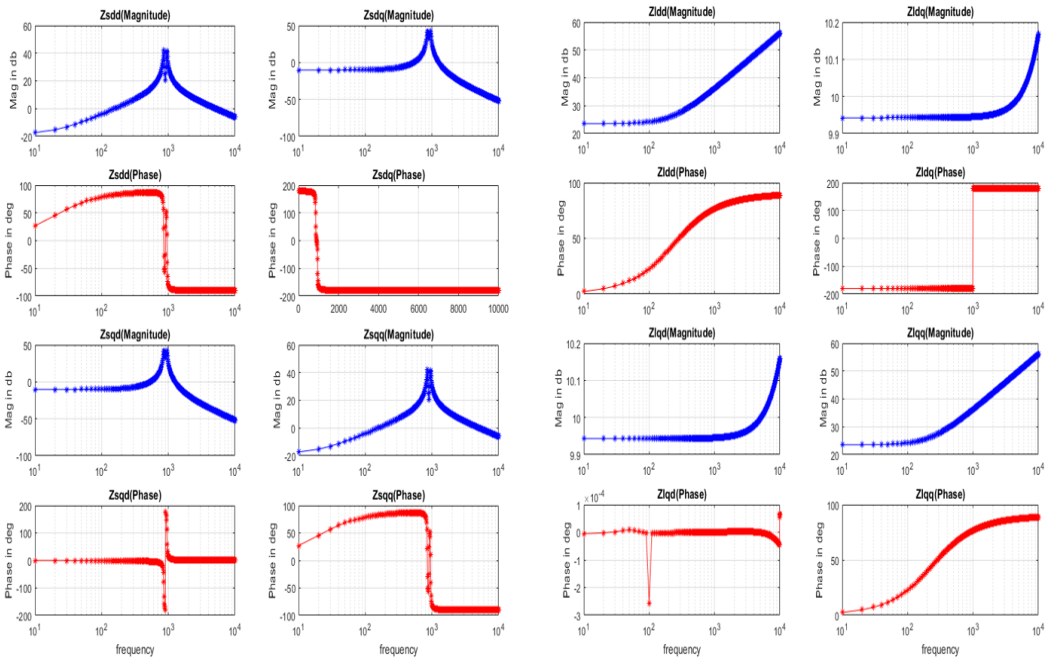


Fig. PWM-VSI with RL load and the impedance estimation algorithm in dq-domain for the VSI using multi-tone perturbation



(b)

Fig. (a) Output impedances in dq- domain of PWM-VSI with RL load (b) input dq-Impedances of RL-load

Synchronous frame (dq-frame) impedances of the three phase VSI with RL load using multi-tone shunt injection algorithm estimated in MATLAB/Simulink platform is depicted in the above Fig. The small signal stability of the multi machine power system of the petrochemical plant is being carried out using General Nyquist-stability Criteria (GNC).

Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported the necessity for an analytical tools which is capable of predicting voltage collapse in complex networks by identifying voltage-weak points and areas susceptible to voltage instability. Once the critical points are identified, application of FACTS devices to improve the voltage stability margin, to handle the scenario of sudden change in the load and sudden power variability solar-based generations, becomes possible. A bus participation factor is defined to rank the system buses based on the voltage-weak points. This could help to determine the placement of any compensators to improve the voltage profile of a network.

In addition, Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported that a + holomorphic embedded power flow (HEPF) method has been extended to study the power flow behaviour of a meshed network at the distribution side, which is typified as having high resistance/reactance values and low voltages. The emergence of many distributed generations would mean that the grid has the potential to become less radial and more meshed, thus being sustainable locally. The paradigm change in this manner would require faster and error-free solutions of the power-flow problem that facilitate practical decision-making, especially for a computer loaded with online algorithms whose operations are contingent on the power-flow solution. A meshed micro-gird is modelled as shown in in the figure on the next page, and the fast non-iterative power-flow technique (HEPF) is applied to the modelled network to validate the algorithm's effectiveness for high R/X network.

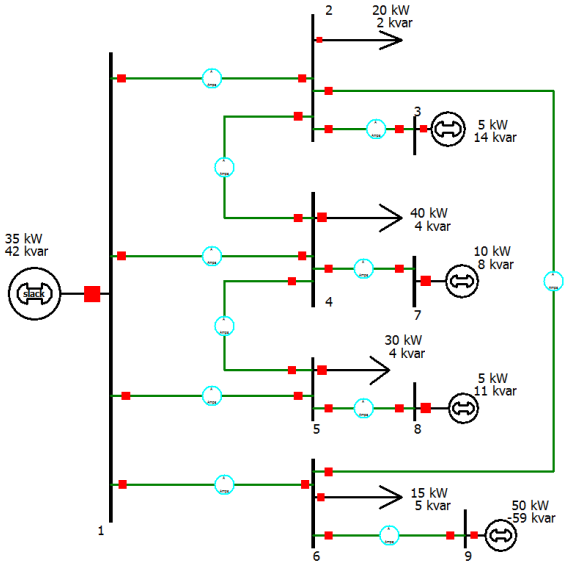
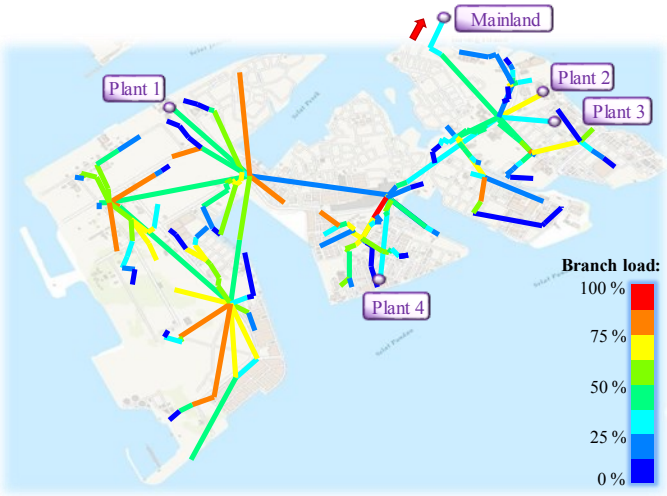


Fig. PowerWorld model of the meshed distribution system. The results from PowerWorld and that of HEPF have been found nearly the same.

Dr Bhagyesh Vijay (RF, NTU, IRP4) reported on the development of a new hybrid global optimization framework for nonlinear optimal power flow problems *as well as on the* development of the decentralized nonlinear MPC scheme for the multimachine power system. In addition he is studying the Development of a scalable sequential linear programming approach for nonlinear optimal power flow problem.



Dr Rèmy RIGO-MARIANI (RF, IRP4, NTU) reported on the progress of the modelling of the Jurong Island Power System and the implementation of an environmental unit commitment problem. The objective is to minimize the CO_2 emissions while feeding the loads and fulfilling operating constraints. In addition, he and fellow research colleagues investigated the opportunity of energy storage as well as photovoltaic generation and estimated their impact on the grid emission factor improvements (in term of kg of CO_2 per MWh generated). The objective is to establish a case study that will be further used to investigate optimal methods for grid planning with distributed generation as well as load control. The obtained results show a good consistency with the values advised by the Energy Market Authority in Singapore with a grid emissions factor of 411 kg/MWh while considering only natural gas for power generation. The main contributions so far are:

- The models for combined cycle power plants and estimation of CO_2 emissions depending on the operating point.
- A detailed, parametrised model for the electrical grid including rules of connexion of heavy consumers and updated information for the generation on site (collaboration with Dr Eddy FOO Yi Singh, Co-PI, IRP3 & IRP4, NTU).
- A mixed integer linear formulation for the environmental power dispatch problem as well as a tightened version that allows reducing the computational time.

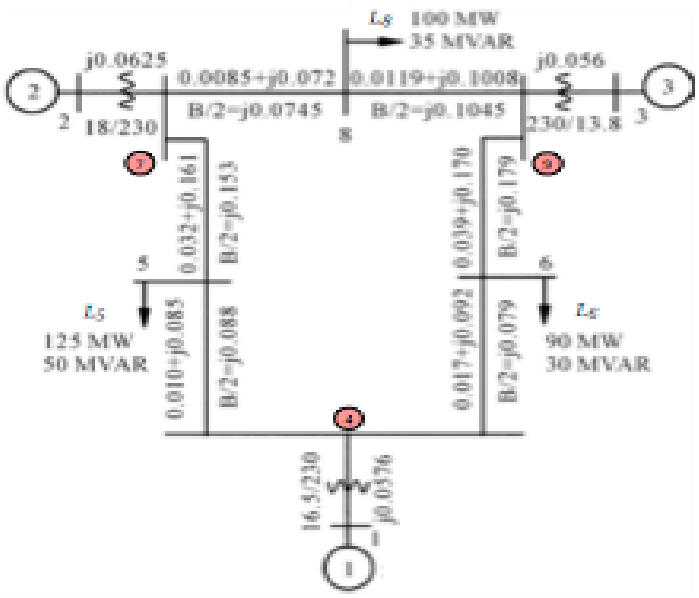
- The fulfilment of AC power flow constraints along the scheduling horizon (i.e. one day) with the Jump and Shift method.

A paper describing this work has been accepted for the ACEPT conference (Singapore, October 2017), and another paper has been accepted for the *CREATE* special issue of *Energy Technology.*

Dr Prakash Kumar RAY (RF, NTU, IRP4, has been working on detection, identification and mitigation of power quality issues in microgrids and petrochemical plants. Identification of islanding and power quality disturbances plays an important role in improving the performance, stability and reliability of power systems. Hence, fast detection and subsequent classification of disturbances is essential for providing protection to the power system and connected equipment. Signal processing techniques such as wavelet transform (WT), independent component analysis (ICA), S-transform and their modified transforms are applied for detecting disturbances. Subsequently, techniques like support vector machines, extreme learning machines, decision tree, deep learning etc. are applied for correct classification of the disturbance type to devise suitable mitigation and protection techniques for improvements in system performance. These studies are carried out initially on a microgrid and then extended to larger power systems and petrochemical plants such as the biodiesel plant. These systems are tested under different steady-state and transient operating conditions. The steady-state and transient behaviours of the plant apart from power quality (PQ) issues are studied in case of changes in the chemical process inputs in the petrochemical plant. Different types of disturbances are studied in MATLAB as well as OPAL-RT using software tools such as Hypersim and eMEGASim. The study aims to correlate changes in load observed in the power system to changes in actual chemical processes happening within the petrochemical plant, thereby building bridges between chemical plant processes and electrical power system to improve the overall system performance and efficiency. Mr Karmakar Gourab, an MSc student at School of EEE, NTU, has signed up dissertation project, ISM-DISS-01414, **Transient and Power Quality Analysis in Petrochemical Plants.** He will be working closely with Dr Prakash Kumar RAY (RF, NTU, IRP4) who serves as a co-supervisor of the MSc project.

WP 4.5: Model building, integration and maintenance

Prof Jan Maciejowski (PI, CAM, IRP4) reported that an investigation into the mathematical characterisation of *inverse response* in dynamical systems, namely an initial response in the opposite direction to the final response. Such responses make systems difficult to control. While this investigation is primarily a foundational contribution to system theory, inverse responses occur in real systems. In the context of electrical power systems they are commonly associated with drum boilers used for raising steam for turbine-driven generators, and with some wind-turbine configurations. This work was presented at the annual workshop of the European Network on System Identification, Lyon, France, September 2017.



WP 4.6: Demonstration of proposed algorithms on pilot scale

Dr FOO Yi Shyh Eddy (Co-PI, NTU, IRP3 & IRP4) has been working with Mr Ashok KRISHNAN (PhD student, NTU, IRP4) and researchers in IRP3 to examine the coupling between the chemical process and electrical power system models that will enable combined analysis of both domains. The bio-diesel plant is chosen as an exemplar petrochemical plant for developing this relationship. The chemical process model and electrical power system model were developed in Aspen Plus and OPAL -RT's Hypersim respectively. Currently, the impact of changes in chemical process inputs on the electrical power system stability are being studied. Additionally, Dr FOO Yi Shyh Eddy (Co-PI, IRP3 & IRP4, NTU) is collaborating with Dr Prakash Kumar RAY (RF, NTU, IRP4) on studying the impact of changes in chemical process inputs on power quality in the biodiesel plant model. Dr FOO Yi Shyh Eddy (Co-PI, IRP3 & IRP4, NTU) has also been working with Ashok KRISHNAN (PhD student, IRP4, NTU) on load management strategies for industrial microgrids. In this, the deployment of loads in industrial units can be optimally scheduled based on the electricity price. Furthermore, Dr FOO has also been working to finalize the purchase of power amplifiers for the OPAL-RT system at NTU. The tendering process is under evaluation and an order will be placed with the winning vendor shortly. The purchase of power amplifiers will boost the PHIL (Power Hardware-in-the-Loop) capabilities of the OPAL-RT system at NTU. It allows real power to be exchanged between the OPAL-RT and physical real world equipment. This enhanced capability will allow the OPAL-RT to be linked with the microgrid testbed at the Clean Energy Research Lab in NTU. The microgrid can thus be 'virtually' expanded to a larger network. Dr Foo also completed the purchase of the eFPGASIM, an advanced software module on the OPAL-RT. The eFPGASIM enhances the OPAL-RT's capabilities in performing fast simulations, especially for power electronic circuits.

