CAMBRIDGE CARES

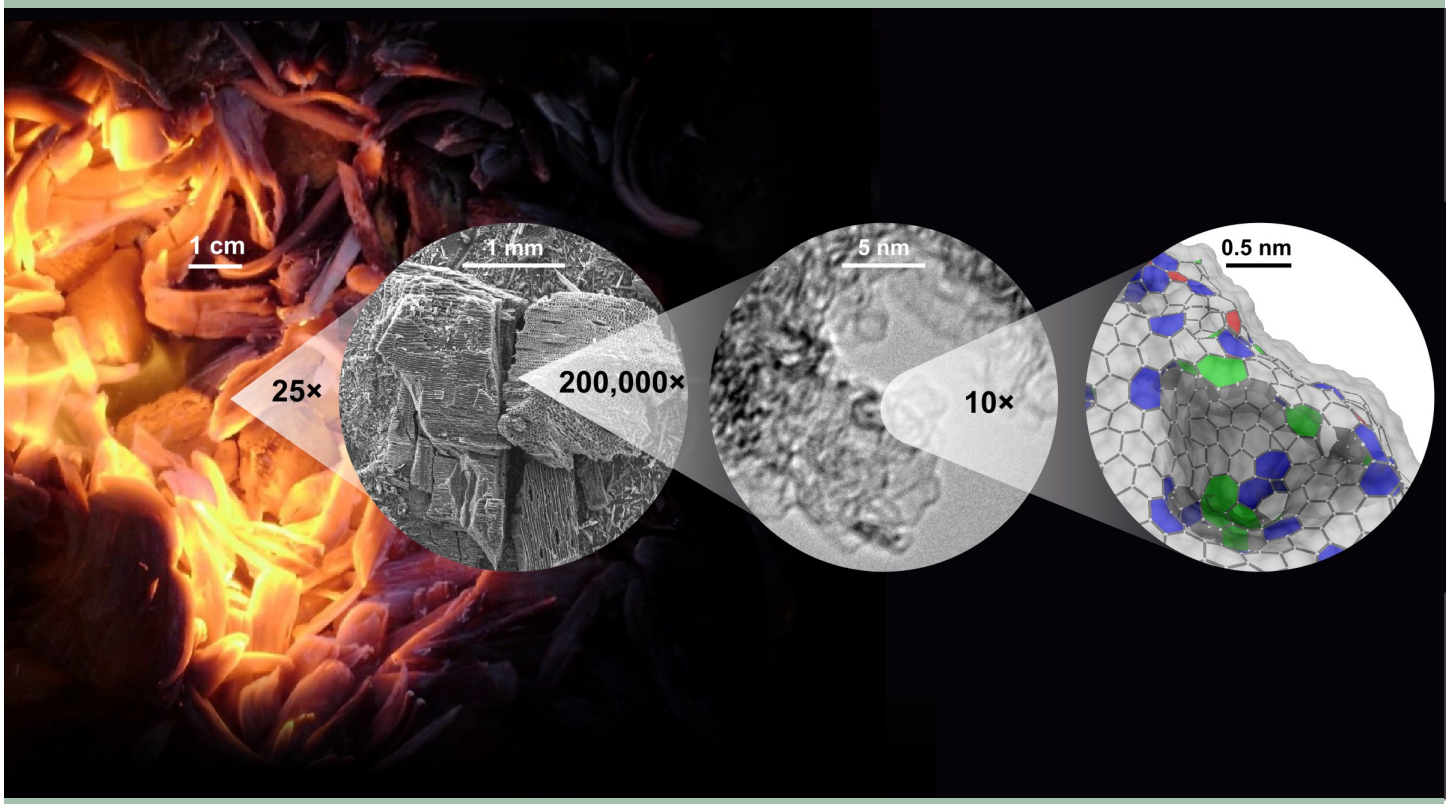
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH AND EDUCATION IN SINGAPORE LTD.

Biannual Research Report

November 2017 — April 2018

CAM.CREATE C4T

Cambridge Centre for Carbon Reduction in Chemical Technology



CREATE

Campus for Research Excellence And Technological Enterprise

University of Cambridge

Nanyang Technological University

National University of Singapore

Cover figure

The structure of charcoal at various length scales —from the macroscale to the nanoscale (Jacob MARTIN, PhD student, CAM, IRP3 CARES C4T).

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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

Prof. Markus Kraft

CARES Director

April 2018

I am very pleased to present the 8th 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). The last six months have been a particularly busy and fruitful time for our programme as we plan the next five years of work with our second phase of funding beginning in November. We are also celebrating the commencement of our first Intra-CREATE project.

Phase 2

Since our last biannual report, we have submitted a proposal to the National Research Foundation (NRF) for our next five years of research. I'm happy to report that we had a positive and constructive interview with NRF at the end of December and are currently finalising the details of our next research phase with a proposed start date of 1 November 2018. Phase 2 research will include a new Interdisciplinary Research Programme (IRP) on how we can best integrate and apply our research to industry here in Singapore (IRP Better Business) and a new separate IRP for the J-Park Simulator (part of IRP3 in Phase 1). The current IRP4 programme on the Jurong Island electrical sub-network will cease in its current form, but we hope the new Grid 2.0 programme run by NRF will be able to pick up some of this work and benefit from the outputs of the current programme. The new IRP4 will focus on waste heat utilisation.

PIs in residence

Prof. Alexei LAPKIN has now successfully completed his six-month stay in Singapore, spending time in the CARES office while also serving as an Adjunct Professor at NUS where he gave undergraduate lectures as part of a new course on advanced reaction engineering. We also enjoyed a shorter visit from Dr Adrian FISHER (CAM, IRP2) in March. During their visits Prof. LAPKIN and Dr FISHER were able to develop relationships with potential collaborators, including various A*STAR Institutes and industry. In addition, they of course enjoyed the opportunity to spend time in person with Singapore-based CARES members.

Intra-CREATE

CARES' first Intra-CREATE programme, eCO_2EP ("A table top chemical factory for the reduction of CO_2 to value added chemicals") commenced in January 2018 with a kick-off meeting held in Singapore. The kick-off meeting was attended by representatives from A*STAR institutes (IMRE and SIMTech) and local industry. The meeting set out the context of the project (large-scale chemical storage of energy and independent routes to ethylene and propylene) and identified potential future collaborators and partners. The next face-to-face consortium meeting will be held in Singapore in June. We are looking forward to seeing the first results of this programme later this year.

Highlights

One of our main highlights of 2017 was the CREATE 10th Anniversary Symposium in early December. This was a wonderful event, attended by former President of Singapore Dr Tony TAN and Singapore Finance Minister Mr HENG Swee Keat. I chaired a session on energy during which Dr LIM Mei Qi (Project Officer, NTU, IRP3) gave an excellent presentation on the J-Park Simulator along with contributions from several other CREATE entities. Several of our PhD students had the opportunity to present posters and to discuss their work with the wider community.

CARES C4T research continues to fill the development pipeline, with two promising patents filed recently. The first is a provisional patent is for a high-shear microreactor for nanomaterial synthesis, filed by Nick JOSE (PhD student, CAM, IRP1) and Prof. Alexei LAPKIN (PI, CAM, IRP1). Nick and Alexei are hoping to commercialise this via a spin-off based in Singapore. The second patent is for the production of lactic acid from glycerol via electrosynthesis, filed by Prof. Zhichuan XU (Co-PI, NTU, IRP2), Dr Chencheng DAI (RF, NTU, IRP2) and Dr Adrian FISHER (PI, CAM, IRP2).

Conferences and external presentations

We had several researchers attend conferences around the world to present their work. Two of our members, both NTU Research Fellows with IRP1, attended the 2017 Annual Meeting of the American Institute of Chemical Engineers (AIChE), held in Minneapolis, USA during October/November – Dr Quang Thang (Victor) TRINH presented one talk while Dr Jithin John VARGHESE gave two, all covering some of latest research from across IRP1. Two of our IRP4 researchers, Jan MACIEJOWSKI (PI, CAM) and Bhagyesh PATIL (RF, NTU) attended the IEEE Conference on Decision and Control in Melbourne, Australia, and presented a paper. Also in IRP4, Yuhao SUN (Senior RF, NTU) presented a paper and also hosted a session on distributed generation and smart grids at the 12th IEEE International Conference on Power Electronics and Drive Systems. Vishvak KANNAN (PhD student, NUS, IRP2) presented a poster at the COMSOL conference Singapore, November 2017, entitled "Analysis of current at the surface of a rocking disk electrode".

CARES C4T members have been busy presenting our research to the wider public and more general audiences. Prof. Alexei LAPKIN (PI, CAM, IRP1) presented a seminar at the CREATE PI seminar series in November. The topic of his talk was "First Principles Process Models for Design of Intensified Catalytic Processes." In addition, one of our PhD students (Jacob MARTIN, CAM, IRP3) visited a local primary school in January to give a science demonstration complete with explosions and plenty of dry ice.

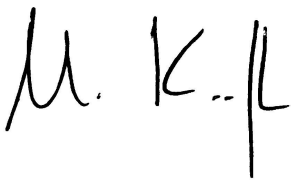
Visitors

We have been fortunate to have had a number of guest seminars from Visiting Scientists since our last report, covering a range of topics from nanoparticles to hydrogen fuels. For a full report on our Visiting Scientist programme, please see Appendix 2. We were also glad to host members of the Singapore Oxford and Cambridge Society, who visited in September to learn more about the programme and have a tour of our laboratories.