Other Activities and Achievements

- Dr Anthony TRAN (SRF, NTU, IRP4) has been awarded 'Honorary Visiting Fellow' status by the University of Technology, Sydney (UTS), Australia.
- Prof Jan MACIEJOWSKI (PI, CAM, IRP4) completed his "long stay" in Singapore during the reporting period.
- Prof. Jan MACIEJOWSKI gave a lecture promoting Engineering as a career to secondary-school children attending a "STEP" camp at NUS in May 2017.
- Dr FOO Yi Shyh Eddy (Co-PI, NTU, IRP3 & IRP4) presented a paper titled 'Hybrid Model Predictive Control Framework for the Thermal Unit Commitment Problem including Start-up and Shutdown Power Trajectories' at the 2017 IFAC World Congress held between 9-14 July, 2017 in Toulouse, France. Dr Foo gratefully acknowledges CARES funding for covering his travel expenses for this conference. The other authors of this paper are Ashok Krishnan and Bhagyesh V. Patil.
- Ashok KRISHNAN (PhD Student, NTU, IRP4) co-authored a paper titled 'A Control Architecture for Optimal Power Sharing between Interconnected Microgrids',17PESGM1290, which was presented at the 2017 IEEE PES General Meeting held between 16-20 July, 2017 at Chicago, IL, USA. The other authors of this paper are L. P. M. I. Sampath, Kalpesh Chaudhari, H. B. Gooi and Abhisek Ukil. The paper was selected as one of the Best Conference Papers by the IEEE PES Technical Review Committee.
- The paper, "Hierarchical EMS for Aggregated BESSs in Energy and Performance-based Regulation Markets", Co-authored by Dr Tian Zhang, Dr Shuaixun Chen, Professors Hoay Beng Gooi and Jan Maciejowski and was accepted earlier by IEEE Transactions on Power Systems, was presented by Professor Gooi at the 2017 IEEE PES General Meeting held between 16-20 July, 2017 at Chicago, IL, USA. A related energy storage paper, "Sizing of Energy Storage for Microgrids", published in IEEE Transactions on Smart Grid, and presented by Professor Gooi in the IEEE PES GM2012 has been placed in the top 1% of its academic field as of March/April 2017 based on data from Essential Science Indicators and a highly cited threshold for the field and publication year. This can be viewed using the citation report of Web of Science.
- Dr FOO Yi Shyh Eddy (Co-PI, NTU, IRP3 & IRP4) delivered a lecture on Power Hardware-in-the-Loop as part of the short course titled 'Improving Reliability and Economic Performance of Microgrids'. The short course was held on 27 July 2017 at NTU's Clean Energy Research Lab. The short course was jointly organized by the School of Electrical and Electronic Engineering, NTU and IEEE Singapore Section. About 30 people participated in the short course.

3.4.3 Scientific output of IRP4

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP4 during the reporting period. A full list of publications during the period may be found in Appendix A.

Short-term Electricity Price Forecasting with Empirical Mode Decomposition based Ensemble Kernel Machines

Xueheng, Qui, P.N., Suganthan, Gehan A.J, Amaratunga

https://doi.org/10.1016/j.procs.2017.05.055

Abstract:

Short-term electricity price forecasting is a critical issue for the operation of both electricity markets and power systems. An ensemble method composed of Empirical Mode Decomposition (EMD), Kernel Ridge Regression (KRR) and Support Vector Regression (SVR) is presented in this paper. For this purpose, the electricity price signal was first decomposed into several intrinsic mode functions (IMFs) by EMD, followed by a KRR which was used to model each extracted IMF and predict the tendencies. Finally, the prediction results of all IMFs were combined by an SVR to obtain an aggregated output for electricity price. The electricity price datasets from Australian Energy Market Operator (AEMO) are used to test the effectiveness of the proposed EMD-KRR-SVR approach. Simulation results demonstrated attractiveness of the proposed method based on both accuracy and efficiency.

Oblique Random Forest Ensemble via Least Square Estimation for Time Series Forecasting

Xueheng, Qui, Le Zhang, Ponnuthurai Nagaratnam, Suganthan Gehan A.J. Amaratunga

https://doi.org/10.1016/j.ins.2017.08.060

Abstract:

Recent studies in Machine Learning indicates that the classifiers most likely to be the bests are the random forests. As an ensemble classifier, random forest combines multiple decision trees to significant decrease the overall variances. Conventional random forest employs orthogonal decision tree which selects one “optimal” feature to split the data instances within a non-leaf node according to impurity criteria such as Gini impurity, information gain and so on. However, orthogonal decision tree may fail to capture the geometrical structure of the data samples. Motivated by this, we make the first attempt to study the oblique random forest in the context of time series forecasting. In each node of the decision tree, instead of the single “optimal” feature based orthogonal classification algorithms used by standard random forest, a least square classifier is employed to perform partition. The proposed method is advantageous with respect to both efficiency and accuracy. We empirically evaluate the proposed method on eight generic time series datasets and five electricity load demand time series datasets from the Australian Energy Market Operator and compare with several other benchmark methods.

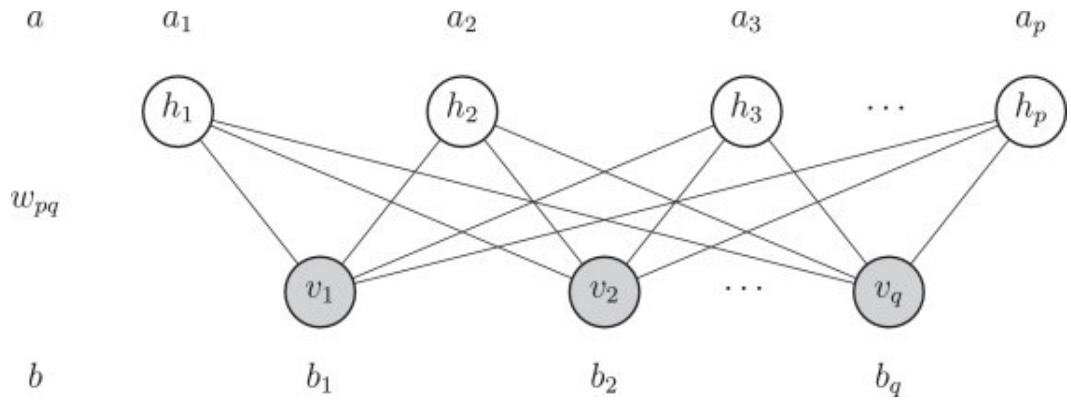


Illustration of Schematic Diagram of a Restricted Boltzmann Machine (RBM).

Minimizing Harmonic Distortion in Power System with Optimal Design of Hybrid Active Power Filter using differential evolution

Partha, Biswas, Ponnuthurai, Suganthan, Gehan, Amaratunga

Doi: 10.1016/j.asoc.2017.08.031

Abstract:

Hybrid active power filter (HAPF) is an advanced form of harmonic filter combining advantages of both active and passive filters. In HAPF, selection of active filter gain, passive inductive and capacitive reactances, while satisfying system constraints on individual and overall voltage and current harmonic distortion levels, is the main challenge. To optimize HAPF parameters, this paper proposes an approach based on differential evolution (DE) algorithm called L-SHADE. SHADE is the success history based parameter adaptation technique of DE optimization process for a constrained, multimodal non-linear objective function. L-SHADE improves the performance of SHADE with linearly reducing the population size in successive generations. The study herein considers two frequently used topologies of HAPF for parameter estimation. A single objective function consisting of both total voltage harmonic distortion (VTHD) and total current harmonic distortion (ITHD) is formulated and finally harmonic pollution (HP) is minimized in a system comprising of both non-linear source and non-linear loads. Several case studies of a selected industrial plant are performed. The output results of L-SHADE algorithm are compared with a similar past study and also with other well-known evolutionary algorithms.

Decomposition based multi-objective evolutionary algorithm for windfarm layout optimization

Partha, Biswas, Ponnuthurai, Suganthan, Gehan, Amaratunga

doi: 10.1016/j.renene.2017.08.041

Abstract:

An efficient windfarm layout to harness maximum power out of the wind is highly desirable from technical and commercial perspectives. A bit of flexibility on layout gives leeway to the designer of

windfarm in planning facilities for erection, installation and future maintenance. This paper proposes an approach where several options of optimized usable windfarm layouts can be obtained in a single run of decomposition based multi-objective evolutionary algorithm (MOEA/D). A set of Pareto optimal vectors is obtained with objective as maximum output power at minimum wake loss i.e. at maximum efficiency. Maximization of both output power and windfarm efficiency are set as two objectives for optimization. The objectives thus formulated ensure that in any single Pareto optimal solution the number of turbines used are placed at most optimum locations in the windfarm to extract maximum power available in the wind. Case studies with actual manufacturer data for wind turbines of same as well as different hub heights and with realistic wind data are performed under the scope of this research study.

Variance Analysis of Robust State Estimation in Power Systems using Influence Function

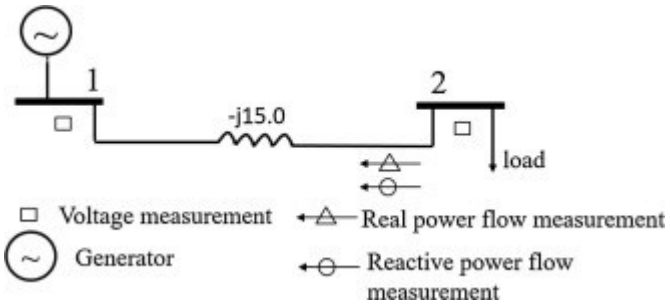
Weng Khuen, Ho, Tengpeng, Chen, Keck Voon, Ling, Lu, Sun

http://www.sciencedirect.com/science/article/pii/S0142061517301941

Abstract:

An analytical equation is derived using influence function approximation to calculate the variance of the state estimate for traditional robust state estimators such as the Quadratic-Constant, Quadratic-Linear, Square-Root, Schweppe-Huber Generalized-M and Multiple-Segment estimator. The equation gives insights into the precision of the estimation. Using the equation, the variance of a state estimate can be expressed as a function of measurement noise variances enabling the selection of sensors for a specified estimator precision. It can also be used to search for the optimum estimator parameters to give the minimum sum of variances. The well-known Weighted-Least-Squares variance formula is a special case of the equation and simulations on the IEEE 14-bus system are given to show the usefulness of the equation.

A simple example for power system state estimation with voltage measurements V1,V2 , real and reactive power flow measurements P21,Q21



Minimizing THD of Multilevel Inverters with Optimal Values of DC Voltages and Switching Angles using LSHADE-EpSin algorithm

Partha, Biswas, Noor, Awad, Ponnuthurai, Suganthan, Mostafa, Ali, Gehan, Amaratunga

Dio: 10.1109/CEC.2017.7969298

Abstract:

Multilevel inverters are mainly used for DC to AC power conversion and these inverters can be clas-

sified into types current source inverter (CSI) and voltage source inverter (VSI). Voltage source inverters are more common in power industry to convert lower levels of DC voltages into higher levels of AC voltages. In the process of conversion widely implemented pulse width modulated (PWM) switching technique of DC sources introduces harmonics in inverter output voltage. Total harmonic distortion (THD) is a measure of harmonic pollution in the power system and it is observed that variations in both DC voltages and switching angles of inverter affect the THD of inverter output voltage. Cascaded multilevel symmetric inverters ideally have DC sources all equal and constant. This paper considers inverters where DC sources can be unequal, a justifiable and realistic supposition. Optimal values of DC voltages and switching angles, which minimize THD level, are found using evolutionary algorithm. An advanced form of Differential Evolution (DE), called LSHADE-EpSin, is applied for the optimization problem. SHADE is a success history based parameter adaptation technique of DE. LSHADE improves the performance of SHADE with linearly reducing the population size in successive generations. LSHADE-EpSin introduces an additional adaptation technique for control parameters of the evolutionary algorithm. The algorithm has successfully been implemented for higher levels of inverters considered in the scope of our research study.

Optimal Placement of Wind Turbines in a Windfarm using L-SHADE algorithm

Partha, Biswas, Ponnuthurai, Suganthan, Gehan, Amaratunga

Doi: 10.1109/CEC.2017.7969299

Abstract:

Generations from several sources in an electrical network are to be optimally scheduled for economical and efficient operation of the network. Optimal power flow problem is formulated with all relevant system parameters including generator outputs and solved subsequently to obtain the optimal settings. The network may consist of conventional fossil fuel generators as well as renewable sources like wind power generators and solar photovoltaic. Classical optimal power flow itself is a highly non-linear complex problem with non-linear constraints. Incorporating intermittent nature of solar and wind energy escalates the complexity of the problem. This paper proposes an approach to solve optimal power flow combining stochastic wind and solar power with conventional thermal power generators in the system. Weibull and lognormal probability distribution functions are used for forecasting wind and solar photovoltaic power output respectively. The objective function considers reserve cost for overestimation and penalty cost for underestimation of intermittent renewable sources. Besides, emission factor is also included in objectives of selected case studies. Success history based adaptation technique of differential evolution algorithm is adopted for the optimization problem. To handle various constraints in the problem, superiority of feasible solutions constraint handling technique is integrated with success history based adaptive differential evolution algorithm. The algorithm thus combined and constructed gives optimum results satisfying all network constraints.

A.1 Publications

This list shows all C4T publications with CREATE acknowledgement since the beginning of the programme.