Features

This report features articles from two of our members that give further insight into the applications of some of the work being done at CARES, while covering the science behind the concepts. Dr SUN Libo (RF, NTU, IRP2) explains how carbon dioxide can be converted into other useful materials and VO Chi Hung (PhD student, NUS, IRP3) looks at the role of microbes in storing excess carbon. If you would like to stay up to date on our latest news and research, do take a look at our website, where our new Communications Officer has been reporting our events and scientific updates (www.cares.cam.ac.uk).

I hope I have encouraged you to read more about CARES' latest work and achievements in this report. As ever, please do get in touch if you have any questions or see opportunity for collaboration.



Prof. Markus Kraft, CARES Director

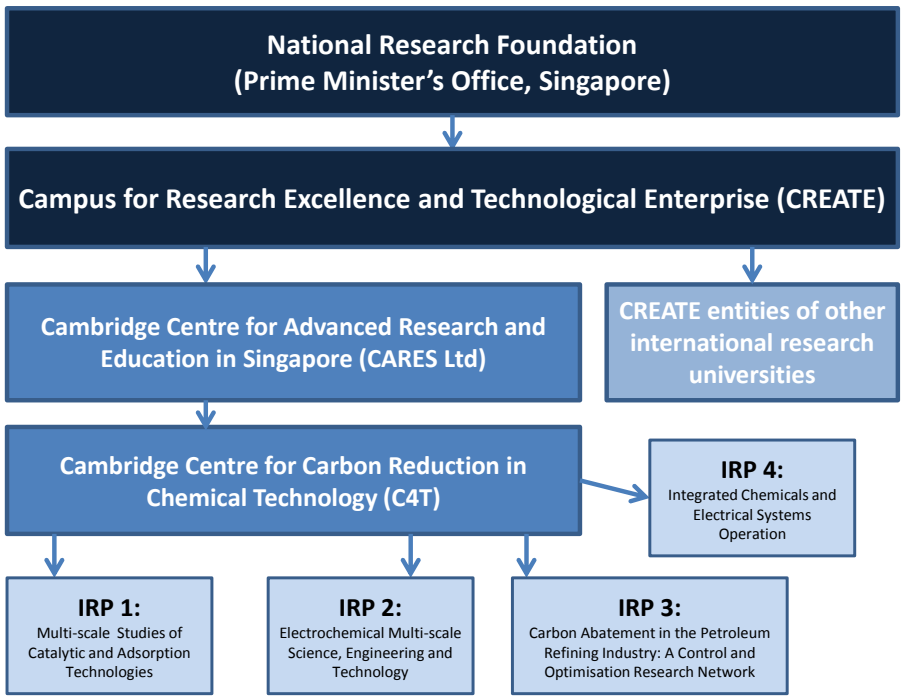
April 2018

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 interaction between 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)

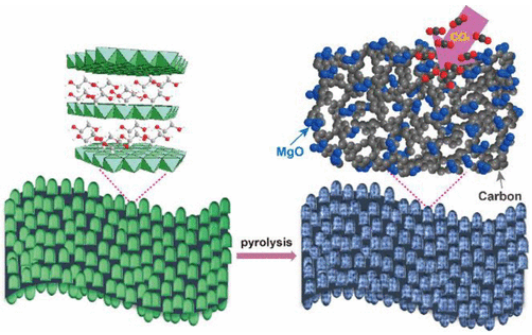
2.1 IRP1: Hierarchical Nanocomposite by the Integration of Reduced Graphene Oxide and Amorphous Carbon with Ultrafine MgO Nanocrystallites for Enhanced CO_2 Capture

Ping Li and Hua Chun Zeng

DOI: 10.1021/acs.est.7b03308

Abstract:

Exploring efficient and low-cost solid sorbents is essential for carbon capture and storage. Herein, a novel class of high-performance CO_2 adsorbent (rGO@MgO/C) is engineered based on the controllable integration of reduced graphene oxide (rGO), amorphous carbon and MgO nanocrystallites. The optimised rGO@MgO/C nanocomposite exhibits remarkable CO_2 capture capacity (up to 31.5 wt % at 27 °C, 1 bar CO_2, and 22.5 wt % under the simulated flue gas), fast sorption rate and strong process durability. The enhanced capture capability of CO_2 is the best among all of the MgO-based sorbents reported so far. The high performance of rGO@MgO/C nanocomposite can be ascribed to the hierarchical architecture and special physicochemical features, including the sheet-on-sheet sandwich-like structure, ultrathin nanosheets with abundant nanopores, large surface area and highly dispersed ultrafine MgO nanocrystallites (ca. 3 nm in size), together with the rGO sheets and in situ generated amorphous carbon that serve as a dual carbon support and protectant system with which to prevent MgO nanocrystallites from agglomeration. In addition, the CO_2-uptake capacity at intermediate temperatures (e.g. 350 °C) can be further improved threefold through alkali metal salt promotion treatment. This work provides a facile and effective strategy with which to engineer advanced graphene-based functional nanocomposites with rationally designed compositions and architectures for potential applications in the field of gas storage and separation.



IRP1: ZIF-67-Derived Nanoreactors for Controlling Product Selectivity in CO_2 Hydrogenation

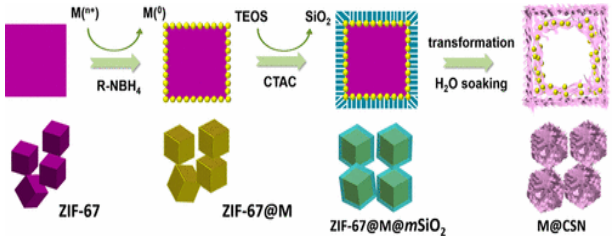
Guowu Zhan and Hua Chun Zeng

DOI: 10.1021/acscatal.7b01827

Abstract:

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, of which catalysts lie at the heart. However, our fundamental understanding of the correlation between catalyst structures and product selectivity is still limited because in most cases the catalyst structures in nanoscale are not well-defined. Herein, we report the design and synthesis of nanoreactors by phase transformations of sandwich-structured ZIF-67@Pt@*m*SiO_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 mazelike 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 catalysed by the nearby cobalt site. It was found that the overall "long retention time" for feed gases on catalysts significantly affected the product distribution. Thus, the specific activity (in the form of turnover frequency) of the nanoreactor having prolonged diffusion paths was

around six times as much as that of other comparative catalysts with shorter diffusion paths. This work contributes insights to the CO_2 hydrogenation to methane over bifunctional nanoreactors with designed structures.



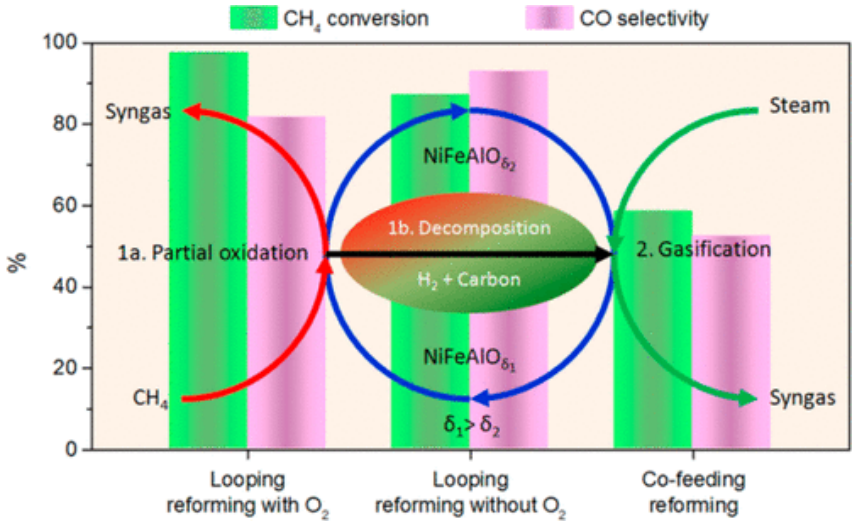
IRP1: High-Performance Ni–Fe Redox Catalysts for Selective CH_4 to Syngas Conversion via Chemical Looping

Jijiang Huang, Wen Liu, Yanhui Yang and Bin Liu

DOI: 10.1021/acscatal.7b03964

Abstract:

In traditional steam reforming of CH_4, the CH_4 conversion and its selectivity to CO and H_2 are thermodynamically limited. In this work, we designed a series of Ni–Fe redox catalysts with varying Ni/Fe ratios. The Ni–Fe redox catalysts could function as oxygen carriers to selectively convert CH_4 to syngas via chemical looping. The selectivity to CO was dramatically enhanced via a selective conversion route of CH_4 to C and H_2 in the reduction, followed by C gasification to syngas with hot steam. Taking the advantages of the highly reactive Ni species for CH_4 activation and Fe species for water splitting, together with the resulting NiFe alloy in the reduced catalyst for catalytic CH_4 decomposition, high CH_4 conversion up to 97.5% and CO selectivity up to 92.9% were achieved at 900 °C with productivity of CO and H_2 of 9.6 and 29.0 mol kg−1, respectively, on equimolar Ni–Fe catalyst.



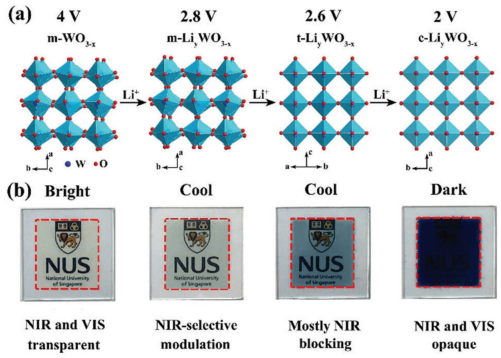
2.2 IRP2: Monoclinic Oxygen-Deficient Tungsten Oxide Nanowires for Dynamic and Independent Control of Near-Infrared and Visible Light Transmittance

Shengliang Zhang, Sheng Cao, Tianran Zhang, Qiaofeng Yao, Adrian C. Fisher and Jim Yang Lee

DOI: 10.1039/C7MH01128H

Abstract:

The transmittance of near-infrared (NIR) and visible (VIS) light spectral regions can be dynamically and independently controlled using a single-component material – monoclinic oxygen-deficient tungsten oxide nanowires, without the need for compositing with other electrochromic materials. A localised surface plasmon resonance and phase-transition assisted mechanism and bandgap transition electrochromism are individually responsible for the modulation of the NIR and VIS light transmissions.



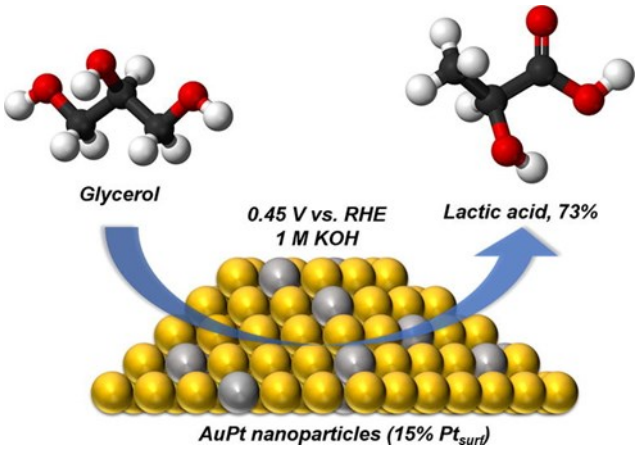
IRP2: Electrochemical Production of Lactic Acid from Glycerol Oxidation Catalyzed by AuPt Nanoparticles

Chencheng Dai, Libo Sun, Hanbin Liao, Bahareh Kherzi, Richard D. Webster, Adrian C. Fisher and Zhichuan J. Xu

DOI: 10.1016/j.jcat.s017.10.010

Highlights:

- Lactic acid is produced by glycerol electro-oxidation with high selectivity.
- AuPt catalyst with Au-riched surface exhibits the highest lactic acid selectivity.
- Lower applied potential for glycerol oxidation enhances lactic acid selectivity.
- Higher KOH concentration improves lactic acid selectivity and glycerol conversion.
- Glycerol concentration has a disregardable influence on lactic acid selectivity.



Abstract:

The production of valuable chemicals from relatively inexpensive feedstocks utilising electrochemical methods has been attracting widespread attention in recent years as it is highly efficient, decentralised, environmentally friendly and can operate at room temperature and pressure. Currently, the industrial production of lactic acid is mainly based on bio-fermentation. This has drawbacks including severe conditions, unfriendliness to the environment, low efficiency and the requirement of expensive equipment, but these can potentially be overcome by electrochemical methods. Herein, we report for the first time the preparation of lactic acid at room temperature and pressure from the one-pot electro-oxidation of glycerol, a byproduct from biodiesel production. AuPt nanoparti-

cles with different surface compositions were employed in this work to optimise the catalysis performance, and the glycerol oxidation was operated at a series of applied potentials, pH and glycerol concentration. The optimal lactic acid selectivity was 73%, obtained with Au-enriched surface at applied potential of 0.45 V vs. RHE.

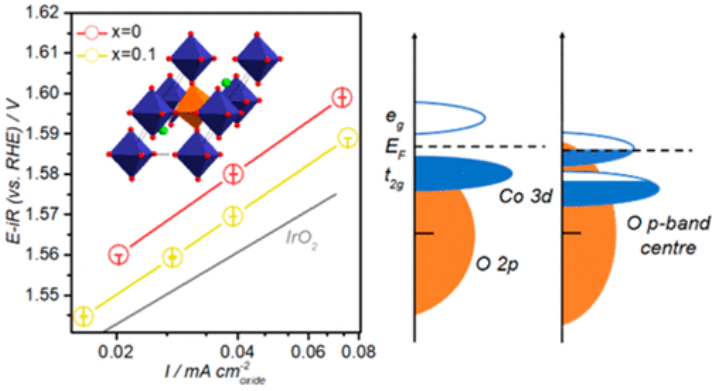
IRP2: Tailoring the Co 3d-O 2p Covalency in $LaCoO_3$ by Fe Substitution To Promote Oxygen Evolution Reaction

Yan Duan, Shengnan Sun, Shibo Xi, Xiao Ren, Ye Zhou, Ganlu Zhang, Haitao Yang, Yonghua Du and Zhichuan J. Xu

DOI: 10.1021/acs.chemmater.7b04534

Abstract:

$LaCoO_3$ is an active, stable catalyst in alkaline solution for oxygen evolution reaction (OER). With its lower cost, it is a potential alternative to precious metal oxides like IrO_2 and RuO_2 in water electrolysis. However, room still remains for improving its activity according to recent understandings of OER on perovskite oxides. In this work, Fe substitution has been introduced in $LaCoO_3$ to boost its OER performance. Density function theory (DFT) calculations verified that the enhanced performance originates from the enhanced Co 3d-O 2p covalency with 10 at% Fe substitution in $LaCoO_3$. Both DFT calculations and Superconducting Quantum Design (SQUID) magnetometer (MPMS-XL) showed a Co^{3+} spin state transition from generally low spin state (LS: $t_{2g}^6 e_g^0$, S = 0) to a higher spin state with the effect of 10 at% Fe substitution. X-ray absorption near-edge structure (XANES) supports DFT calculations on an insulator to half-metal transition with 10 at% Fe substitution, induced by spin state transition. The half-metallic $LaCo_{0.9}Fe_{0.1}O_3$ possesses increased overlap between Co 3d and O 2p states, which results in enhanced covalency and promoted OER performance. This finding enlightens a new way of tuning the metal–oxygen covalency in oxide catalysts for OER.



IRP2: Revealing the Dominant Chemistry for Oxygen Reduction Reaction on Small Oxide Nanoparticles

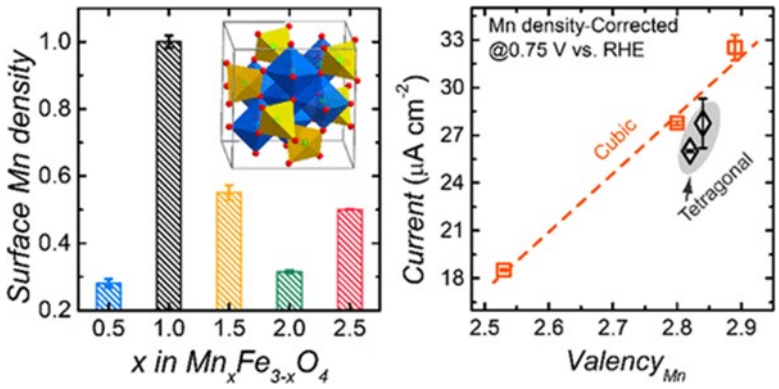
Ye Zhou, Shibo Xi, Jingxian Wang, Shengnan Sun, Chao Wei, Zhenxing Feng, Yonghua Du and Zhichuan J. Xu

DOI: 10.1021/acscatal.7b03864

Abstract:

Bulk chemistry has been successfully used as a descriptor for oxygen reduction reaction (ORR) activities of various metal oxides. However, as the size of oxides becomes small, bulk chemistry may not be sufficient to describe the activities. Here, we report a systematic study on Mn-substituted ferrite $Mn_xFe_{3-x}O_4$ (x = 0.5–2.5) nanoparticles and the roles of surface Mn in determining their ORR activities. Gradual Mn substitution induced changes in Mn valence and crystal structure.

However, there is no remarkable correlation that can be found between their bulk chemistry and ORR activities. Instead, the surface Mn density and valency were found to play dominant roles in determining the ORR. This work shows that, at a small particle size, the bulk chemistry of oxides may not be the descriptor for their electrochemical properties. Due to the significantly high surface/bulk ratio, the surface chemistry has to be carefully characterised to interpret the activities of oxide nanoparticles.



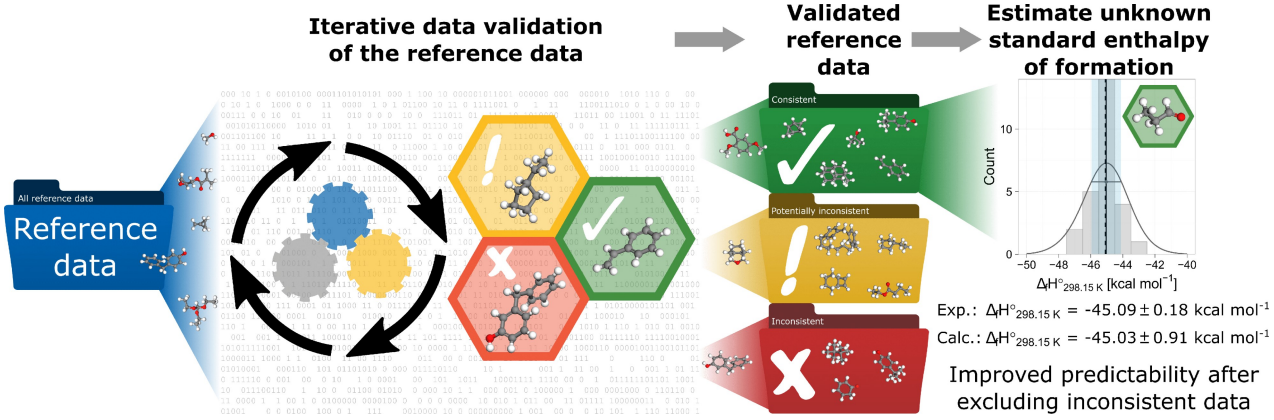
2.3 IRP3: A Systematic Method to Estimate and Validate Enthalpies of Formation Using Error-Cancelling Balanced Reactions