A1.1 Joint IRP Publications

IRP1 and IRP3

- Amaniampong, Prince N., Quang Thang Trinh, Kaixin Li, Samir H. Mushrif, Yu Hao, and Yanhui Yang. 2017. 'Porous Structured CuO-CeO2 Nanospheres for the Direct Oxidation of Cellobiose and Glucose to Gluconic Acid'. *Catalysis Today*, January. doi:10.1016/j.cattod.2017.01.009.
- Amaniampong, Prince N., Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, and Samir H. Mushrif. 2015. 'Biomass Oxidation: Formyl C H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves'. *Angewandte Chemie International Edition* 54 (31): 8928–33. doi:10.1002/anie.201503916.
- Amaniampong, Prince Nana, Amin Yoosefi Booshehri, Xinli Jia, Yihu Dai, Bo Wang, Samir H. Mushrif, and Armando Borgna. 2015. 'High-Temperature Reduction Improves the Activity of Rutile TiO2 Nanowires-Supported Gold-Copper Bimetallic Nanoparticles for Cellobiose to Gluconic Acid Conversion'. *Applied Catalysis A: General* 505 (September): 16–27. doi:10.1016/j.apcata.2015.07.027.
- Azadi, Pooya, George Brownbridge, Immanuel Kemp, Sebastian Mosbach, John S. Dennis, and Markus Kraft. 2015. 'Microkinetic Modeling of the Fischer-Tropsch Synthesis over Cobalt Catalysts'. *ChemCatChem* 7 (1): 137–43. doi:10.1002/cctc.201402662.
- Amaniampong, P. N., Booshehri, A. Y., Jia, X., Dai, Y., Wang, B., Mushrif, S. H., & Borgna, A. (2015). High-temperature reduction improves the activity of rutile TiO2 nanowires-supported gold-copper bimetallic nanoparticles for cellobiose to gluconic acid conversion. *Applied Catalysis A: General*, *505*, 16–27. https://doi.org/10.1016/j.apcata.2015.07.027
- Amaniampong, P. N., Trinh, Q. T., Wang, B., Borgna, A., Yang, Y., & Mushrif, S. H. (2015). Biomass Oxidation: Formyl C H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves. *Angewandte Chemie International*

IRP1 and IRP2

- Xie, Ming Shi, Bao Yu Xia, Yawei Li, Ya Yan, Yanhui Yang, Qiang Sun, Siew Hwa Chan, Adrian Fisher, and Xin Wang. 2016. 'Amino Acid Modified Copper Electrodes for the Enhanced Selective Electroreduction of Carbon Dioxide towards Hydrocarbons'. *Energy Environ. Sci.* doi:10.1039/C5EE03694A.
- Yan, Yibo, Jianwei Miao, Zhihong Yang, Fang-Xing Xiao, Hong Bin Yang, Bin Liu, and Yanhui Yang. 2015. 'Carbon Nanotube Catalysts: Recent Advances in Synthesis, Characterization and Applications'. *Chem. Soc. Rev.* 44 (10): 3295–3346. doi:10.1039/C4CS00492B

IRP1 and IRP4

- Yang, Shiliang, Andy Cahyadi, Yuhao Sun, Jingwei Wang, and Jia Wei Chew. n.d. 'CFD–DEM Investigation into the Scaling up of Spout-Fluid Beds via Two Interconnected Chambers'. *AIChE Journal*. doi:DOI:10.1002/aic.15188.
- Yang, Shiliang, Yuhao Sun, Jingwei Wang, Andy Cahyadi, and Jia Wei Chew. n.d. 'Influence of Operating Parameters and Flow Regime on Solid Dispersion Behavior in a Gas–solid Spout-Fluid Bed'. *Chemical Engineering Science* 142: 112–25. doi:http://dx.doi.org/10.1016/j.ces.2015.11.038.

- Yang, Shiliang, Yuhao Sun, Liangqi Zhang, Ya Zhao, and Jia Wei Chew. 2016. 'Numerical Investigation on the Effect of Draft Plates on Spouting Stability and Gas-Solid Characteristics in a Spout-Fluid Bed'. *Chemical Engineering Science*, March. doi:10.1016/j.ces.2016.03.010.
- Yang, S., Cahyadi, A., Sun, Y., Wang, J., & Chew, J. W. (n.d.). CFD–DEM investigation into the scaling up of spout-fluid beds via two interconnected chambers. *AIChE Journal*. https://doi.org/DOI:10.1002/aic.15188

IRP3 and IRP4

- Chen, Tengpeng, Dexiang Zhou, Tri Tran, Catharine Kastner, K-V. Ling, K-J. Tseng, and Jan M. Maciejowski. 2015. 'Distributed Moving Horizon Estimation for Power Systems'. In , 1–5. IEEE. doi:10.1109/PESGM.2015.7286281.
- Li, Kaixin, Zhihong Yang, Jun Zhao, Junxi Lei, Xinli Jia, Samir H. Mushrif, and Yanhui Yang. 2015. 'Mechanistic and Kinetic Studies on Biodiesel Production Catalyzed by an Efficient Pyridinium Based Ionic Liquid'. *Green Chem.* 17 (8): 4271–80. doi:10.1039/C5GC00976F.
- Trinh, Quang Thang, Arghya Banerjee, Yanhui Yang, and Samir H. Mushrif. 2016. 'Sub-Surface Boron-Doped Copper for Methane Activation and Coupling: First-Principles Investigation of the Structure, Activity, and Selectivity of the Catalyst'. *The Journal of Physical Chemistry C* 121 (2): 1099–1112. doi:10.1021/acs.jpcc.6b09236.

A.1.1 IRP1— MUSCAT

- Amaniampong, P. N., Booshehri, A. Y., Jia, X., Dai, Y., Wang, B., Mushrif, S. H., & Borgna, A. (2015). High-temperature reduction improves the activity of rutile TiO2 nanowires-supported gold-copper bimetallic nanoparticles for cellobiose to gluconic acid conversion. *Applied Catalysis A: General*, *505*, 16–27. https://doi.org/10.1016/j.apcata.2015.07.027
- Cahyadi, A., Anantharaman, A., Yang, S., Karri, S. B. R., Findlay, J. G., Cocco, R. A., & Chew, J. W. (n.d.). Review of cluster characteristics in circulating fluidized bed (CFB) risers. *Chemical Engineering Science*, (158), 70–95.
- Chan, M. S., Liu, W., Ismail, M., Yang, Y., Scott, S., & Dennis, J. (2016). Improving hydrogen yields, and hydrogen: steam ratio in the chemical looping production of hydrogen using Ca 2 Fe 2 O 5. *Chemical Engineering Journal*, *296*, 406–411. https://doi.org/10.1016/j.cej.2016.03.132
- Chen, H., Dai, Y., Jia, X., Yu, H., & Yang, Y. (2016). Highly selective gas-phase oxidation of ethanol to ethyl acetate over bi-functional Pd/zeolite catalysts. *Green Chemistry*. https://doi.org/10.1039/C5GC02593A
- Chunmiao, J., Jiajian, G., Yihu, D., Jia, Z., & Yanhui, Y. (n.d.). The thermodynamics analysis and experimental validation for complicated systems in CO_2 hydrogenation process. *Journal of Energy Chemistry*, *25*(6), 1027–1037. https://doi.org/10.1016/j.jechem.2016.10.003
- Dai, Y., Wang, Y., Liu, B., & Yang, Y. (2015). Metallic Nanocatalysis: An Accelerating Seamless Integration with Nanotechnology. *Small*, *11*(3), 268–289. https://doi.org/10.1002/smll.201400847
- Dai, Y., Wu, X., Tang, Y., Yang, Y., Gong, X., & Fan, J. (2015). Selectivity switching resulting in the formation of benzene by surface carbonates on ceria in catalytic gas-phase oxidation of benzyl alcohol. *Chemical Communications*, *52*(13), 2827–2830. https://doi.org/10.1039/C5CC08904B
- Daniel, H., Dr Polina, Y., Dr Parminder K., H., Artur M., S., & Prof Alexei A., L. (2017). A Multi-objective Optimization Including Results of Life Cycle Assessment in Developing Biorenewables-Based Processes. *ChemSusChem*. https://doi.org/10.1002/cssc.201700927
- Dou, J., Sheng, Y., Choong, C., Chen, L., & Zeng, H. C. (2017). Silica Nanowires Encapsulated Ru Nano particles as Stable Nanocatalysts for Selective Hydrogenation of CO_2 to CO. *Applied*

Catalysis B: Environmental, *219*, 580–591. https://doi.org/https://doi.org/10.1016/j.apcatb.2017.07.083

- Dunstan, M., Maugeri, S., Liu, W., Tucker, M., Taiwo, O., Gonzalez, B., … Grey, C. (2016). In situ studies of materials for high temperature CO_2 capture and storage. *Faraday Discussion*. https://doi.org/10.1039/C6FD00047A
- Dunstan, M. T., Jain, A., Liu, W., Ong, S. P., Liu, T., Lee, J., … Grey, C. P. (2016). Large scale computational screening and experimental discovery of novel materials for high temperature CO_2 capture. *Energy & Environmental Science*. https://doi.org/10.1039/C5EE03253A
- González, B., Liu, W., Sultan, D. S., & Dennis, J. S. (2016). The effect of steam on a synthetic Ca-based sorbent for carbon capture. *Chemical Engineering Journal*, *285*, 378–383. https://doi.org/10.1016/j.cej.2015.09.107
- He, C., Wang, K., Giannis, A., Yang, Y., & Wang, J.-Y. (2015). Products evolution during hydrothermal conversion of dewatered sewage sludge in sub- and near-critical water: Effects of reaction conditions and calcium oxide additive. *International Journal of Hydrogen Energy*, *40* (17), 5776–5787. https://doi.org/10.1016/j.ijhydene.2015.03.006
- He, C., Wang, K., Yang, Y., Amaniampong, P. N., & Wang, J.-Y. (2015). Effective Nitrogen Removal and Recovery from Dewatered Sewage Sludge Using a Novel Integrated System of Accelerated Hydrothermal Deamination and Air Stripping. *Environmental Science & Technology*, *49*(11), 6872–6880. https://doi.org/10.1021/acs.est.5b00652
- He, C., Zhao, J., Yang, Y., & Wang, J.-Y. (2016). Multiscale characteristics dynamics of hydrochar from hydrothermal conversion of sewage sludge under sub- and near-critical water. *Bioresource Technology*, *211*, 486–493. https://doi.org/10.1016/j.biortech.2016.03.110
- Ismail, M., Liu, W., Chan, M. S. C., Dunstan, M. T., & Scott, S. A. (2016). Synthesis, Application, and Carbonation Behavior of Ca2Fe2O5 for Chemical Looping H2 Production. *Energy & Fuels*, *30*(8), 6220–6232. https://doi.org/10.1021/acs.energyfuels.6b00631
- Ismail, M., Liu, W., Dunstan, M. T., & Scott, S. A. (2016). Development and performance of iron based oxygen carriers containing calcium ferrites for chemical looping combustion and production of hydrogen. *International Journal of Hydrogen Energy*, *41*(7), 4073–4084. https://doi.org/10.1016/j.ijhydene.2015.11.066
- Jijiang, H., Wen, L., & Yanhui, Y. (2017). Phase interactions in Mg-Ni-Al-O oxygen carriers for chemical looping applications. *Chemical Engineering Journal*, *326*, 470–476. https://doi.org/https://doi.org/10.1016/j.cej.2017.05.176
- Jithin John, V., & Samir H., M. (2017). Insights into the C-H Bond Activation on NiO Surfaces: The Role of Nickel and Oxygen Vacancies of Low Valent Dopants on the Reactivity and Energetics. *Journal of Physical Chemistry C*, *2017*, *121 (33),* pp 17969–17981. https://doi.org/DOI: 10.1021/acs.jpcc.7b05226
- Li, K., Yang, Z., Zhao, J., Lei, J., Jia, X., Mushrif, S. H., & Yang, Y. (2015). Mechanistic and kinetic studies on biodiesel production catalyzed by an efficient pyridinium based ionic liquid. *Green Chem.*, *17*(8), 4271–4280. https://doi.org/10.1039/C5GC00976F
- Li, P., & Zeng, H. C. (2016). Ultrafine Alloy Nanoparticles Converted from 2D Intercalated Coordination Polymers for Catalytic Application. *Advanced Functional Materials*, 5658–5668. https://doi.org/10.1002/adfm.201601174
- Li, P., & Zeng, H. C. (2017a). Advanced Oxygen Evolution Catalysis by Bimetallic Ni-Fe Phosphide Nanoparticles Encapsulated in Nitrogen, Phosphorus, and Sulfur Tri-Doped Porous Carbon. *Chemical Communications*, *53*(44), 6025–6028. https://doi.org/10.1039/C7CC03005C
- Li, P., & Zeng, H. C. (2017b). Sandwich-like Nanocomposite of CoNiOx/Reduced Graphene Oxide for Enhanced Electrocatalytic Water Oxidation. *Advanced Functional Materials, Vol. 27 (2017) Pp. 1606325-35.*, *27*(13), 1606325. https://doi.org/10.1002/adfm.201606325
- Li, P., & Zeng, H. C. (2017c). Synthetic Architecture of MgO/C Nanocomposite from Hierarchical-Structured Coordination Polymer towards Enhanced CO_2 Capture. *ACS Appl. Mater. Interfaces*, *9*. https://doi.org/10.1021/acsami.6b14960

- Li, P., & Zeng, H. C. (n.d.). Immobilization of Metal–Organic Framework Nanocrystals for Advanced Design of Supported Nanocatalysts. *ACS Appl. Mater. Interfaces*, *8*, 29551–29564. https://doi.org/10.1021/acsami.6b11775
- Liangqi ZHANG, J. W. C. (2017). Forcing scheme analysis for the axisymmetric lattice Boltzmann method under incompressible limit. *PHYSICAL REVIEW E*, *95*, 043311.
- Liangqi ZHANG, J. W. C. (n.d.). Alternative kinetic theory based lattice Boltzmann model for incompressible axisymmetric flows. *Computers and Mathematics with Applications*, *72*, 2751–2772.
- Liangqi ZHANG, S. Y., & Jia Wei Chew. (2016). Consistent lattice Boltzmann methods for incompressible axisymmetric flows. *PHYSICAL REVIEW E*, *94*, 023302.
- Liu, W., González, B., Dunstan, M. T., Saquib Sultan, D., Pavan, A., Ling, C. D., … Dennis, J. S. (2016). Structural evolution in synthetic, Ca-based sorbents for carbon capture. *Chemical Engineering Science*, *139*, 15–26. https://doi.org/10.1016/j.ces.2015.09.016
- Liu, W., Ismail, M., Dunstan, M. T., Hu, W., Zhang, Z., Fennell, P. S., … Dennis, J. S. (2015). Inhibiting the interaction between FeO and Al_2O_3 during chemical looping production of hydrogen. *RSC Adv.*, *5*(3), 1759–1771. https://doi.org/10.1039/C4RA11891J
- Sheng, Y., & Zeng, H. C. (2015a). Monodisperse Aluminosilicate Spheres with Tunable Al/Si Ratio and Hierarchical Macro-Meso-Microporous Structure. *ACS Applied Materials & Interfaces*, *7*(24), 13578–13589. https://doi.org/10.1021/acsami.5b03011
- Sheng, Y., & Zeng, H. C. (2015b). Structured Assemblages of Single-Walled 3d Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts. *Chemistry of Materials*, *27*(3), 658–667. https://doi.org/10.1021/cm502691s
- Tan, Y. C., & Zeng, H. C. (2016). Self-templating Synthesis of Hollow Spheres of MOFs and Their Derived Nanostructures. *Chemical Communications*, *52*.
- Trinh, Q. T., Hirao, H., Mondal, J., Singuru, R., Banerjee, B., Reddy, B. M., … Rao, B. G. (2016). Integrated Experimental and Theoretical Study of Shape-Controlled Catalytic Oxidative Coupling of Aromatic Amines over CuO Nanostructures. *ACS Omega*, *1*(6), 1121–1138. https://doi.org/10.1021/acsomega.6b00331
- Xi, B., Tan, Y. C., & Zeng, H. C. (2015). A General Synthetic Approach for Integrated Nanocatalysts of Metal-Silica@ZIFs. *Chemistry of Materials*, *28*(1), 326–336. https://doi.org/10.1021/acs.chemmater.5b04147
- Yan, Y., Dai, Y., Wang, S., Jia, X., Yu, H., & Yang, Y. (2016). Catalytic applications of alkali-functionalized carbon nanospheres and their supported Pd nanoparticles. *Applied Catalysis B: Environmental*, *184*, 104–118. https://doi.org/10.1016/j.apcatb.2015.11.024
- Yan, Y., Miao, J., Yang, Z., Xiao, F.-X., Yang, H. B., Liu, B., & Yang, Y. (2015). Carbon nanotube catalysts: recent advances in synthesis, characterization and applications. *Chem. Soc. Rev.*, *44*(10), 3295–3346. https://doi.org/10.1039/C4CS00492B
- Yang, S., Cahyadi, A., Sun, Y., Wang, J., & Chew, J. W. (n.d.). CFD–DEM investigation into the scaling up of spout-fluid beds via two interconnected chambers. *AIChE Journal*. https://doi.org/DOI:10.1002/aic.15188
- Yang, S., Sun, Y., Wang, J., Cahyadi, A., & Chew, J. W. (n.d.). Influence of operating parameters and flow regime on solid dispersion behavior in a gas–solid spout-fluid bed. *Chemical Engineering Science*, *142*, 112–125. https://doi.org/http://dx.doi.org/10.1016/j.ces.2015.11.038
- Yang, S., Sun, Y., Zhang, L., & Chew, J. W. (n.d.-a). Computational Study of the Effect of Draft Plates on the Solid Behavior in a Spout-Fluid Bed. *Industrial & Engineering Chemistry Research*, *49*(55), 12598–12615.
- Yang, S., Sun, Y., Zhang, L., & Chew, J. W. (n.d.-b). Improving the operational stability of the multi-chamber spout-fluid bed via the insertion of a submerged partition plate. *AIChE Journal*, *2*(63), 485–500.
- Yang, S., Sun, Y., Zhang, L., Zhao, Y., & Chew, J. W. (2016). Numerical investigation on the