Philipp Buerger, Jethro Akroyd, Sebastian Mosbach and Markus Kraft

DOI: 10.1016/j.combustflame.2017.08.013

Abstract:

This paper presents an automated framework that uses overlapping subsets of reference data to systematically derive an informed estimate of the standard enthalpy of formation of chemical species and assess the consistency of the reference data. The theory of error-cancelling balanced reactions (EBRs) is used to calculate estimates of the standard enthalpy of formation. Individual EBRs are identified using linear programming. The first part of the framework recursively identifies multiple EBRs for specified target species. A distribution of estimates can then be determined for each species from which an informed estimate of the enthalpy is derived. The second part of the framework



iteratively isolates inconsistent reference data and improves the prediction accuracy by excluding such data. The application of the framework is demonstrated for test cases from organic and inorganic chemistry, including transition metal complexes. Its application to a set of 920 carbon, hydrogen and oxygen containing species resulted in a rapid decrease of the mean absolute error for estimates of the enthalpy of formation of each species due to the identification and exclusion of inconsistent reference data. Its application to titanium-containing species identified that the available reference values of TiOCl and $TiO(OH)_2$ are inconsistent and need further attention. Revised values are calculated for both species. A comparison with popular high-level quantum chemistry methods shows that the framework is able to use affordable density functional theory (DFT) calculations to deliver highly accurate estimates of the standard enthalpy of formation, comparable to high-level quantum chemistry methods for both hydrocarbons and transition metal complexes.

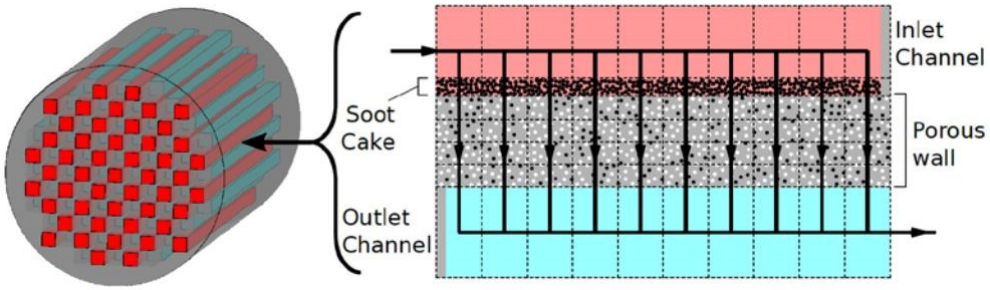
IRP3: Modelling of Secondary Particulate Emissions during the Regeneration of Diesel Particulate Filters

Chung Ting Lao, Jethro Akroyd, Nick Eaves and Markus Kraft

DOI: 10.1016/j.egypro.2017.12.245

Abstract:

Significant nanoparticle emission during the regeneration of Diesel Particulate Filters (DPFs) has been observed in experiments. A numerical reactive-flow model is coupled with a sectional particle method and phenomenological filtration model to describe the behaviour of the DPF, and in particular the evolution of soot particle size distribution. The ability of the model to predict the pressure drop and flow profile in the DPF is critically assessed against experimental and simulated results from the literature. The capability to describe the impact of oxidative fragmentation on the size distribution of trapped particles is demonstrated. The model is shown to be able to qualitatively describe the decrease in average soot particle size during regeneration which will allow better prediction of particle number emissions.



Single channel model representation of a monolithic diesel particulate filter (DPF).

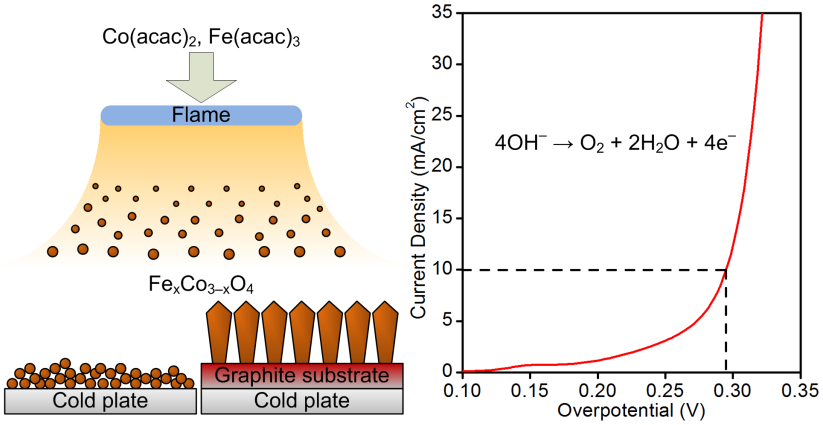
IRP3: Co_3O_4 and $Fe_xCo_{3-x}O_4$ Nanoparticles/Films Synthesized in a Vapor-Fed Flame Aerosol Reactor for Oxygen Evolution

Sheng Yuan, Maria L. Botero, Manoel Y. Manuputty, Markus Kraft and Rong Xu

DOI: 10.1021/acsaem.7b00172

Abstract:

Synthesis of earth-abundant nanocatalysts for the oxygen evolution reaction (OER) has depended largely on highly diluted, batchwise wet chemical methods, leaving it a challenge to improve throughput and sustainability of the process. Herein, we demonstrate for the first time the production of Co_3O_4 and $Fe_xCo_{3-x}O_4$ nanoparticles using vapour-fed flame aerosol synthesis (VFAS), a continuous and scalable process requiring minimal waste treatment. In 1 M KOH, the catalysts exhibit stable OER overpotentials of 295 mV at 10 mA/cm^2 and Tafel slopes down to 38 mV/dec, which are comparable to the performances of wet-chemically derived benchmark (Fe-doped) Co_3O_4 catalysts. The high activity is attributed to ultrafine particle size of ⟨Dp⟩ = 3.1–4.4 nm and rich surface defects. Furthermore, nanostructured Co_3O_4 and $Fe_xCo_{3-x}O_4$ films can be conveniently grown on graphite substrates by VFAS and serve as OER electrodes without further treatment. Remarkably, the morphology of the films can be easily tuned from columnar to granular by varying precursor concentration in feed gas, achieving optimal utilisation of catalytic materials with a hierarchical structure consisting of elongated nanoparticulate building blocks.



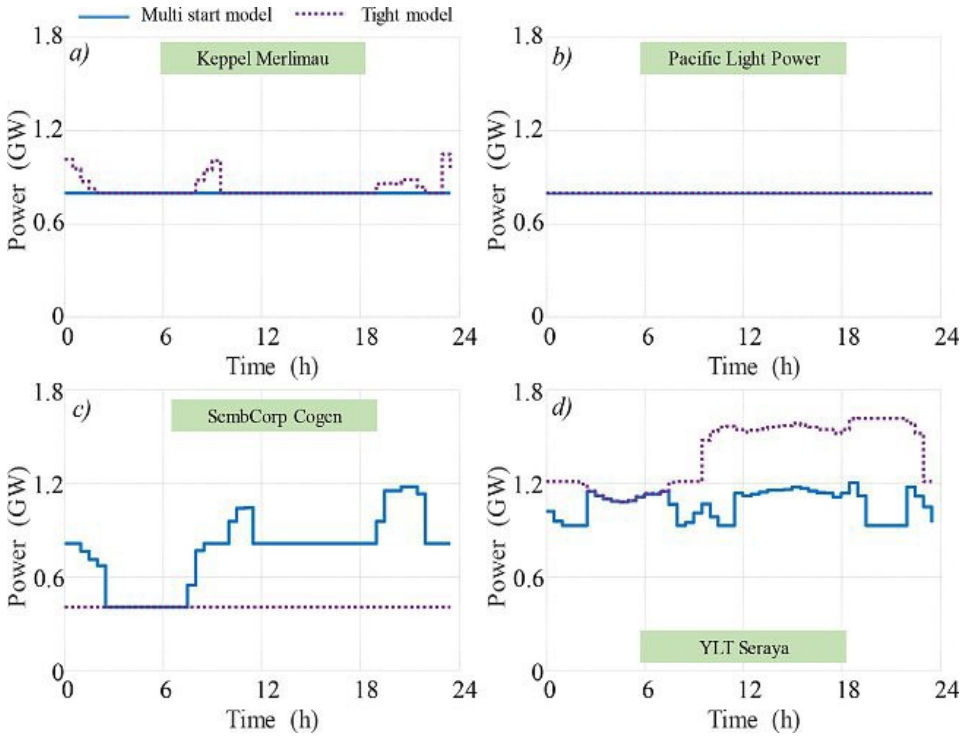
2.4 IRP4: A Generic Method to Model CO_2 Emission Performances of Combined-Cycle Power Plants for Environmental Unit Commitment

Rémy Rigo-Mariani, K. V. Ling and Jan M. Maciejowski

DOI: 10.1002/ente.201700552

Abstract:

This paper proposes a generic methodology for combined cycle gas turbine modelling. The main objectives are the estimation of the CO_2 emissions for specific units and their integration in an environmental power dispatch that considers several plants. First, a design procedure aims at calibrating the model using the information available from the manufactures. Off-design points are also investigated to estimate the CO_2 emissions for the whole operating range of the units. The obtained CO_2-cost results show a good consistency with the emission coefficients found in the literature for that type of unit. Then, those CO_2 costs are used as input parameters for a unit commitment problem. Mixed-integer linear programming formulation minimises the global emissions for a set of different units on Jurong Island in Singapore. The grid emission factor obtained for the simulated network displays values close to the registered field data, which validates the developed model. Finally, a tightened formulation for the power-dispatch problem is introduced. The objective is to reduce the computational time while guaranteeing good performance of the returned solutions.



Tight model results in comparison to the multi-start model for the different power plants on Jurong Island (Singapore): a) KPL, b) PLP, c) SMB and d) SRY.

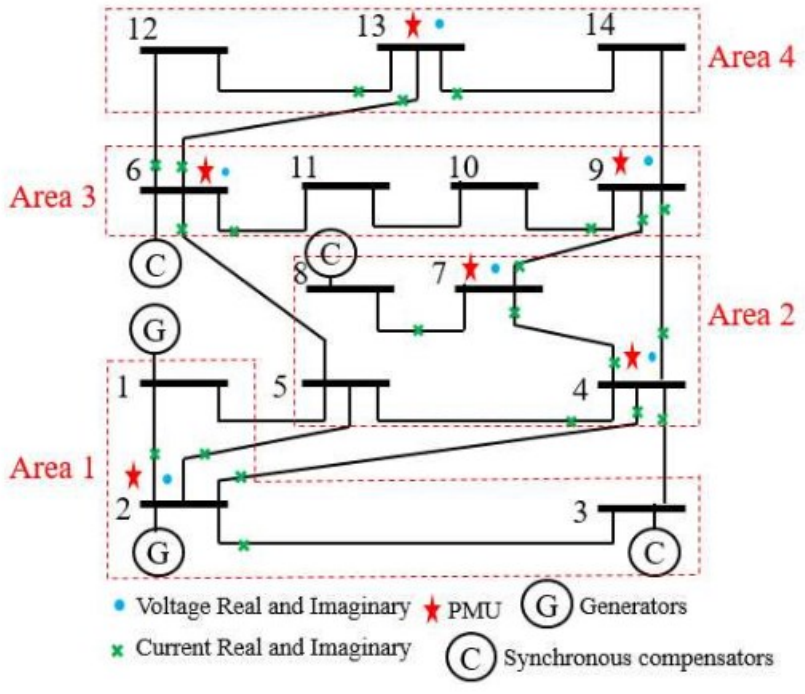
IRP4: Distributed State Estimation Using a Modified Partitioned Moving Horizon Strategy for Power Systems

Tengpeng Chen, Yi Shyh Eddy Foo, K.V Ling and Xuebing Chen

DOI: 10.3390/s17102310

Abstract:

In this paper, a distributed state estimation method based on moving horizon estimation (MHE) is proposed for the large-scale power system state estimation. The proposed method partitions the power systems into several local areas with non-overlapping states. Unlike the centralised approach where all measurements are sent to a processing centre, the proposed method distributes the state estimation task to the local processing centres where local measurements are collected. Inspired by the partitioned moving horizon estimation (PMHE) algorithm, each local area solves a smaller optimisation problem to estimate its own local states by using local measurements and estimated results from its neighbouring areas. In contrast with PMHE, the error from the process model is ignored in our method. The proposed modified PMHE (mPMHE) approach can also take constraints on states into account during the optimisation process such that the influence of the outliers can be further mitigated. Simulation results on the IEEE 14-bus and 118-bus systems verify that our method achieves comparable state estimation accuracy but with a significant reduction in the overall computation load.



IEEE 14-bus system with phasor measurement units (PMUs).

IRP4: Optimal Power Flow Solutions Using Differential Evolution Algorithm Integrated with Effective Constraint Handling Techniques

Partha Biswas, Ponnuthurai Suganthan, Rammohan Mallipeddi and Gehan Amaratunga

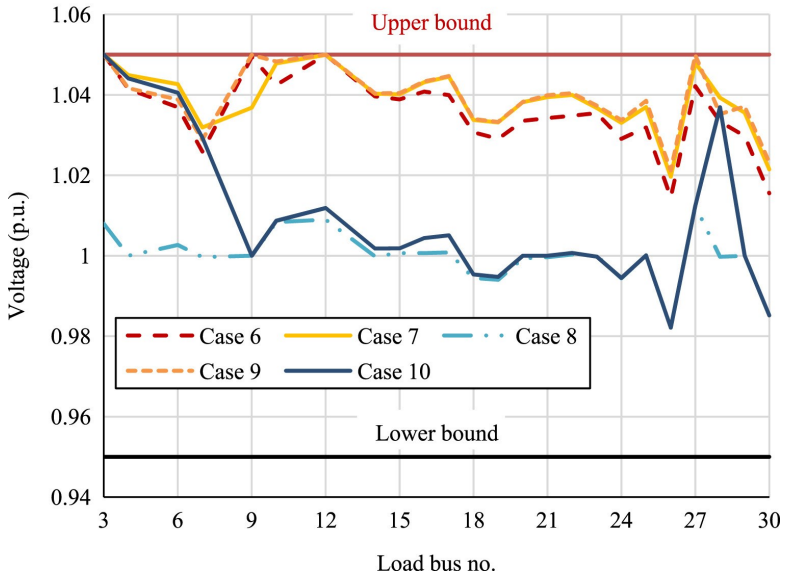
DOI: 10.1016/j.engappai.2017.10.019

Highlights:

- Optimal power flow problems for IEEE 30, 57 and 118-bus systems are studied.
- Several single and multi-objective case studies are performed.
- Performances of 3-constraint handling techniques are analysed.
- Differential evolution (DE) is used as basic search algorithm.
- Results are compared with most recent studies and improvement is observed.

Abstract:

Optimal power flow (OPF) is a highly non-linear complex optimisation problem where the steady state parameters of an electrical network need to be determined for its economical and efficient operation. The complexity of the problem escalates with the ubiquitous presence of constraints in the problem. Solving OPF remains a popular but challenging task among power system researchers. In last couple of decades, numerous evolutionary algorithms (EAs) have been applied to find optimal solutions with different objectives of OPF. However, the search method adopted by EAs is unconstrained. An extensively used methodology to discard infeasible solutions found during the search process is the static penalty function approach. The process requires appropriate selection of penalty coefficients decided largely by a tedious trial and error method. This paper presents performance evaluation of proper constraint handling (CH) techniques — superiority of feasibly solutions (SF), self-adaptive penalty (SP) and an ensemble of these two constraint handling techniques (ECHT) with differential evolution (DE) being the basic search algorithm, on the problem of OPF. The methods are tested on standard IEEE 30, IEEE 57 and IEEE 118-bus systems for several OPF objectives such as cost, emission, power loss, voltage stability etc. Single objective and weighted sum multi-objective cases of OPF are studied under the scope of this literature. Simulation results are analysed and compared with most recent studies on the problem.

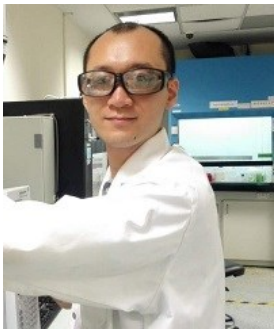


IEEE 30-bus system – voltage profiles of load buses for best solutions of case 6 to case 10.

2.5 Focus on Impact

In the fourth of a CARES C4T series of short articles focusing on the potential real world impact of the programme's research, Dr SUN Libo explores a new, more efficient method of converting carbon dioxide into other useful materials, while VO Chi Hung discusses the role that microbes play in storing excess carbon.

Focus on Impact: Single-Atom Catalysts for More Efficient Conversion of CO_2



DR Sun Libo received his PhD thesis under the supervision of Prof. YU Jihong in State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, China. His PhD research focused on the synthesis of porous materials, including mesoporous and microporous materials, metal-organic frameworks and porous organic polymers.

For his current Cambridge CARES project, his interest has turned to electrochemical areas and he is now focused on CO_2 reduction and oxygen evolution, with complex or single-atom catalysts.

The problem of climate change is currently attracting widespread attention due to its negative impact on people around the world. Disasters like glacial melting, sea level rise, changing ecosystems, increased droughts and floods and deadly heat waves are no longer hypothetical ideas but real threats to society. It is widely accepted that the emission of greenhouse gases like carbon dioxide (CO_2) from the burning of fossil fuels, agriculture and deforestation, mainly initiated by humans, is the main culprit of climate change. An observable temperature increase has accompanied these fossil fuel emissions and the concentration of CO_2 in the atmosphere has increased from 350 ppm (the upper safety limit) in 1990 to around 400 ppm today. Furthermore, the depletion of the non-renewable fossil fuels due to the world's fast economic development and population growth is contributing to an energy crisis while rapidly increasing CO_2 emissions into the atmosphere. It is time to develop new paths to obtain the world's required energy, while at the same time reducing our harmful emissions.

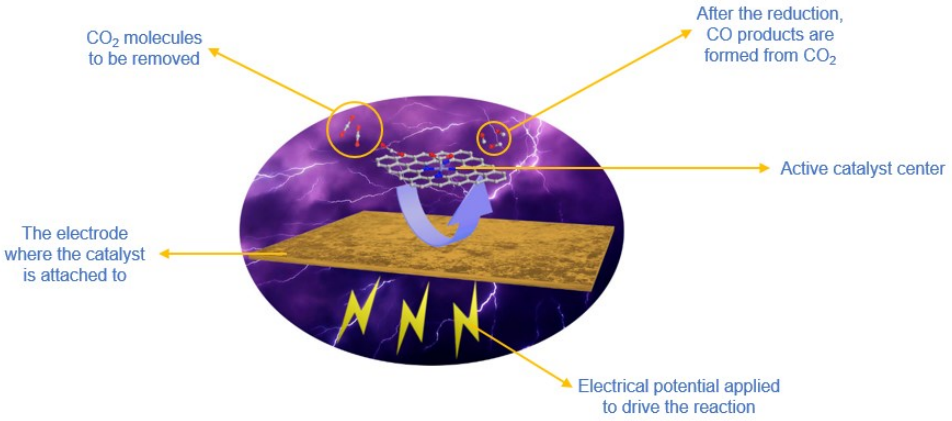
Numerous methods have been devised in an effort to solve this problem, including the development of novel, clean and renewable energies (e.g. wind, solar and tide) and ways to decrease the concentration of atmospheric CO_2. Harnessing these alternative energies can partly replace the use of fossil fuels. In addition, CO_2 capture and sequestration (CCS) techniques are being explored to decrease the amount of CO_2 released into the atmosphere. However, fossil fuel is still irreplaceable and makes up more than 80% of total energy consumed per year, while CCS techniques are imperfect solutions due to their expensive price, high energy consumption and the required storage space.