effect of draft plates on spouting stability and gas-solid characteristics in a spout-fluid bed. *Chemical Engineering Science*. https://doi.org/10.1016/j.ces.2016.03.010

- Yang, S., Zhang, K., & Chew, J. W. (2015). Computational study of spout collapse and impact of partition plate in a double slot-rectangular spouted bed. *AIChE Journal*, n/a-n/a. https://doi.org/10.1002/aic.14973
- Yang, Shiliang, W., Jingwei, & Cahyadi, Andy, C., Jia Wei. (n.d.). DEM Study of Granular Flow Characteristics in the Active and Passive Regions of a Three-dimensional Rotating Drum. *AIChE Journal*. https://doi.org/http://dx.doi.org/10.1002/aic.15315
- Yibo Yan, Kaixin Li, Yihu Dai, Jun Zhao, Xiaoping Chen, Yong Yan, … Jong-Min Lee. (2016). Controlled Synthesis of 3D Nanoplate-Assembled La2O3 Hierarchical Microspheres for Enzyme-Free Detection of Hydrogen Peroxide. *ADVANCED MATERIALS INTERFACES*, *3*(14). https://doi.org/10.1002/admi.201500833
- Yibo Yan, Kaixin Li, Yihu Dai, Xiaoping Chen, Jun Zhao, Yanhui Yang, & Jong-Min Lee. (2016). Synthesis of 3D mesoporous samarium oxide hydrangea microspheres for enzyme-free sensor of hydrogen peroxide. *ELECTROCHIMICA ACTA*, *208*, 231–237. https://doi.org/10.1016/j.electacta.2016.05.037
- Yong, Y., Yihu, D., Hong, H., Yunbo, X., & Yanhui, Y. (n.d.). A novel W-doped Ni-Mg mixed oxide catalyst for CO_2 methanation. *Applied Catalysis B: Environmental*, *196*, 108–116. https://doi.org/10.1016/j.apcatb.2016.05.016
- Zhan, G. W., & Zeng, H. C. (2016). An Alternative Synthetic Approach for Macro-Meso-Microporous Metal–Organic Framework via 'Domain Growth' Mechanism. *Chem. Commun.*, *52*, 8432–8435. https://doi.org/10.1039/C6CC03555H
- Zhan, G. W., & Zeng, H. C. (2017). Smart Nanocatalysts with Streamline Shapes. *ACS Central Science*, *3*(7), 794–799. https://doi.org/10.1021/acscentsci.7b00216
- Zhan, G., Yec, C. C., & Zeng, H. C. (2015). Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts. *Chemistry - A European Journal*, *21*(5), 1882–1887. https://doi.org/10.1002/chem.201405697
- Zhan, G., & Zeng, H. (2016a). Integrated Nanocatalysts with Mesoporous Silica/Silicate and Microporous MOF Materials. *Coordination Chemistry Reviews*. https://doi.org/10.1016/j.ccr.2016.03.003
- Zhan, G., & Zeng, H. (2016b). Synthesis and Functionalization of Oriented Metal-Organic Framework Nanosheets: Toward a Series of Two-dimensional Catalysts. *Advanced Functional Materials*, *26*(19), 3268–3281. https://doi.org/10.1002/adfm.201505380
- Zhan, G., & Zeng, H. C. (2016c). Charge-Switchable Integrated Nanocatalysts for Substrate-Selective Degradation in Advanced Oxidation Processes. *Chemistry of Materials*, *28*, 4572–4582. https://doi.org/10.1021/acs.chemmater.6b01128
- Zhan, G., & Zeng, H. C. (2017). Alternative synthetic approaches for metal–organic frameworks: transformation from solid matters. *Chem. Commun.*, *53*, 72–81. https://doi.org/10.1039/C6CC07094A
- Zhan, G., & Zeng, H. C. (n.d.). Alternative synthetic approaches for metal–organic frameworks: transformation from solid matters. *Chemical Communications*. https://doi.org/10.1039/C6CC07094A
- Zhao, J., Zhou, C., He, C., Dai, Y., Jia, X., & Yang, Y. (2015). Efficient dehydration of fructose to 5-hydroxymethylfurfural over sulfonated carbon sphere solid acid catalysts. *Catalysis Today*. https://doi.org/10.1016/j.cattod.2015.07.005
- Zhou, C., Guo, Z., Dai, Y., Jia, X., Yu, H., & Yang, Y. (2016). Promoting role of bismuth on carbon nanotube supported platinum catalysts in aqueous phase aerobic oxidation of benzyl alcohol. *Applied Catalysis B: Environmental*, *181*, 118–126. https://doi.org/10.1016/j.apcatb.2015.07.048
- Zhou, Y., & Zeng, H. (2016a). Alumina-Supported Metal Catalysts inside a Mesoporous Aluminum-Silicate Shell: Nanoscale Reactors Prepared through Transformation of MIL-96(Al) Nano-

crystals. *ChemCatChem*, *8*(7), 1283–1287. https://doi.org/10.1002/cctc.201600062

- Zhou, Y., & Zeng, H. C. (2015). Kinetically Controlled Growth of Fine Gold Nanofractals from Au(I) via Indirect Galvanic Replacement Reaction. *ACS Applied Materials & Interfaces*, *7*(38), 21552–21561. https://doi.org/10.1021/acsami.5b06818
- Zhou, Y., & Zeng, H. C. (2016b). Transition Ions Induced Coalescence: Stitching Au Nanoclusters into Tubular Au-Based Nanocomposites. *Small*, *12*(19), 2652–2664. https://doi.org/10.1002/smll.201503881
- Zhou, Y., & Zeng, H. C. (2017). Synthesis, Self-Assembly, Transformation, and Functionalization of Nanoscale Artificial Allophane Spherules for Catalytic Applications. *Chemistry of Materials*, *29*(14), 6076–6086. https://doi.org/10.1021/acs.chemmater.7b01956
- Zhou, Y., & Zeng, H. C. (n.d.). Metal-Hydroxide and Au-Nanocluster Interfaces: Enhancing Catalyst Activity and Stability for Oxygen Evolution Reaction. *J. Phys. Chem. C*, *120*(51), 29348–29357. https://doi.org/10.1021/acs.jpcc.6b11102

A.1.2 IRP2— EMSET

- Ahn, S. D., Frith, P. E., Fisher, A. C., Bond, A. M., & Marken, F. (2014). Mass transport and modulation effects in rocking dual-semi-disc electrode voltammetry. *Journal of Electroanalytical Chemistry*, *722–723*, 78–82. https://doi.org/10.1016/j.jelechem.2014.02.018
- Bahareh, K., Adrian C., F., & Martin, P. (2017). CO_2 reduction: the quest for electrocatalytic materials. *Journal of Materials Chemistry A.*, 8230–8246. https://doi.org/10.1039/C6TA09875D
- Chao, W., Zhenxing, F., Günther G., S., James, B., Yang, S.-H., & Zhichuan J., X. (2017). Cations in Octahedral Sites: A Descriptor for Oxygen Electrocatalysis on Transition-Metal Spinels. *Advanced Materials*.
- Chen, R., Sun, G., Yang, C., Zhang, L., Miao, J., Tao, H., … Liu, B. (2016). Achieving stable and efficient water oxidation by incorporating NiFe layered double hydroxide nanoparticles into aligned carbon nanotubes. *Nanoscale Horiz.*, *1*(2), 156–160. https://doi.org/10.1039/C5NH00082C
- Chen, R., Wang, H.-Y., Miao, J., Yang, H., & Liu, B. (2015). A flexible high-performance oxygen evolution electrode with three-dimensional NiCo2O4 core-shell nanowires. *Nano Energy*, *11*, 333–340. https://doi.org/10.1016/j.nanoen.2014.11.021
- Dai, C., Chan, C.-W. I., Barrow, W., Smith, A., Song, P., Potier, F., … Lawrence, N. S. (2016). A Route to Unbuffered pH Monitoring: A Novel Electrochemical Approach. *Electrochimica Acta*, *190*, 879–886. https://doi.org/10.1016/j.electacta.2016.01.004
- Dai, C., Crawford, L. P., Song, P., Fisher, A. C., & Lawrence, N. S. (n.d.). A novel sensor based on electropolymerized substituted-phenols for pH detection in unbuffered systems. *RSC Advances*, *2015*(5), 104048–104053. https://doi.org/10.1039/c5ra22595g
- Dai, C., Song, P., Wadhawan, J. D., Fisher, A. C., & Lawrence, N. S. (2015). Screen Printed Alizarin-Based Carbon Electrodes: Monitoring pH in Unbuffered Media. *Electroanalysis*, *27*(4), 917–923. https://doi.org/10.1002/elan.201400704
- Dejan, U., Anthony J.R., P., & Richard D., W. (2017). Regional transport, source apportionment and health impact of PM10 bound polycyclic aromatic hydrocarbons in Singapore's atmosphere. *Environmental Pollution*, *229*, 984–993. https://doi.org/https://doi.org/10.1016/j.envpol.2017.07.086
- Gu, Y., & Fisher, A. C. (2013). An ac voltammetry approach for the detection of droplets in microfluidic devices. *The Analyst*, *138*(16), 4448. https://doi.org/10.1039/c3an00822c
- Hanbin, L., Chao, W., Jingxian, W., Adrian, F., Thirumany, S., Zhenxing, F., & Zichuan J., X. (2017). A Multisite Strategy for Enhancing the Hydrogen Evolution Reaction on a Nano-Pd Surface in Alkaline Media. *Advanced Energy Materials*. https://doi.org/10.1002/aenm.201701129

- Hu, N., Zhang, L., Yang, C., Zhao, J., Yang, Z., Wei, H., … Xu, Z. J. (2016). Three-dimensional skeleton networks of graphene wrapped polyaniline nanofibers: an excellent structure for high-performance flexible solid-state supercapacitors. *Scientific Reports*, *6*, 19777. https://doi.org/10.1038/srep19777
- Huang, B., Shao, H., Liu, N., Xu, Z. J., & Huang, Y. (2015). From fish scales to highly porous N-doped carbon: a low cost material solution for CO $_2$ capture. *RSC Adv.*, *5*(107), 88171–88175. https://doi.org/10.1039/C5RA16745K
- Inglesby, A. E., & Fisher, A. C. (2013). Downstream application of a microbial fuel cell for energy recovery from an Arthrospira maxima fed anaerobic digester effluent. *RSC Advances*, *3* (38), 17387. https://doi.org/10.1039/c3ra42277a
- Jiong, W., Hua, Z., & Xin, W. (2017). Recent Methods for the Synthesis of Noble-Metal-Free Hydrogen-Evolution Electrocatalysts: From Nanoscale to Sub-nanoscale. *Small Methods*. https://doi.org/10.1002/smtd.201700118
- Jiong, W., Xiaoming, G., Zhaolin, L., Larissa, T., Wei, X., & Xin, W. (2017). Heterogeneous Electrocatalyst with Molecular Cobalt Ions Serving as the Center of Active Sites. *Jouranl of the American Chemical Society 2017*, *139*(5), 1878–1884. https://doi.org/10.1021/jacs.6b10307
- Khezri, B., Chan, Y. Y., Tiong, L. Y. D., & Webster, R. D. (2015). Annual air pollution caused by the Hungry Ghost Festival. *Environ. Sci.: Processes Impacts*. https://doi.org/10.1039/C5EM00312A
- Larissa, T., Mingshi, X., Donghwan, K., & Xin, W. (2017). Ag containing porous Au structures as highly selective catalysts for glycolate and formate. *Catalysis Science and Technology 2017*. https://doi.org/10.1039/C6YO2580C
- Larissa, T., Mingshi, X., Zhaolin, L., Xiaoming, G., Yizhong, L., Wenmei, E. F., & Xin, W. (2016). Copper-Modified Gold Nanoparticles as Highly Selective Catalysts for Glycerol Electro-Oxidation in Alkaline Solution. *Chemcatchem*, *8*. https://doi.org/http://dx.doi.org/10.1002/cctc.201600725
- Latiff, N. M., Teo, W. Z., Sofer, Z., Fisher, A. C., & Pumera, M. (2015). The Cytotoxicity of Layered Black Phosphorus. *Chemistry - A European Journal*, n/a-n/a. https://doi.org/10.1002/chem.201502006
- Latiff, N., Teo, W. Z., Sofer, Z., Huber, Š., Fisher, A. C., & Pumera, M. (2015). Toxicity of layered semiconductor chalcogenides: beware of interferences. *RSC Adv.*, *5*(83), 67485–67492. https://doi.org/10.1039/C5RA09404F
- Lee, J. H. Q., Lauw, S. J. L., & Webster, R. D. (2016). The electrochemical reduction of carbon dioxide (CO_2) to methanol in the presence of pyridoxine (vitamin B6). *Electrochemistry Communications*, *64*, 69–73. https://doi.org/10.1016/j.elecom.2016.01.016
- Li, N., Thia, L., & Wang, X. (2014). A CO_2-responsive surface with an amidine-terminated self-assembled monolayer for stimuli-induced selective adsorption. *Chemical Communications*, *50*(30), 4003. https://doi.org/10.1039/c4cc00412d
- Li, N., Wang, H.-B., Thia, L., Wang, J.-Y., & Wang, X. (2015). Enzymatic-reaction induced production of polydopamine nanoparticles for sensitive and visual sensing of urea. *The Analyst*, *140*(2), 449–455. https://doi.org/10.1039/C4AN01900H
- Li, N., Yan, Y., Xia, B.-Y., Wang, J.-Y., & Wang, X. (2014). Novel tungsten carbide nanorods: An intrinsic peroxidase mimetic with high activity and stability in aqueous and organic solvents. *Biosensors and Bioelectronics*, *54*, 521–527. https://doi.org/10.1016/j.bios.2013.11.040
- Liao, H., Fisher, A., & Xu, Z. J. (2015). Surface Segregation in Bimetallic Nanoparticles: A Critical Issue in Electrocatalyst Engineering. *Small*, *11*(27), 3221–3246. https://doi.org/10.1002/smll.201403380
- Lim, R. J., Xie, M., Sk, M. A., Lee, J.-M., Fisher, A., Wang, X., & Lim, K. H. (2014). A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalysts. *Catalysis Today*, *233*, 169–180. https://doi.org/10.1016/j.cattod.2013.11.037
- Liu, Y., Liao, H., Zhou, Y., Du, Y., Wei, C., Zhao, J., … Xu, Z. J. (2015). Fe2O3 Nanoparticle/

SWCNT Composite Electrode for Sensitive Electrocatalytic Oxidation of Hydroquinone. *Electrochimica Acta*, *180*, 1059–1067. https://doi.org/10.1016/j.electacta.2015.09.046

- Malcolm E., T., Shu Jun, N., Kwok Kiong, C., Sher Li, G., Natalie F., S., Yu Rong, K., & Prof Dr Richard D., W. (2016). Impurities in Nitrile Solvents Commonly Used for Electrochemistry, and their Effects on Voltammetric Data. *ChemElectroChem*, *3(11)*, 1753–1759. https://doi.org/10.1002/celc.201600597
- Naziah M. Latiff, Carmen C. Mayorga-Martinez, Lu Wang, Zdenek Sofer, Adrian C.Fisher, & Martin Pumera. (n.d.). Microwave irradiated N- and B,Cl-doped graphene: Oxidation method has strong influence on capacitive behavior. *2017*, *9*, 204–211. https://doi.org/http://dx.doi.org/10.1016/j.apmt.2017.07.006
- Naziah M. Latiff, Lu Wang, Carmen C. Mayorga-Martinez, Zdeněk Sofer, Adrian C. Fisher, & Martin Pumera. (n.d.). Valence and oxide impurities in MoS 2 and WS 2 dramatically change their electrocatalytic activity towards proton reduction. *2016*, *8*, 16752–16760. https://doi.org/10.1039/c6nr03086f
- Naziah M. Latiff, Zdenek Sofer, Adrian C. Fisher, & Martin Pumera. (2016, December 7). *Cytotoxicity of Exfoliated Layered Vanadium Dichalcogenides*. Retrieved from http://onlinelibrary.wiley.com/doi/10.1002/chem.201604430/abstract
- Ng, F.-L., Jaafar, M. M., Phang, S.-M., Chan, Z., Salleh, N. A., Azmi, S. Z., … Periasamy, V. (2014). Reduced Graphene Oxide Anodes for Potential Application in Algae Biophotovoltaic Platforms. *Scientific Reports*, *4*, 7562. https://doi.org/10.1038/srep07562
- Ng, F.-L., Phang, S.-M., Periasamy, V., Yunus, K., & Fisher, A. C. (2014). Evaluation of Algal Biofilms on Indium Tin Oxide (ITO) for Use in Biophotovoltaic Platforms Based on Photosynthetic Performance. *PLoS ONE*, *9*(5), e97643. https://doi.org/10.1371/journal.pone.0097643
- Peng Song, Adrian C. Fisher, Jay D. Wadhawan, Joshua J. Cooper, Haydn J. Ward, & Nathan S. Lawrence. (n.d.). A mechanistic study of the EC' mechanism – the split wave in cyclic voltammetry and square wave voltammetry. *RSC Advances*, *2016*(6), 70237. https://doi.org/10.1039/c6ra08723j
- Rui, G., Zdenek, S., & Martin, P. (2017). Black Phosphorus Rediscovered: From Bulk to Monolayer. *Angew. Chemie Int. Ed. 2017*. https://doi.org/10.1002/anie.201610512
- Shengnan, S., Libo, S., Shibo, X., Yonghua, D., M.U, A. P., Zilong, W., … Zhichuan J., X. (2017). Electrochemical oxidation of C3 saturated alcohols on Co3O4 in alkaline. *Electronica Acta*, *228*, 1830194. https://doi.org/http://dx.doi.org/10.1016/j.electacta.2017.01.086
- Sun, S., & Xu, Z. J. (2015). Composition dependence of methanol oxidation activity in nickel–cobalt hydroxides and oxides: an optimization toward highly active electrodes. *Electrochimica Acta*, *165*, 56–66. https://doi.org/10.1016/j.electacta.2015.03.008
- Sun, S., Zhou, Y., Hu, B., Zhang, Q., & Xu, Z. J. (2016). Ethylene Glycol and Ethanol Oxidation on Spinel Ni-Co Oxides in Alkaline. *Journal of The Electrochemical Society*, *163*(2), H99–H104. https://doi.org/10.1149/2.0761602jes
- Sunyhik D. Ahn, K. S., H.Viet Nguyen, E. B., Jim Yang Lee, X. G., Adrian C. Fisher, P. E. F., & Frank Marken. (2015). Hydrodynamic Voltammetry at a Rocking Disc Electrode: Theory versus Experiment. *Electrochimica Acta*, *188*, 837–844. https://doi.org/10.1016/j.electacta.2015.11.143
- Tao, H. B., Fang, L., Chen, J., Bin, H. Y., Gao, J., Miao, J., … Liu, B. (2016). Identification of Surface Reactivity Descriptor for Transition Metal Oxides in Oxygen Evolution Reaction. *Journal of the American Chemical Society*, *138*(31), 9978–9985. https://doi.org/10.1021/jacs.6b05398
- Tianran, Z., Xiaoming, G., Zhao, Z., Nguk Neng, T., Zhaolin, L., Adrian, F., & Jim Yang, L. (2017). Improving the Electrochemical Oxygen Reduction Activity of Manganese Oxide Nanosheets with Sulfurization-Induced Nanopores. *ChemCatChem*. https://doi.org/10.1002/cctc.201701192
- Vengadesh, P., Ciniciato, G. P. M. K., Zhijian, C., Musoddiq, M., Fisher, A. C., & Yunus, K.

(2015). Capillary force assisted fabrication of DNA templated silver wires. *RSC Adv.*, *5*(11), 8163–8166. https://doi.org/10.1039/C4RA16448B

- Wang, H., Thia, L., Li, N., Ge, X., Liu, Z., & Wang, X. (2015a). Pd Nanoparticles on Carbon Nitride–Graphene for the Selective Electro-Oxidation of Glycerol in Alkaline Solution. *ACS Catalysis*, *5*(6), 3174–3180. https://doi.org/10.1021/acscatal.5b00183
- Wang, H., Thia, L., Li, N., Ge, X., Liu, Z., & Wang, X. (2015b). Selective electro-oxidation of glycerol over Au supported on extended poly(4-vinylpyridine) functionalized graphene. *Applied Catalysis B: Environmental*, *166–167*, 25–31. https://doi.org/10.1016/j.apcatb.2014.11.009
- Wang, H., Xie, M., Thia, L., Fisher, A., & Wang, X. (2014). Strategies on the Design of Nitrogen-Doped Graphene. *The Journal of Physical Chemistry Letters*, *5*(1), 119–125. https://doi.org/10.1021/jz402416a
- Wang, H.-Y., Hsu, Y.-Y., Chen, R., Chan, T.-S., Chen, H. M., & Liu, B. (2015). Ni^{3+} -Induced Formation of Active NiOOH on the Spinel Ni-Co Oxide Surface for Efficient Oxygen Evolution Reaction. *Advanced Energy Materials*, *5*(10), n/a-n/a. https://doi.org/10.1002/aenm.201500091
- Wang, H.-Y., Hung, S.-F., Chen, H.-Y., Chan, T.-S., Chen, H. M., & Liu, B. (2016). In Operando Identification of Geometrical-Site-Dependent Water Oxidation Activity of Spinel Co_3O_4. *Journal of the American Chemical Society*, *138*(1), 36–39. https://doi.org/10.1021/jacs.5b10525
- Wang, L. P., Yu, L., Satish, R., Zhu, J., Yan, Q., Srinivasan, M., & Xu, Z. (2014). High-performance hybrid electrochemical capacitor with binder-free Nb_2O_5 @graphene. *RSC Advances*, *4*(70), 37389. https://doi.org/10.1039/C4RA06674J
- Wang, L. P., Yu, L., Wang, X., Srinivasan, M., & Xu, Z. J. (2015). Recent developments in electrode materials for sodium-ion batteries. *J. Mater. Chem. A*, *3*(18), 9353–9378. https://doi.org/10.1039/C4TA06467D
- Wang, L. P., Zhao, Y., Wei, C., Wong, C., Srinivasan, M., & Xu, Z. J. (2015). Polycrystalline zinc stannate as an anode material for sodium-ion batteries. *J. Mater. Chem. A*, *3*(26), 14033–14038. https://doi.org/10.1039/C5TA02734A
- Wei, C., Lee, P. S., & Xu, Z. (2014). A comparison of carbon supports in MnO_2 /C supercapacitors. *RSC Advances*, *4*(59), 31416. https://doi.org/10.1039/C4RA04914D
- Xia, B. Y., Wu, H. B., Li, N., Yan, Y., Lou, X. W. D., & Wang, X. (2015). One-Pot Synthesis of Pt-Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties. *Angewandte Chemie International Edition*, *54*(12), 3797–3801. https://doi.org/10.1002/anie.201411544
- Xiao, F.-X., Pagliaro, M., Xu, Y.-J., & Liu, B. (2016). Layer-by-layer assembly of versatile nanoarchitectures with diverse dimensionality: a new perspective for rational construction of multilayer assemblies. *Chemical Society Reviews*, *11*(45,3088-3121). https://doi.org/10.1039/C5CS00781J
- Xiao, P., Ge, X., Wang, H., Liu, Z., Fisher, A., & Wang, X. (2015). Novel Molybdenum Carbide-Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution. *Advanced Functional Materials*, *25*(10), 1520–1526. https://doi.org/10.1002/adfm.201403633
- Xiao, P., Sk, M. A., Thia, L., Ge, X., Lim, R. J., Wang, J.-Y., … Wang, X. (2014). Molybdenum phosphide as an efficient electrocatalyst for the hydrogen evolution reaction. *Energy Environ. Sci.*, *7*(8), 2624–2629. https://doi.org/10.1039/C4EE00957F
- Xie, M. S., Xia, B. Y., Li, Y., Yan, Y., Yang, Y., Sun, Q., … Wang, X. (2016). Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons. *Energy Environ. Sci.* https://doi.org/10.1039/C5EE03694A
- Yan, Y., Miao, J., Yang, Z., Xiao, F.-X., Yang, H. B., Liu, B., & Yang, Y. (2015). Carbon nanotube catalysts: recent advances in synthesis, characterization and applications. *Chem. Soc. Rev.*, *44*(10), 3295–3346. https://doi.org/10.1039/C4CS00492B