Another solution is to convert CO_2 into other useful chemicals. A great many techniques to implement this have been explored, including electrochemical and biological options. Among the current methods being developed, electrochemical CO_2 reduction is the most attractive due to its simple operating conditions and the diversity of chemicals it can produce. This process uses electricity to convert CO_2 to a number of other chemicals and can be an energy-saving process. Electrochemical CO_2 reduction uses electricity applied across electrodes (one positive and one negative) to drive a chemical reaction that wouldn't otherwise occur. The products of these reactions usually include organic feedstocks like formic acid (CH_2O_2), carbon monoxide (CO) and methanol (CH_3OH), and other hydrocarbons like methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6). Electrochemical CO_2 reduction can both reduce CO_2 emissions into the environment and produce useful fuel sources.

The latest research has shown that in a standard electrochemical setup, a small change in the relative electrical potential of the solid and liquid phases can give a greatly improved reaction rate, requiring a lower amount of energy to get started, when compared with other methods mentioned above. Using this reaction, researchers have found that metals like indium, tin and lead tend to produce formic acid, while silver, gold, palladium and zinc may produce carbon monoxide. Copper is unique as it can produce a series of different products, including C1-C2 hydrocarbons with different selectivity. Despite the versatility and low energy requirements of electrochemical CO_2 reduction, the technique is not yet perfect. We are still searching for excellent catalysts that are economical, have a low activation energy to initiate the reaction, a high selectivity to designated product, longer stability and a high current density during the process.

A possible candidate for this is single-atom catalysts, which have drawn much interest over the last few years. In such catalysts, the metal active sites are evenly dispersed onto the substrates, which means a highly efficient use of metal to the atomic level. Standard electrochemical reduction techniques incorporate materials of varying surface orientations, which can affect the amount of organic feedstock produced. In single-atom catalysts, however, the even dispersion of atoms on the substrate gives a fast and highly uniform production rate. Some factors need to be considered when fabricating such catalysts:

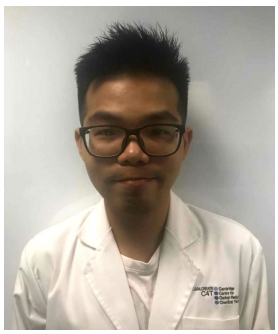
One, all the atoms should be exposed to the surface of the substrate, which means the electrochemical surface area should be large enough to react with electrolytes directly, and diminish the mass transport to the inside layers of catalysts. Two, the substrate should be conductive, helping to make the charge transfer more efficient, so carbon-based, or element-doped carbon can be an ideal substrate. Three, the stability and durability of catalysts needs to be considered, as a large overpotential (excess energy) may induce the single atoms to aggregate during the process. Four, the mass loading should be as large as possible while keeping a highly dispersed structure, and thus a higher current density. Finally and most importantly, to understand the reaction mechanism of such single-atom catalysts, there is no doubt that the synergistic effects between the substrate and the metal atoms used may contribute to performance and efficiency.



A diagram showing the process of electrochemical CO_2 reduction on a single-atom catalyst.

Based on the points mentioned above, we aim to develop single-atom catalysts with uniform and large loading efficiency, high conductivity and better stability and durability. We have therefore selected a nitrogen-doped carbon substrate to prepare single-atom metals with transition metals (such as iron, cobalt, nickel and copper) to form metal-nitrogen-carbon catalysts. Such catalysts can better utilise atoms, exhibit higher selectivity during the tests, reduce wasted energy and increase stability. One catalyst that we are currently investigating could exhibit higher selectivity towards carbon monoxide, above 90%, in the testing range of -0.65 to -1.05 V versus the standard reversible hydrogen electrode.

Future research promises continual improvements to these catalysts. Eventually, the technology will have developed to the point where there can be large-scale application in areas such as the petroleum refinery industry. Cleaning up and transforming some of the waste produced by refineries through electrochemical reduction is one of many ways in which we can reduce our atmospheric carbon dioxide levels and mitigate the damaging effects of climate change.



VO Chi Hung's research focuses on the construction and utilisation of a metabolic model for the methanogen M. maripaludis S2, an organism capable of capturing CO_2 and producing methane.

Knowledge gained from the study of this organism will allow genetic modification to enhance its CO_2 capture capabilities. A promising application of this study is the use of a bioreactor to convert CO_2 into useful fuels or other organic products.

Focus on Fundamental Science: Microbes, Carbon Fixation and Genome-Scale Metabolic Modelling

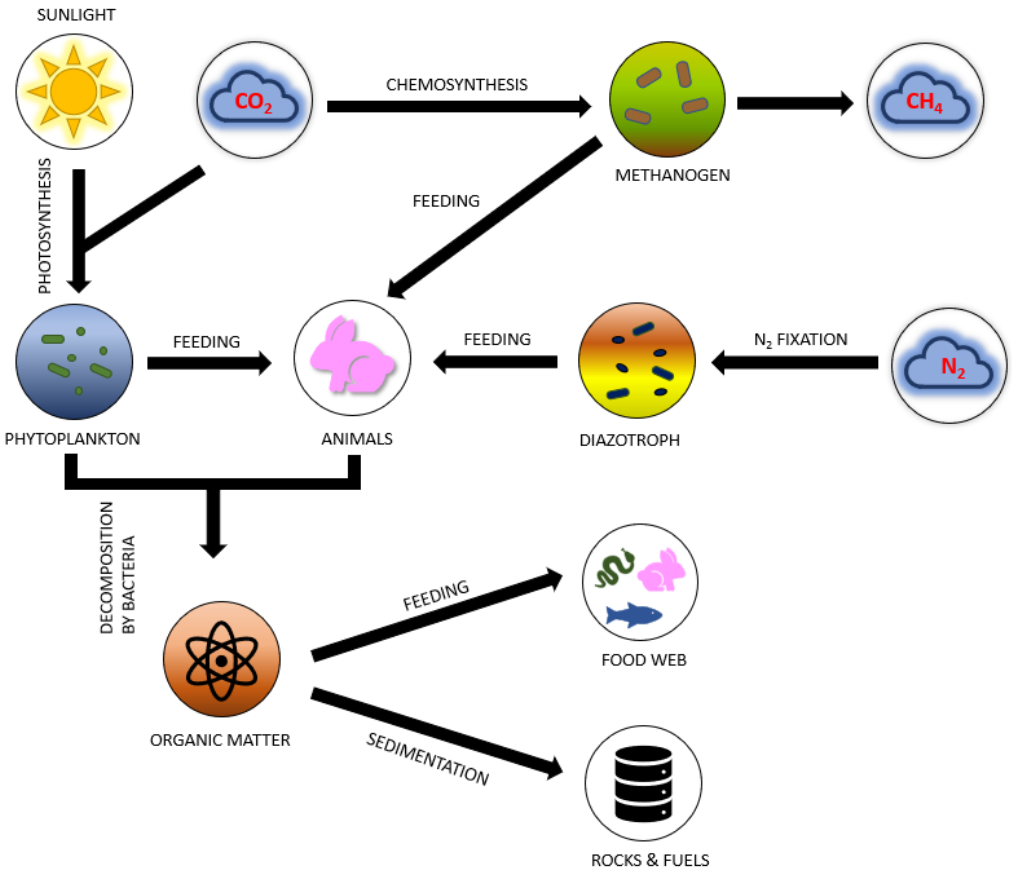
It is widely accepted that the current level of carbon dioxide gas in the atmosphere is changing the Earth's climate, with the negative effects being seen around the world. Climate change is a large-scale problem, with many equivalent, large-scale initiatives in place to try and reduce carbon emissions, make carbon-producing processes more efficient and even remove tonnes of carbon dioxide from the atmosphere. There is, however, another method that could play a disproportionately large part in reducing our carbon dioxide levels: microbes.

Microbes are a diverse group of microscopic organisms which are invisible to the naked eye. They are typically about 0.2 to 10 micrometres in size (10 to 1000 times smaller than the thickness of a strand of human hair). Microbes can live in various habitats: soil, the sea, lakes, ponds, swamps, the atmosphere and even man-made surfaces. Many microbes also live on and inside the bodies of other organisms, for instance the cyanobacteria in lichens growing on tree barks, the gastrointestinal microbiota in the digestive systems of humans and animals, the skin flora on the epidermis. In fact, there are as many microbes on and inside our bodies as the number of human cells we have. Some microbes, called extremophiles, even adapt to survive in extreme environments like hot springs, hydrothermal vents, oceanic trenches, deserts, permafrost and rocks deep in the Earth's crust.