- Yan, Y., Thia, L., Xia, B. Y., Ge, X., Liu, Z., Fisher, A., & Wang, X. (2015). Construction of Efficient 3D Gas Evolution Electrocatalyst for Hydrogen Evolution: Porous FeP Nanowire Arrays on Graphene Sheets. *Advanced Science*, n/a-n/a. https://doi.org/10.1002/advs.201500120
- Yan, Y., Xia, B., Ge, X., Liu, Z., Wang, J.-Y., & Wang, X. (2013). Ultrathin MoS_2 Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution. *ACS Applied Materials & Interfaces*, *5*(24), 12794–12798. https://doi.org/10.1021/am404843b
- Yan, Y., Xia, B., Li, N., Xu, Z., Fisher, A., & Wang, X. (2015). Vertically oriented MoS_2 and WS_2 nanosheets directly grown on carbon cloth as efficient and stable 3-dimensional hydrogen-evolving cathodes. *J. Mater. Chem. A*, *3*(1), 131–135. https://doi.org/10.1039/C4TA04858J
- Yan, Y., Xia, B., Xu, Z., & Wang, X. (2014). Recent Development of Molybdenum Sulfides as Advanced Electrocatalysts for Hydrogen Evolution Reaction. *ACS Catalysis*, *4*(6), 1693–1705. https://doi.org/10.1021/cs500070x
- Yan, Y., Xia, B. Y., Ge, X., Liu, Z., Fisher, A., & Wang, X. (2015). A Flexible Electrode Based on Iron Phosphide Nanotubes for Overall Water Splitting. *Chemistry - A European Journal*, *21*(50), 18062–18067. https://doi.org/10.1002/chem.201503777
- Yang, H. B., Miao, J., Hung, S.-F., Chen, J., Tao, H. B., Wang, X., … Liu, B. (2016). Identification of catalytic sites for oxygen reduction and oxygen evolution in N-doped graphene materials: Development of highly efficient metal-free bifunctional electrocatalyst. *Science Advances*, *2*(4,e1501122). https://doi.org/DOI: 10.1126/sciadv.1501122
- Yi, Z., Luyuan, P. W., Moulay, T. S., Zhenxing, F., Yann, L., Adrian, F., … Zichuan, X. (2016). A Review on Design Strategies for Carbon Based Metal Oxides and Sulfides Nanocomposites for High Performance Li and Na Ion Battery Anodes. *Advanced Energy Materials*. https://doi.org/10.1002/aenm.201601424
- Yu, L., Wang, L. P., Xi, S., Yang, P., Du, Y., Srinivasan, M., & Xu, Z. J. (2015). β-FeOOH: An Earth-Abundant High-Capacity Negative Electrode Material for Sodium-Ion Batteries. *Chemistry of Materials*, *27*(15), 5340–5348. https://doi.org/10.1021/acs.chemmater.5b01747
- Yu, L., Wei, C., Yan, Q., & Xu, Z. J. (2015). Controlled synthesis of high-performance β-FeOOH anodes for lithium-ion batteries and their size effects. *Nano Energy*, *13*, 397–404. https://doi.org/10.1016/j.nanoen.2015.03.003
- Yu, L., Xi, S., Wei, C., Zhang, W., Du, Y., Yan, Q., & Xu, Z. (2015). Superior Lithium Storage Properties of β-FeOOH. *Advanced Energy Materials*, *5*(6), n/a-n/a. https://doi.org/10.1002/aenm.201401517
- Zhao, Y., Feng, Z., & Xu, Z. J. (2015). Yolk–shell Fe_2O_3 ⊙ C composites anchored on MWNTs with enhanced lithium and sodium storage. *Nanoscale*, *7*(21), 9520–9525. https://doi.org/10.1039/C5NR01281C
- Zhao, Y., Wei, C., Sun, S., Wang, L. P., & Xu, Z. J. (2015). Reserving Interior Void Space for Volume Change Accommodation: An Example of Cable-Like MWNTs@SnO_2@C Composite for Superior Lithium and Sodium Storage. *Advanced Science*, *2*(6), n/a-n/a. https://doi.org/10.1002/advs.201500097
- Zhao, Y., Wu, W., Li, J., Xu, Z., & Guan, L. (2014). Encapsulating MWNTs into Hollow Porous Carbon Nanotubes: A Tube-in-Tube Carbon Nanostructure for High-Performance Lithium-Sulfur Batteries. *Advanced Materials*, *26*(30), 5113–5118. https://doi.org/10.1002/adma.201401191

A.1.3 IRP3 — CAPRICORN

- .Amaniampong, P. N., Trinh, Q. T., Wang, B., Borgna, A., Yang, Y., & Mushrif, S. H. (2015). Biomass Oxidation: Formyl C□H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves. *Angewandte Chemie International Edition*, *54*(31), 8928–8933. https://doi.org/10.1002/anie.201503916
- Azadi, P., Brownbridge, G., Kemp, I., Mosbach, S., Dennis, J. S., & Kraft, M. (2015). Microki-

netic Modeling of the Fischer-Tropsch Synthesis over Cobalt Catalysts. *ChemCatChem*, *7*(1), 137–143. https://doi.org/10.1002/cctc.201402662

- Azadi, P., Brownbridge, G., Mosbach, S., Inderwildi, O., & Kraft, M. (2015). Simulation and life cycle assessment of algae gasification process in dual fluidized bed gasifiers. *Green Chem.*, *17* (3), 1793–1801. https://doi.org/10.1039/C4GC01698J
- Azadi, P., Brownbridge, G., Mosbach, S., Smallbone, A., Bhave, A., Inderwildi, O., & Kraft, M. (2014). The carbon footprint and non-renewable energy demand of algae-derived biodiesel. *Applied Energy*, *113*, 1632–1644. https://doi.org/10.1016/j.apenergy.2013.09.027
- Azadi, P., Brownbridge, G. P. E., Mosbach, S., Inderwildi, O. R., & Kraft, M. (2014). Production of Biorenewable Hydrogen and Syngas via Algae Gasification: A Sensitivity Analysis. *Energy Procedia*, *61*, 2767–2770. https://doi.org/10.1016/j.egypro.2014.12.302
- Boje, A., Akroyd, J., Sutcliffe, S., Edwards, J., & Kraft, M. (2017). Detailed population balance modelling of TiO2 synthesis in an industrial reactor. *Chemical Engineering Science*, *164*, 219–231. https://doi.org/http://dx.doi.org/10.1016/j.ces.2017.02.019
- Botero, M. L., Adkins, E. M., González-Calera, S., Miller, H., & Kraft, M. (2016). PAH structure analysis of soot in a non-premixed flame using high-resolution transmission electron microscopy and optical band gap analysis. *Combustion and Flame*, *164*, 250–258. https://doi.org/10.1016/j.combustflame.2015.11.022
- Botero, M. L., Chen, D., González-Calera, S., Jefferson, D., & Kraft, M. (2016). HRTEM evaluation of soot particles produced by the non-premixed combustion of liquid fuels. *Carbon*, *96*, 459–473. https://doi.org/10.1016/j.carbon.2015.09.077
- Botero, M. L., Mosbach, S., Akroyd, J., & Kraft, M. (2015). Sooting tendency of surrogates for the aromatic fractions of diesel and gasoline in a wick-fed diffusion flame. *Fuel*, *153*, 31–39. https://doi.org/10.1016/j.fuel.2015.02.108
- Botero, M. L., Mosbach, S., & Kraft, M. (2014). Sooting tendency of paraffin components of diesel and gasoline in diffusion flames. *Fuel*, *126*, 8–15. https://doi.org/10.1016/j.fuel.2014.02.005
- Botero, M. L., Mosbach, S., & Kraft, M. (2016). Sooting tendency and particle size distributions of n-heptane/toluene mixtures burned in a wick-fed diffusion flame. *Fuel*, *169*, 111–119. https://doi.org/10.1016/j.fuel.2015.12.014
- Botero, M. L., Selmer, A., Watson, R., Bansal, M., & Kraft, M. (2016). Cambridge weblabs: A process control system using industrial standard SIMATIC PCS 7. *Education for Chemical Engineers*, *16*, 1–8. https://doi.org/10.1016/j.ece.2016.04.001
- Brownbridge, G., Azadi, P., Smallbone, A., Bhave, A., Taylor, B., & Kraft, M. (2014). The future viability of algae-derived biodiesel under economic and technical uncertainties. *Bioresource Technology*, *151*, 166–173. https://doi.org/10.1016/j.biortech.2013.10.062
- Buerger, P., Akroyd, J., Martin, J., & Kraft, M. (2017). A Big Data Framework to Validate Thermodynamic Data for Chemical Species. *Combustion and Flame*, *176*, 584–591. https://doi.org/10.1016/j.combustflame.2016.11.006
- Buerger, P., Nurkowski, D., Akroyd, J., & Kraft, M. (2017). A kinetic mechanism for the thermal decomposition of titanium tetraisopropoxide. *Proceedings of the Combustion Institute*, *36*(1), 1019–1027. https://doi.org/10.1016/j.proci.2016.08.062
- Buerger, P., Nurkowski, D., Akroyd, J., Mosbach, S., & Kraft, M. (2015). First-Principles Thermochemistry for the Thermal Decomposition of Titanium Tetraisopropoxide. *The Journal of Physical Chemistry A*, *119*(30), 8376–8387. https://doi.org/10.1021/acs.jpca.5b01721
- Camacho, J., Singh, A. V., Wang, W., Shan, R., Yapp, E. K. Y., Chen, D., … Wang, H. (2016). Soot particle size distributions in premixed stretch-stabilized flat ethylene–oxygen–argon flames. *Proceedings of the Combustion Institute*. https://doi.org/10.1016/j.proci.2016.06.170
- Chen, D., Akroyd, J., Mosbach, S., & Kraft, M. (2015). Surface reactivity of polycyclic aromatic hydrocarbon clusters. *Proceedings of the Combustion Institute*, *35*(2), 1811–1818. https://doi.org/10.1016/j.proci.2014.06.140

- Chen, D., Akroyd, J., Mosbach, S., Opalka, D., & Kraft, M. (2015). Solid–liquid transitions in homogenous ovalene, hexabenzocoronene and circumcoronene clusters: A molecular dynamics study. *Combustion and Flame*, *162*(2), 486–495. https://doi.org/10.1016/j.combustflame.2014.07.025
- Chen, D., Totton, T. S., Akroyd, J., Mosbach, S., & Kraft, M. (2014a). Phase change of polycyclic aromatic hydrocarbon clusters by mass addition. *Carbon*, *77*, 25–35. https://doi.org/10.1016/j.carbon.2014.04.089
- Chen, D., Totton, T. S., Akroyd, J. W. J., Mosbach, S., & Kraft, M. (2014b). Size-dependent melting of polycyclic aromatic hydrocarbon nano-clusters: A molecular dynamics study. *Carbon*, *67*, 79–91. https://doi.org/10.1016/j.carbon.2013.09.058
- Dezhi, Z., Wenming, Y., Jing, L., Kun Lin, T., & Markus, K. (n.d.). Combustion modeling in RCCI engines with a hybrid characteristic time combustion and closed reactor model. *Accepted - In Press*. https://doi.org/10.1016/j.apenergy.2017.08.137
- Garud, S., Karimi, I., & Kraft, M. (2016). Smart Adaptive Sampling for Surrogate Modelling. *Computer Aided Chemical Engineering*, *38*, 631–636. https://doi.org/10.1016/B978-0-444-63428-3.50110-7
- Garud, S. S., Karimi, I. A., & Kraft, M. (2016). Smart Sampling Algorithm for Surrogate Model Development. *Computers and Chemical Engineering*, *96*, 103–114. https://doi.org/10.1016/j.compchemeng.2016.10.006
- Garud, S. S., Karimi, I. A., & Kraft, M. (2017). Design of Computer Experiments: A Review. *Computers and Chemical Engineering*, *106*, 71–95. https://doi.org/https://doi.org/10.1016/j.compchemeng.2017.05.010
- Grančič, P., Martin, J. W., Chen, D., Mosbach, S., & Kraft, M. (2016). Can nascent soot particles burn from the inside? *Carbon*. https://doi.org/10.1016/j.carbon.2016.08.025
- Han, J., Wang, D., Du, Y., Xi, S., Chen, Z., Yin, S., … Xu, R. (2015). Polyoxometalate immobilized in MIL-101(Cr) as an efficient catalyst for water oxidation. *Applied Catalysis A: General*. https://doi.org/10.1016/j.apcata.2015.10.015
- Kastner, C. A., Lau, R., & Kraft, M. (2015). Quantitative tools for cultivating symbiosis in industrial parks; a literature review. *Applied Energy*, *155*, 599–612. https://doi.org/10.1016/j.apenergy.2015.05.037
- Lee, K. F., Davidson, J. F., Akroyd, J., & Kraft, M. (2014). Lifting a buried object: Reverse hopper theory. *Chemical Engineering Science*, *105*, 198–207. https://doi.org/10.1016/j.ces.2013.11.002
- Lee, K. F., Dosta, M., McGuire, A., Mosbach, S., Wagner, W., Heinrich, S., & Kraft, M. (2017). Development of a multi-compartment population balance model for high-shear wet granulation with Discrete Element Method. *Computers & Chemical Engineering*, *99*, 171–184. https://doi.org/10.1016/j.compchemeng.2017.01.022
- Lee, K. F., Mosbach, S., Kraft, M., & Wagner, W. (2015). A multi-compartment population balance model for high shear granulation. *Computers & Chemical Engineering*, *75*, 1–13. https://doi.org/10.1016/j.compchemeng.2015.01.009
- Lee, K. F., Patterson, R., Wagner, W., & Kraft, M. (2015). Stochastic weighted particle methods for population balance equations with coagulation, fragmentation and spatial inhomogeneity. *Journal of Computational Physics*, *303*, 1–18. https://doi.org/10.1016/j.jcp.2015.09.031
- Li, C., Du, Y., Wang, D., Yin, S., Tu, W., Chen, Z., … Xu, R. (2017). Unique P-Co-N Surface Bonding States Constructed on g-C3N4 Nanosheets for Drastically Enhanced Photocatalytic Activity of H2 Evolution. *Advanced Functional Materials*, *27*(4), 1604328. https://doi.org/10.1002/adfm.201604328
- Li, J., Yang, W., An, H., Zhou, D., & Kraft, M. (2016). Application of Dynamic φ–T Map: Analysis on a Natural Gas/Diesel Fueled RCCI Engine. *Journal of Engineering for Gas Turbines and Power*, *138*(9), 092803. https://doi.org/10.1115/1.4032712

- Lindberg, C., Akroyd, J., & Kraft, M. (2017). Developing breakage models relating morphological data to the milling behaviour of flame synthesised titania particles. *Chemical Engineering Science*, *166*, 53–65. https://doi.org/10.1016/j.ces.2017.03.016
- Manuputty, M. Y., Akroyd, J., Mosbach, S., & Kraft, M. (2017). Modelling TiO2 formation in a stagnation flame using method of moments with interpolative closure. *Combustion and Flame*, *178*, 135–147.
- Martin, J., McIntosh, G., Arul, R., Oosterbeek, R., Kraft, M., & Soehnel, T. (2017). Giant fullerene formation through thermal treatment of fullerene soot. *Carbon*, *125*, 132–138. https://doi.org/https://doi.org/10.1016/j.carbon.2017.09.045
- McGuire, A., Lee, K. F., Dosta, M., Mosbach, S., Rosenboom, J.-G., Heinrich, S., & Kraft, M. (2017). Compartmental residence time estimation in batch granulators using a colourimetric image analysis algorithm and Discrete Element Modelling. *Advanced Powder Technology*, *28* (9), 2239–2255. https://doi.org/https://doi.org/10.1016/j.apt.2017.06.005
- Menz, W. J., Brownbridge, G. P. E., & Kraft, M. (2014). Global sensitivity analysis of a model for silicon nanoparticle synthesis. *Journal of Aerosol Science*, *76*, 188–199. https://doi.org/10.1016/j.jaerosci.2014.06.011
- Mosbach, S., Hong, J. H., Brownbridge, G. P. E., Kraft, M., Gudiyella, S., & Brezinsky, K. (2014). Bayesian Error Propagation for a Kinetic Model of n-Propylbenzene Oxidation in a Shock Tube. *International Journal of Chemical Kinetics*, *46*(7), 389–404. https://doi.org/10.1002/kin.20855
- Mosbach, S., & Kraft, M. (2015). Influence of experimental observations on n-propylbenzene kinetic parameter estimates. *Proceedings of the Combustion Institute*, *35*(1), 357–365. https://doi.org/10.1016/j.proci.2014.05.061
- Mosbach, S., Menz, W., & Kraft, M. (n.d.). Outlier analysis for a silicon nanoparticle population balance model. *Combustion and Flame*, *177*, 89–97. https://doi.org/http://dx.doi.org/10.1016/j.combustflame.2016.12.006
- Nurkowski, D., Buerger, P., Akroyd, J., & Kraft, M. (2015). A detailed kinetic study of the thermal decomposition of tetraethoxysilane. *Proceedings of the Combustion Institute*, *35*(2), 2291–2298. https://doi.org/10.1016/j.proci.2014.06.093
- Nurkowski, D., Buerger, P., Akroyd, J., Mosbach, S., & Kraft, M. (2016). Skeletal chemical mechanism of high-temperature TEOS oxidation in hydrogen–oxygen environment. *Combustion and Flame*, *166*, 243–254. https://doi.org/10.1016/j.combustflame.2016.01.025
- Nurkowski, D., Jasper, A., Akroyd, J., & Kraft, M. (2017). Theoretical study of the Ti-Cl bond cleavage reaction in TiCl4. *Zeitschrift Fuer Physikalische Chemie*, *231*(9), 1489–1506. https://doi.org/https://doi.org/10.1515/zpch-2016-0866
- Nurkowski, D., Klippenstein, S. J., Georgievskii, Y., Verdicchio, M., Jasper, A. W., Akroyd, J., … Kraft, M. (2015). Ab initio Variational Transition State Theory and Master Equation Study of the Reaction (OH)3SiOCH2 + CH3 ⇌ (OH)3SiOC2H5. *Zeitschrift Für Physikalische Chemie*, *229* (5). https://doi.org/10.1515/zpch-2014-0640
- Pan, M., Sikorski, J., Akroyd, J., Mosbach, S., Lau, R., & Kraft, M. (2016). Design technologies for eco-industrial parks: from unit operations to processes, plants and industrial networks. *Applied Energy*, *175*, 305–323. https://doi.org/10.1016/j.apenergy.2016.05.019
- Pan, M., Sikorski, J., Kastner, C. A., Akroyd, J., Mosbach, S., Lau, R., & Kraft, M. (2015). Applying Industry 4.0 to the Jurong Island Eco-industrial Park. *Energy Procedia*, *75*, 1536–1541. https://doi.org/10.1016/j.egypro.2015.07.313
- Sikorski, J., Brownbridge, G., Garud, S., Mosbach, S., Karimi, I., & Kraft, M. (2016). Parameterisation of a biodiesel plant process flow sheet model. *Computers & Chemical Engineering*, *95*, 108–122. https://doi.org/10.1016/j.compchemeng.2016.06.019
- Sikorski, J., Haughton, J., & Kraft, M. (2017). Blockchain technology in the chemical industry: Machine-to-machine electricity market. *Applied Energy*, *195*, 234–246. https://doi.org/http://dx.doi.org/10.1016/j.apenergy.2017.03.039

- Tianhua, Z., Yonghua, D., Danping, W., Shengming, Y., Wenguang, T., Zhong, C., … Rong, X. (2017). Phosphonate-Based Metal–Organic Framework Derived Co–P–C Hybrid as an Efficient Electrocatalyst for Oxygen Evolution Reaction, *7*(9), 6000–6007. https://doi.org/10.1021/acscatal.7b00937
- Wang, B., Mosbach, S., Schmutzhard, S., Shijin Shuai, Huang, Y., & Kraft, M. (2016). Modelling soot formation from wall films in a gasoline direct injection engine using a detailed population balance model. *Applied Energy*, *163*, 154–166. https://doi.org/10.1016/j.apenergy.2015.11.011
- Wenguang, T., You, X., Jiajia, W., Bowei, Z., Tianhua, Z., Shengming, Y., … Rong, X. (2017). Investigating the Role of Tunable Nitrogen Vacancies in Graphitic Carbon Nitride Nanosheets for Efficient Visible-Light-Driven H2 Evolution and CO_2 Reduction, *5*(8), 7260–7268. https://doi.org/10.1021/acssuschemeng.7b01477
- Wu, S., Yapp, E., Akroyd, J., Mosbach, S., Xu, R., Yang, W., & Kraft, M. (2017). Extension of moment projection method to the fragmentation process. *Journal of Computational Physics*, *335*, 516–534. https://doi.org/10.1016/j.jcp.2017.01.045
- Wu, S., Yapp, E., Akroyd, J., Mosbach, S., Yang, W., & Kraft, M. (2017). A moment projection method for population balance dynamics with a shrinkage term. *Journal of Computational Physics*, *330*, 960–980. https://doi.org/10.1016/j.jcp.2016.10.030
- Xu, Y., Kraft, M., & Xu, R. (2016). Metal-Free Carbonaceous Electrocatalysts and Photocatalysts for Water Splitting. *Chemical Society Reviews*.
- Xu, Y., Tu, W., Zhang, B., Yin, S., Huang, Y., Kraft, M., & Xu, R. (2017). Nickel Nanoparticles Encapsulated in Few-Layer Nitrogen-Doped Graphene Derived from Metal–Organic Frameworks as Efficient Bifunctional Electrocatalysts for Overall Water Splitting. *Advanced Materials*, 1605957. https://doi.org/10.1002/adma.201605957
- Yang, W., An, H., Li, J., Zhou, D., & Kraft, M. (2015). Impact of Urea Direct Injection on NOx Emission Formation of Diesel Engines Fueled by Biodiesel (p. V002T04A005). ASME. https://doi.org/10.1115/ICEF2015-1059
- Yapp, E. K. Y., Patterson, R. I. A., Akroyd, J., Mosbach, S., Adkins, E. M., Miller, J. H., & Kraft, M. (2016). Numerical simulation and parametric sensitivity study of optical band gap in a laminar co-flow ethylene diffusion flame. *Combustion and Flame*, *167*, 320–334. https://doi.org/10.1016/j.combustflame.2016.01.033
- Yapp, E. K. Y., Wells, C. G., Akroyd, J., Mosbach, S., Xu, R., & Kraft, M. (2017). Modelling PAH curvature in laminar premixed flames using a detailed population balance model. *Combustion and Flame*, *176*, 172–180. https://doi.org/10.1016/j.combustflame.2016.10.004
- Yin, S., Han, J., Zou, Y., Zhou, T., & Xu, R. (2016). A highly efficient noble metal free photocatalytic hydrogen evolution system containing MoP and CdS quantum dots. *Nanoscale*, *8*(30), 14438–14447. https://doi.org/10.1039/C6NR00989A
- Yu, W., Yang, W., Mohan, B., Tay, K., Zhao, F., Zhang, Y., … Lou, K. (2016). Numerical and Experimental Study on Internal Nozzle Flow and Macroscopic Spray Characteristics of a Kind of Wide Distillation Fuel (WDF) - Kerosene. *SAE International*, *2016-1–839*. https://doi.org/10.4271/2016-01-0839
- Zhang, C., Zhou, L., Chhabra, P., Garud, S., Aditya, K., Romagnoli, A., … Kraft, M. (2016). A novel methodology for the design of waste heat recovery network in eco-industrial park using techno-economic analysis and multi-objective optimization. *Applied Energy*, *184*, 88–102. https://doi.org/10.1016/j.apenergy.2016.10.016
- Zhang, W., Zhou, T., Hong, J., & Xu, R. (2016). MoS3 loaded TiO2 nanoplates for photocatalytic water and carbon dioxide reduction. *Journal of Energy Chemistry*. https://doi.org/10.1016/j.jechem.2016.01.016
- Zhang, W., Zhou, T., Zheng, J., Hong, J., Pan, Y., & Xu, R. (2015). Water-Soluble MoS3 Nanoparticles for Photocatalytic H2 Evolution. *ChemSusChem*, *8*(8), 1464–1471. https://doi.org/10.1002/cssc.201500067

- Zhou, D., Yang, W., An, H., Li, J., & Kraft, M. (2016). An Enhanced Primary Reference Fuel Mechanism Considering Conventional Fuel Chemistry in Engine Simulation. *Journal of Engineering for Gas Turbines and Power*, *138*(9), 092804. https://doi.org/10.1115/1.4032713

A.1.4—ICESO

- Bhagyesh V. Patil. (2015). The Bernstein branch-and-prune constrained global optimization algorithm for MINLPs. In *Proceedings of the 6th International Conference on Mathematical Aspects of Computer and Information Sciences (MACIS'15)*. Berlin, Germany.
- B.Y, Q., J.J, L., Y.S, Z., & P.N, S. (2017). Solving dynamic economic emission dispatch problem considering wind power by multi-objective differential evolution with ensemble of selection method. *Natural Computing*, 1–9. https://doi.org/10.1007/s11047-016-9598-6
- B.Y, Q., J.J, L., Y.S, Z., Z.Y, W., & P.N, S. (2016). Economic emission dispatch problems with stochastic wind power using summation based multi-objective evolutionary algorithm. *Information Sciences*, *351*, 48–66. https://doi.org/http://dx.doi.org/10.1016/j.ins.2016.01.081
- Chen, T., Zhou, D., Tran, T., Kastner, C., Ling, K.-V., Tseng, K.-J., & Maciejowski, J. M. (2015). Distributed Moving Horizon Estimation for power systems (pp. 1–5). IEEE. https://doi.org/10.1109/PESGM.2015.7286281
- Chen, X., Chen, T., Tseng, K. J., Sun, Y., & Amaratunga, G. (2016). Hybrid approach based on global search algorithm for optimal placement of µPMU in distribution networks (pp. 559–563). IEEE. https://doi.org/10.1109/ISGT-Asia.2016.7796445
- Dang, T. V., Ling, K. V., & Maciejowski, J. M. (2015a). Embedded ADMM-based QP solver for MPC with polytopic constraints (pp. 3446–3451). IEEE. https://doi.org/10.1109/ECC.2015.7331067
- Dang, T. V., Ling, K. V., & Quevedo, D. E. (2015). Event-triggered anytime control with two controllers. In *2015 54th IEEE Conference on Decision and Control (CDC)* (pp. 4157–4162). Osaka, Japan: IEEE. https://doi.org/10.1109/CDC.2015.7402867
- Dang, T-V, K.-V. L. (2014). Moving horizon estimation on a chip. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)* (pp. 431–437). Singapore: IEEE. https://doi.org/10.1109/ICARCV.2014.7064344
- Dang, T-V, T. T., & K-V. Ling. (2015). Numerical Algorithms for Quadratic Programming in Model Predictive Control - An Overview. In *Proceedings of International Conference on Modelling of Complex Systems and Environment* (pp. 1–6). Danang, Vietnam. https://doi.org/10.13140/RG.2.1.1885.4885
- Foo. Eddy, Y. S., Gooi, H. B., & Chen, S. X. (2015). Multi-Agent System for Distributed Management of Microgrids. *IEEE Transactions on Power Systems*, *30*(1), 24–34. https://doi.org/10.1109/TPWRS.2014.2322622
- Krishnanand, K., Joymala, M., & Sanjib Kumar, P. (2015). Selective Harmonic Optimization for Flexible Single-Phase Operation of Cascaded H-Bridge Multilevel Inverters. In *Proceedings of the 1st Power, Communication and Information Technology Conference (PCITC'15)* (pp. 918–923). Bhubaneswar, India: IEEE. https://doi.org/10.1109/PCITC.2015.7438127
- Krishnanand, K. R., Moirangthem, J., Bhandari, S., & Panda, S. K. (2015). Harmonic load modeling for smart microgrids (pp. 68–72). IEEE. https://doi.org/10.1109/ICBEST.2015.7435867
- Lynn, N., Mallipeddi, R., & Suganthan, P. N. (2015). Differential Evolution with Two Subpopulations. In B. K. Panigrahi, P. N. Suganthan, & S. Das (Eds.), *Swarm, Evolutionary, and Memetic Computing* (Vol. 8947, pp. 1–13). Cham: Springer International Publishing. Retrieved from http://link.springer.com/10.1007/978-3-319-20294-5_1
- Moirangthem, J., Krishnanand, K. R., Panda, S. K., & Amaratunga, G. (2016). GIS integrated automation of a near real-time power-flow service for electrical grids (pp. 48–53). IEEE. https://doi.org/10.1109/ICSET.2016.7811755