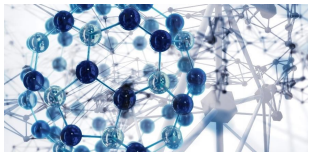
Microbes often live as communities of many different types, and may form biological interactions with higher organisms. The members of the communities may exhibit mutualistic, commensalistic or parasitic behaviours towards one another. Despite their small individual size, microbes collectively represent a significant portion of the global biomass, constituting more than 30% of the total DNA in the biosphere. While the immediate impact of a microbe is on a miniscule scale, their combined action plays a critical role in shaping the macroscopic landscape. Microbes can perform carbon fixation, a process in which carbon dioxide (CO_2) and other inorganic carbon compounds are converted into organic carbon compounds. These carbon compounds are thus incorporated into the structures of the microbes and can be consumed as energy and carbon sources by higher organisms in the ecology. Some other microbes called diazotrophs can convert the inert nitrogen gas in the atmosphere to ammonia and other nitrogen compounds, which serve as the organic nitrogen sources for higher organisms. Other microbial activities include the decomposition and recycling of nutrients, the production of oxygen and methane and the weathering of rocks. As a result, damage at the microbial level may lead to greater instability in the ecosystem as compared to that incurred higher up the food chain. In fact, it is thought that the emergence of oxygen-producing bacteria 2.45 billion years ago altered the atmospheric composition, leading to the mass extinction of anaerobic species.

Microbes that use CO_2 to produce organic compounds are called autotrophs. Examples include phytoplankton and methanogens. Phytoplankton are a group of microbes living on the surface of a body of water such as oceans and lakes. They serve as a large carbon sink while simultaneously producing oxygen through photosynthesis. It has been estimated that phytoplankton contribute half of the photosynthetic activity on Earth, while terrestrial plants account for the remaining half. A well-known example of phytoplankton is green algae, which are now cultivated at an industrial scale (algaculture). These green algae farms do not only contribute to carbon fixation, but also yield chemical feedstock, green fuels, pharmaceutical compounds and can be a food source. Unlike phytoplankton, methanogens do not perform photosynthesis. Instead, they undergo a process called chemosynthesis to convert CO_2 and other simple carbon compounds into methane gas. Methanogens are commonly found in oxygen-free environments such as wetlands and animals' digestive tracts. Methanogens play an integral part in wastewater treatment, in which they work with other microbes to convert organic pollutants into methane.

For large-scale applications of these autotrophs in carbon reduction, it is essential to enhance their carbon fixing capability. In addition, they can be engineered to produce useful chemical compounds to improve the sustainability and profitability of the technology. To achieve these goals, genome-scale metabolic modelling is an excellent tool. A metabolic model is a depiction of all the biochemical reactions occurring inside an organism, together with the associated enzymes and genes. Metabolic models are often constructed from the genome sequence of the organisms. Based on the central idea of molecular biology, DNA specifies RNA, which in turn specifies the proteins being produced. The proteins, often enzymes, determines the biochemical reactions inside an organism.



A detailed genome-scale metabolic model has good predictive power. For instance, the effect on an organism's carbon fixation after changing its feedstocks or living environment can be predicted. A genome-scale metabolic model also allows for identification of certain genes that can be removed from or introduced into the microbes to enhance their carbon fixation capabilities or to produce desired chemical products. The information obtained from a metabolic model influences future research and experiments that could lead to more efficient carbon dioxide fixation methods. There are many ways in which we can mitigate climate change, but the humble microbe might just save the day.



3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

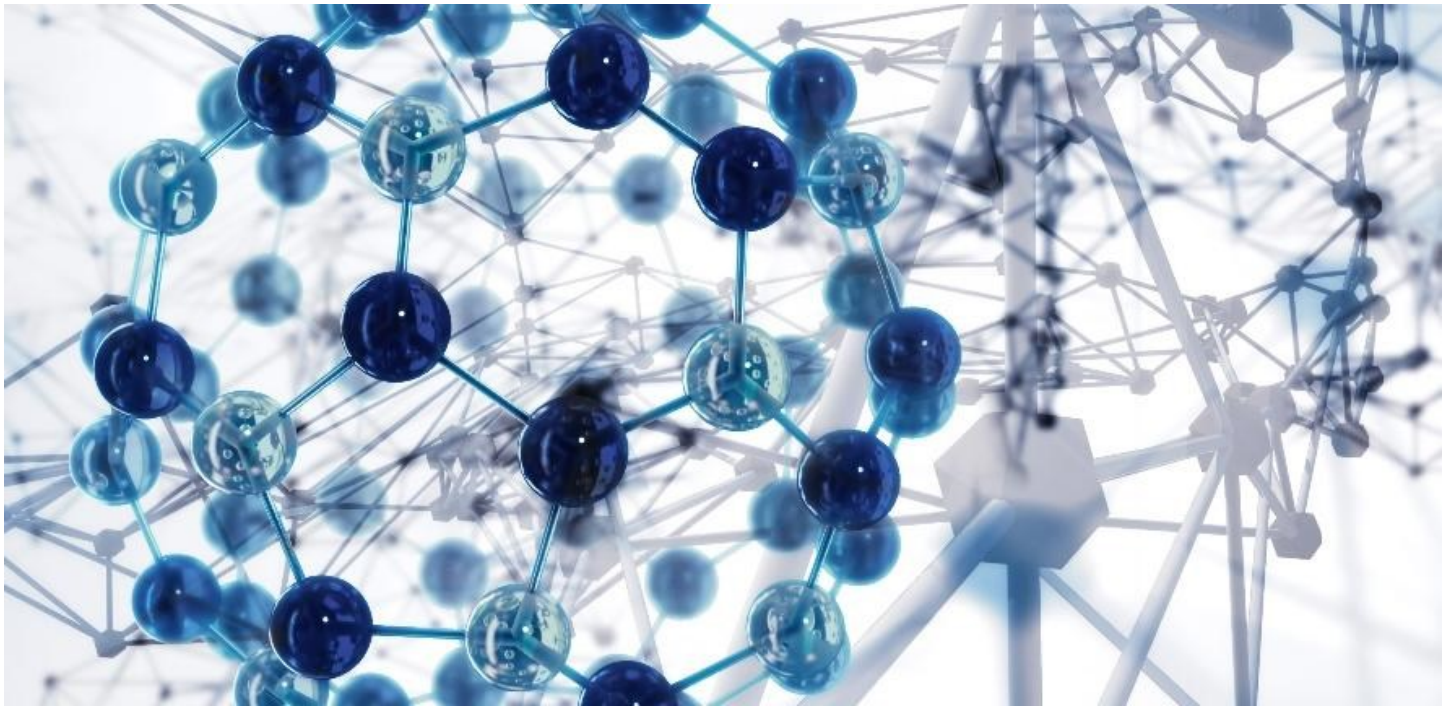
Electrochemical Multi-Scale Science, Engineering and Technology

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 (CAM)

Prof. Samir MUSHRIF (NTU)

Prof. Hua Chun ZENG (NUS)

Prof. Alexei Lapkin

University of Cambridge

PI, IRP1

April 2018

3.1.1 IRP1 Research Overview

The IRP1 project is working on the decarbonisation of the chemical industry through the 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 nanostructuring of heterogeneous catalysts, and translation of the novel catalysts into energy-efficient advanced processes.

The work packages currently in progress are:

WP 1.1: Chemical looping with advanced oxide carriers

WP 1.2: CO_2 methanation and biomass conversion

WP 1.3: New materials and MOFs

WP 1.4: Multi-scale modelling

WP 1.5: Fundamentals of adsorption and PSA

Most projects within IRP1 are maturing towards important milestones, such as patent applications, final papers and the generation of new proposals based on discoveries made during the project and new hypotheses. In the area of bio-feedstocks conversion, the team, comprising researchers from NTU and Cambridge, has completed the study on the mechanism of glycerol hydrogenolysis and the publication is being finalised. There are a number of exciting new functional structured materials emerging from the group of Prof. Hua Chun ZENG (PI, NUS) and in the collaboration with Cambridge we have found a way of scaling up synthesis of some of these materials. One patent has been filed for the process and materials and a second filing is currently being prepared. In this area IRP1 is now exploring potential new collaborations, including with A*STAR institutes. The work on CO_2 capture has progressed significantly over the last few months, with the final commissioning of the pilot scale rig. The team is now generating data and finalising their publications on the new carbon capture cycle.

3.1.2 Update on Work Packages

WP 1.1: Chemical looping with advanced oxide carriers

Jijiang HUANG (PhD student, NTU) worked on the design and preparation of Ni catalysts for dry reforming of methane. This reaction converts two types of greenhouse gases, CO_2 and CH_4, into syngas, which is an important raw material for the production of methanol and gasoline through methanol or Fischer–Tropsch synthesis. Ni-based layered double hydroxides have been synthesised by a co-precipitation method and used as the support for the preparation of the Ni catalysts with various promoters via impregnation, followed by heat treatment. The effect of the promoters on the activation behaviour, reactivity at varied temperatures and long-term stability of the catalysts will be extensively investigated. Special attention will also be paid to the catalytic stability in reduction/regeneration looping cycles.

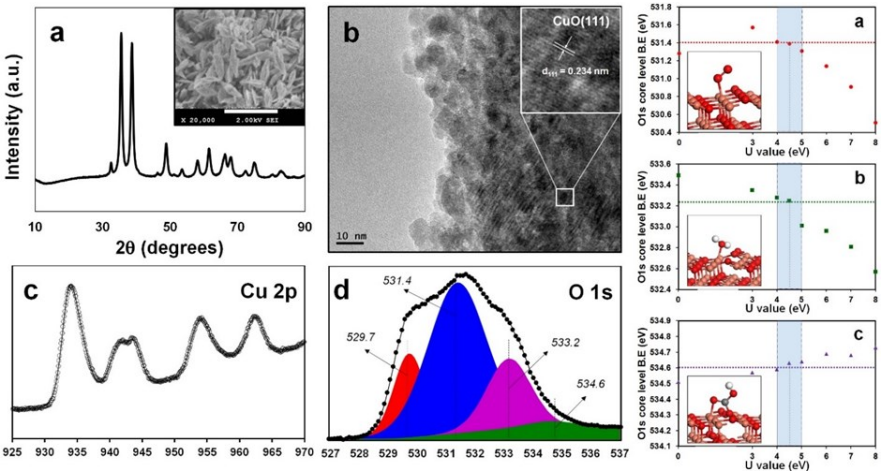


Fig. 1.1: Images and graphs showing metal oxide surface catalysis experiments.