- Partha, B., Noor, A., Ponnuthurai, S., Mostafa, A., & Gehan, A. (06-Jun-17). Minimizing THD of Multilevel Inverters with Optimal Values of DC Voltages and Switching Angles using LSHADE-EpSin algorithm. Presented at the IEEE CEC 2017. https://doi.org/10.1109/CEC.2017.7969298
- Partha, B., Ponnuthurai, S., & Gehan, A. (05-Jun-17). Optimal Placement of Wind Turbines in a Windfarm using L-SHADE algorithm. Presented at the IEEE CEC 2017. https://doi.org/10.1109/CEC.2017.7969299
- Partha, B., Ponnuthurai, S., & Gehan, A. (2017a). Decomposition based multi-objective evolutionary algorithm for windfarm layout optimization. *Renewable Energy, Elsevier*. https://doi.org/10.1016/j.renene.2017.08.041
- Partha, B., Ponnuthurai, S., & Gehan, A. (2017b). Minimizing Harmonic Distortion in Power System with Optimal Design of Hybrid Active Power Filter using differential evolution. *Applied Soft Computing, Elsevier*. https://doi.org/10.1016/j.asoc.2017.08.031
- Partha, B., Ponnuthurai, S., & Gehan, A. (2017c). Optimal power flow solutions incorporating stochastic wind and solar power. *Energy Conversion and Management, Elsevier*. https://doi.org/10.1016/j.enconman.2017.06.071
- Partha, B., Rammohan, M., Ponnuthurai, S., & Gehan, A. (06-Jul-17). A multiobjective approach for optimal placement and sizing of distributed generators and capacitors in distribution network. *Applied Soft Computing, Elsevier*. https://doi.org/10.1016/j.asoc.2017.07.004
- Patil, B. V. (2016). The Bernstein Branch-and-Prune Algorithm for Constrained Global Optimization of Multivariate Polynomial MINLPs. In I. S. Kotsireas, S. M. Rump, & C. K. Yap (Eds.), *Mathematical Aspects of Computer and Information Sciences* (Vol. 9582, pp. 560–575). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-319-32859-1_48
- Patil, B. V., Maciejowski, J., & Ling, K. V. (2016). Nonlinear model predictive control based on Bernstein global optimization with application to a nonlinear CSTR (pp. 471–476). IEEE. https://doi.org/10.1109/ECC.2016.7810329
- Patil, B. V., Sampath, L. P. M. I., Krishnan, A., Ling, K. V., & Gooi, H. B. (2016). Examining the Bernstein global optimization approach to optimal power flow problem (p. 090022). https://doi.org/10.1063/1.4965386
- Qiu, X., Zhang, L., Ren, Y., Suganthan, P., & Amaratunga, G. (2014). Ensemble deep learning for regression and time series forecasting. In *2014 IEEE Symposium on Computational Intelligence in Ensemble Learning (CIEL)* (pp. 1–6). Orlando, FL: IEEE. https://doi.org/10.1109/CIEL.2014.7015739
- Ren, Y., Qiu, X., & Suganthan, P. (2014). Empirical mode decomposition based adaboost-backpropagation neural network method for wind speed forecasting. In *2014 IEEE Symposium on Computational Intelligence in Ensemble Learning (CIEL)* (pp. 1–6). Orlando, FL: IEEE. https://doi.org/10.1109/CIEL.2014.7015741
- Ren Y., X. Q., & P. N. Suganthan, G. A. (2015). Detecting Wind Power Ramp with Random Vector Functional Link (RVFL) Network. In *Proceedings of 2015 IEEE Symposium Series on Computational Intelligence* (pp. 687–694). Cape Town, South Africa: IEEE. https://doi.org/10.1109/SSCI.2015.105
- Ren, Ye, Z., Le, & P. N. Suganthan. (2016). Ensemble Classification and Regression-Recent Developments, Applications and Future Directions. *IEEE Computational Intelligence Magazine*, *11*(1), 41–53. https://doi.org/10.1109/MCI.2015.2471235
- Srinivasa Rao Kamala. (2017). Stability enhancement issues of power grid. In *Communication, Control and Security Challenges for the Smart Grid* (First, Vol. 1, pp. 405–450). London, United Kingdom: The Institution of Engineering and Technology (IET). Retrieved from http://digital-library.theiet.org/content/books/10.1049/pbpo095e_ch14
- T., J., T, R., B.R., A., & Ponnuthurai, N. S. (2016). Economic dispatch using hybrid grey wolf optimizer. *Energy*, *111*, 630–641. https://doi.org/http://dx.doi.org/10.1016/j.energy.2016.05.105
- Tian Zhang, S.-X. C., & Hoay Beng Gooi, J. M. M. (n.d.). A Hierarchical EMS for Aggregated

BESSs in Energy and Performance-based Regulation Markets. *IEEE Transactions on Power Systems*, (99). https://doi.org/10.1109/TPWRS.2016.2598186

- T-P Chen, A. K., & Tri Tran. (2015). Application of Partition-based Moving Horizon Estimation to Power System State Estimation. In *Proceedings of the 7th IEEE PES Asia-Pacific Power and Energy Engineering Conference (PES APPEEC'15)* (pp. 1–5). Brisbane, Australia: IEEE. https://doi.org/10.1109/APPEEC.2015.7380907
- T-P. Chen, T. T., D. Zhou, W.-K. H., & K-V. Ling. (2014). Iterated moving horizon estimation for power systems. In *2014 International Conference on Control, Automation and Information Sciences (ICCAIS)* (pp. 81–86). IEEE. https://doi.org/10.1109/ICCAIS.2014.7020573
- Tran, A. (n.d.). Self-Reliant Control Systems. In *Proceedings of the 5th International Conference on Control, Automation and Information Science (IEEE)*. Seoul, South Korea: IEEE.
- Tran, T. (2015). A New Architecture for Reliable Computerized-Control System via IoT Enabled Connectivity. In *Proceedings of the International Conference on Modelling of Complex Systems and Environment* (pp. 6–9). Danang, Vietnam. https://doi.org/10.13140/RG.2.1.2934.0649
- Tran, T., Maciejowski, J., & Ling, K.-V. (n.d.). A general dissipativity constraint for feedback system synthesis and design. *Systems and Control Letters (Submitted)*.
- Tri Tran. (2014). State feedback control of explicitly-bounded nonlinearly-coupled interconnected systems. In *2014 International Conference on Control, Automation and Information Sciences (ICCAIS)* (pp. 30–35). IEEE. https://doi.org/10.1109/ICCAIS.2014.7020563
- Tri Tran. (2015). Periodic Economic Model Predictive Control with Bounded-State Stability. In *Proceedings of the 5th Australian Control Conference (AUCC'15)* (pp. 253–258). Gold Coast, Australia: IEEE. Retrieved from http://ieeexplore.ieee.org/xpl/articleDetails.jsp?arnumber=7361943&newsearch=true&queryText=Periodic%20Economic%20Model%20Predictive%20Control%20with%20Bounded-State%20Stability
- Tri Tran. (2016). A Private Machine-Cloud Architecture and Self-Reliant Controllers for Operational Technology Systems. In *Proceedings of 2016 International Conference on Control, Automation and Information Sciences* (pp. 214–219). Ansan, Seoul, Korea: IEEE. https://doi.org/10.1109/ICCAIS.2016.7822458
- Tri Tran. (2017a). Application of GDC to the Automatic Generation Control Problem. In *Proceedings of the 6th International Conference on Control, Automation and Information Science (IEEE)*. Thailand: IEEE. Retrieved from http://ieeexplore.ieee.org/xpl/conhome.jsp?punumber=1802677
- Tri Tran. (2017b). Linear Matrix Inequalities for Dissipative Constraints in Stabilization with Relaxed Non-monotonic Lyapunov Function. In *Proceedings of the 6th International Conference on Control, Automation and Information Science (IEEE)*. Thailand: IEEE. Retrieved from http://ieeexplore.ieee.org/xpl/conhome.jsp?punumber=1802677
- Tri Tran. (2017c). Perturbed Cooperative-State Feedback Strategy for Model Predictive Networked Control of Interconnected Systems. *ISA Transactions*. Retrieved from https://www.journals.elsevier.com/isa-transactions
- Tri Tran. (2017d). Stability from the Stabilization with General Dissipativity Constraint. In *Proceedings of the 6th International Conference on Control, Automation and Information Science (IEEE)*. Thailand: IEEE. Retrieved from http://ieeexplore.ieee.org/xpl/conhome.jsp?punumber=1802677
- Tri Tran, D.-X. Z., & K-V. Ling, J. M. (2015). Multiplexed Model Predictive Control of Interconnected Systems. In *Proceedings of IEEE Conference on Decision and Control (CDC'14)* (pp. 15–17). Los Angeles, CA: IEEE. https://doi.org/10.1109/CDC.2014.7040439
- Tri Tran, E. Y. S. F., & K-V. Ling, J. M. (2014). Application of quadratically-constrained model predictive control in power systems. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)* (pp. 193–198). IEEE. https://doi.org/10.1109/ICARCV.2014.7064303

- Tri Tran, J. M. (2016). Control with General Dissipativity Constraint and Non-Monotonic Lyapunov Functions. In *Proceedings of 2016 International Conference on Control, Automation and Information Sciences* (pp. 177–182). Ansan, Seoul, Korea: IEEE. https://doi.org/10.1109/ICCAIS.2016.7822456
- Tri Tran, K.-V. L., & J. Maciejowski. (2014a). Closed-loop development for dissipativity constraint. In *2014 International Conference onControl, Automation and Information Sciences (ICCAIS)* (pp. 24–29). IEEE. https://doi.org/10.1109/ICCAIS.2014.7020562
- Tri Tran, K.-V. L., & J. Maciejowski. (2014b). Model predictive control of nonlinear input-affine systems with feasibility and stability constraints. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)* (pp. 992–997). IEEE. https://doi.org/10.1109/ICARCV.2014.7064441
- Tri Tran, K.-V. L., & J. Maciejowski. (2014c). Model predictive control via quadratic dissipativity constraint. In *2014 IEEE 53rd Annual Conference on Decision and Control (CDC)* (pp. 6689–6694). IEEE. https://doi.org/10.1109/CDC.2014.7040439
- Tri Tran, K.-V. L., & J. Maciejowski. (n.d.). Economic Model Predictive Control - A Review. In *Proceedings of the 31st ISARC, Sydney, Australia* (pp. 35–42). Retrieved from http://www.iaarc.org/publications/2014_proceedings_of_the_31st_isarc_sydney_australia/economic_model_predictive_control_a_review.html
- Tri Tran, Q. P. H. (2014). Dependable control systems with self-recovery constraint. In *2014 International Conference onControl, Automation and Information Sciences (ICCAIS)* (pp. 87–92). IEEE. https://doi.org/10.1109/ICCAIS.2014.7020574
- Tri Tran, Q. P. H. (2015a). Dependable control systems with Internet of Things. *ISA Transactions*. https://doi.org/10.1016/j.isatra.2015.08.008
- Tri Tran, Q. P. H. (2015b). Modeling of Washing Circuits in Mining - A Networked System Approach. In *Proceedings of International Conference on Modelling of Complex Systems and Environment* (pp. 123–131). Danang, Vietnam. https://doi.org/10.13140/RG.2.1.1744.1767
- Tri Tran, T.-P. C. (2015). Dissipativity Constraint for Distributed Power System State Estimation. In *Proceedings of the 4th International Conference on Control, Automation, and Information Science (ICCAIS'15)* (pp. 360–365). Changshu, China: IEEE. https://doi.org/10.1109/ICCAIS.2015.7338693
- Weng Khuen, H., Tengpeng, C., Keck Voon, L., & Lu, S. (2017). Variance Analysis of Robust State Estimation in Power Systems using Influence Function. *ELSEVIER*, *92*, 53–62. https://doi.org/https://doi.org/10.1016/j.ijepes.2017.04.009
- X-B Chen, K.-J. T., & G. Amaratunga. (2015). State Estimation for Distribution Systems using Micro-Synchrophasors. In *Proceedings of the 7th IEEE PES Asia-Pacific Power and Energy Engineering Conference (PES APPEEC'15)* (pp. 1–5). Brisbane, Australia: IEEE. https://doi.org/10.1109/APPEEC.2015.7381051
- Xuebing Chen, Tengpeng Chen, King Jet Tseng, Yuhao Sun, & Amaratunga, G. (2016). Customized optimal μPMU Placement method for distribution networks (pp. 135–140). IEEE. https://doi.org/10.1109/APPEEC.2016.7779485
- Xueheng, Q., Le Zhang, Ponnuthurai Nagaratnam, S., & Gehan A.J., A. (2017). Oblique Random Forest Ensemble via Least Square Estimation for Time Series Forecasting. *Information Sciences*. https://doi.org/https://doi.org/10.1016/j.ins.2017.08.060
- Xueheng, Q., P.N., S., & Gehan A.J, A. (2017). Short-term Electricity Price Forecasting with Empirical Mode Decomposition based Ensemble Kernel Machines. *Procedia Computer Science*, *108*, 1308–1317. https://doi.org/https://doi.org/10.1016/j.procs.2017.05.055
- Yu, C., Wang, Q.-G., Zhang, D., Wang, L., & Huang, J. (2015). System Identification in Presence of Outliers. *IEEE Transactions on Cybernetics*, 1–1. https://doi.org/10.1109/TCYB.2015.2430356

Conference papers given and to be published in proceedings

- Camacho, J., Singh, A. V., Wang, W., Shan, R., Yapp, E. K. Y., Chen, D., … Wang, H. (2016). Soot particle size distributions in premixed stretch-stabilized flat ethylene–oxygen–argon flames. *Proceedings of the Combustion Institute*. https://doi.org/10.1016/j.proci.2016.06.170
- Wenming, Y., Kun Lin, T., & Kah Wai, K. (21-24 August). Impact of Various Factors on the Performance and Emissions of Diesel Engine Fueled by Kerosene and Its Blend with Diesel. Presented at the 9th International Conference on Applied Energy, Cardiff, UK.
- Zhou, D., Yang, W., Li, J., Tay, K. L., Chou, S. K., & Kraft, M. (8-11 October). Efficient Combustion Modelling in RCCI Engine with Detailed Chemistry. Presented at the Internal Conference on Applied Energy, Beijing, China.
- Ashok Krishnan, B. V. P., & H. B. Gooi, K. V. L. (2016). Predictive control based framework for optimal scheduling of combined cycle gas turbines. Presented at the 2016 American Control Conference, Boston MA, USA: IEEE. https://doi.org/10.1109/ACC.2016.7526622
- Ashok Krishnan, B. V. P., P. S. V. Nataraj, J. M., & K. V. Ling. (2017). Model predictive control of a CSTR: A comparative study among linear and nonlinear model approaches. In *2017 Indian Control Conference (ICC)*. Guwahati, India: IEEE. https://doi.org/10.1109/INDIANCC.2017.7846472
- Ashok Krishnan, F. Y. S. E., & Bhagyesh V. Patil. (2017). Hybrid Model Predictive Control Framework for the Thermal Unit Commitment Problem including Start-up and Shutdown Power Trajectories (Vol. 50). Presented at the IFAC 2017 World Congress, Toulouse, France: International Federation of Automatic Control (IFAC).
- Foo Yi Shyh Eddy, G. H. B. (2016, June). *How real is real? Comparative Studies on NTU Microgrid Testbed*. User Conference presented at the RT16 OPAL-RT User Conference, Munich, Germany. Retrieved from http://www.opal-rt.com/sites/default/files/file/Events/RT16/RT16%20GUIDE%20WEB.pdf

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