Dr TRINH (RF, NTU)

Dr Quang Thang (Victor) TRINH (RF, NTU) developed an integrated experimental and theoretical method to investigate metal oxide surface catalysis. Transition metal oxides (TMOs) are widely used in the form of pure, supported and zeolite incorporated structures as catalysts for various industrially important reactions like chemical looping combustion, selective oxidation and dehydrogenation of hydrocarbons to produce various high value chemicals. In investigating metal oxide surface catalysed reactions, determining an appropriate Hubbard U-correction term is a challenge for the density functional theory (DFT) community and identifying realistic reaction intermediates and their corresponding X-ray photoelectron spectroscopy (XPS) shifts is a challenge for the experimental researchers. However, this study demonstrated that if DFT and XPS are applied synergistically, the determination of a Hubbard U value and identification of adsorbate/intermediate species on the surface (and their XPS shifts) can be done concurrently. CuO was used as the model metal oxide and had been synthesised in 2D nanoleaves morphology with single dominant facet of CuO(111)) exposed. By comparing the experimentally observed core-level binding energies with the theoretically derived binding energies of realistically possible adsorbates across the U value range (0–9 eV), the U value between 4–5 eV was revealed to capture the experimental O1s core-level binding energies correctly. This U value differs significantly from the bulk properties fitted U value of 7 eV and is in excellent agreement with our recent DFT+U benchmarking study based on heat of adsorption measurements (*J. Phys. Chem. C*, 2017, 121, 21343). This integrated approach results in identification of the realistic adsorbates, their core level binding energies as well as Hubbard U value determination and thus, establishes a methodology for elucidating complex reaction pathways and computing reaction energetics, adsorbate-surface interactions, whilst benchmarking the U value concurrently.

WP 1.2: CO_2 methanation and biomass conversion

Dr Jithin John VARGHESE (RF, NTU) under the supervision of Prof. Samir H. MUSHRIF (PI, NTU); Ms Liwei Cao (RA, NTU) under the supervision of Prof. Yanhui YANG and Prof. Alexei LAPKIN (PI, CAM); and Mr Christopher ROBERTSON (PhD student, CAM) under the supervision of Prof. Lynn F. GLADDEN (Co-PI, CAM) made significant progress in the investigation of glycerol hydrogenolysis on multi-component catalysts.

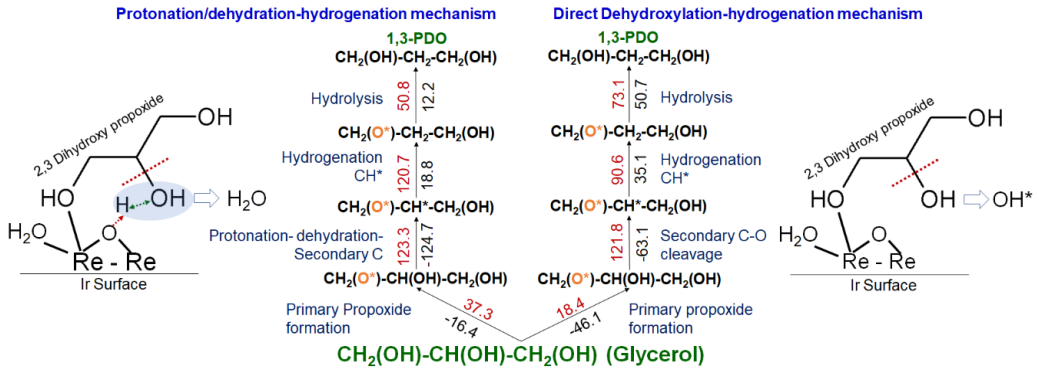


Fig. 1.2: Mechanisms and pathways for the hydrogenolysis of glycerol on ReOx-Ir catalyst.

Dr VARGHESE (RF, NTU)

Combining DFT calculations, spectroscopic characterisation of catalysts, batch catalytic reactions and NMR relaxometry analyses, comprehensive mechanistic insights on selective hydrogenolysis of glycerol on multifunctional ReOx-Ir/SiO_2 catalyst are presented. Sulfuric acid increases the local concentration of glycerol within the catalyst pores, enhancing the glycerol-catalyst interaction and thereby promoting hydrogenolysis of glycerol. The preferential dissociative attachment of glycerol on the partially reduced and Brønsted acid ReOx clusters as primary propoxides facilitates selective removal of the secondary hydroxyl of glycerol. This may be in a direct dehydroxylation mechanism or a proton assisted concerted dehydration mechanism and forms 1,3-propanediol (1,3-PDO) which is the kinetically preferred product. 1-propanol is likely to result from direct sequential hydrogenolysis of glycerol in the initial stages of the reaction and also from subsequent hydrogenolysis of the more reactive 1,2-propanediol which forms from glycerol. On the Ir catalyst (without ReOx), the less favourable dissociative attachment of glycerol and the considerably higher activation barriers for the removal of glycerol hydroxyls result in significantly lower conversion of glycerol than on the ReOx-Ir catalyst. The dehydrogenation-dehydroxylation-hydrogenation pathway on the Ir catalyst leads to formation of the thermodynamically favourable product, 1,2-PDO.

Dr YAN Yong (RF, NTU) reported on the modification of Zn-ZrO catalysts for the hydrogenation of CO_2 into methanol. With the expectation of large-scale production of H_2 at low cost, CO_2 utilisation by hydrogenation into valuable chemicals has attracted much attention, e.g. methanol. However, the popular Cu-based catalysts were sensitive towards particle sintering and thus not industrially preferable. Herein, efforts have been made towards the doping of Cu-free Zn-Zr mixed oxide catalysts by different transient metals via homogeneous precipitation. The catalyst doped by Ce showed no obvious catalytic improvement. Even worse, the stability was deteriorated. On the other hand, Fe-doping decreased the selectivity of CO_2 hydrogenation into methanol, with an increasing tendency for CO formation. Both W and Mo doping revealed an increase in the turnover frequency of CO_2 into methanol. The stability test also showed no deactivation over 120 h on stream. These results suggested that W and Mo doped Zn-Zr catalysts are promising for CO_2 hydrogenation into methanol. The structures of these catalysts will be further characterised.

Dr Christopher ROBERTSON (RF, CAM) reported that NMR relaxometry has been used to investigate competitive adsorption behaviour of water and glycerol in a multifunctional ReO_x-Ir/SiO_2 catalyst. This work is relevant to biomass conversion, where the results have been combined with DFT calculations, spectroscopic characterisation of catalysts and batch catalytic reactions to infer comprehensive mechanistic insights on the selective hydrogenolysis of glycerol on this catalyst. The NMR experiments and a new parameter β, which relates the surface interaction of a reactant (glycerol) to solvent (water) in mixtures, confirm that competitive interactions between glycerol and water are likely responsible for the trends in conversion (as a function of glycerol concentration) observed in the batch catalytic reactions. Furthermore, intra-pellet compositions, as obtained from the NMR analysis, have been used to confirm that glycerol uptake is increased when sulfuric acid is added to the reacting mixture, thereby promoting higher conversions of glycerol.

Dr TRINH applied the integrated DFT and XPS method described in the above-mentioned W.P.1.1 progress report to explain the difference in activities of a CuO nanoleaf catalyst prepared using the novel ultrasound irradiation method (called CuO-US) and the conventional method (called CuO-CM). The ultrasound irradiation method is superior to the conventional method since it provides a fast and efficient synthesis route for the production of highly crystalline, highly pure and uniform 2D CuO nanoleaves (NLs) at room temperature, involves short sonication synthesis time, uses environmentally benign reactants and does not require any surfactant or template as usual, thus simplifying the downstream procedure. Furthermore, CuO NLs prepared using the ultrasound method also have both higher activity and stability than CuO NLs prepared using the conventional method in glycerol selective oxidation to dicarboxylic products (tartronic acid and oxalic acid). Under the iso-conversion comparison, CuO-CM has a lower yield of dicarboxylic acids than CuO-US.

To demonstrate the superior performance of highly crystalline CuO prepared by ultrasound (CuO-US), the recycling of CuO-US and CuO-CM was investigated and a rapid decrease in dicarboxylic acid yields was observed for CuO-CM. The total yield of dicarboxylic acids dropped from 63% to only 7% after six catalytic cycles. Conversely, CuO-US was much more robust than CuO-CM. The total yield of dicarboxylic acids remained higher than 70% up to the fifth catalytic cycle (compared with 78% for the first cycle). The lower activity and stability of CuO-CM than CuO-US could be a result of lower purity, as well as the presence of Cu vacancies on the surface of CuO-CM. Such vacancies may 1) affect the activation of glycerol and hydrogen peroxide, thereby affecting the conversion of glycerol and selectivity towards dicarboxylic acids and 2) may accelerate the reduction of the copper oxide, leading to changes in the crystalline structure of CuO, as was also observed from experiments. DFT simulation was performed to confirm the presence of Cu vacancies in CuO-CM based on the comparison between the O1s XPS spectra of CuO-US and the XPS of CuO-CM.

From the combination of DFT-simulated and experimentally-measured XPS data, it is revealed that the peak at ~531.4 eV in the O1s XPS spectra (Fig. 1.3) corresponds to the adsorbed O_2 molecule and the peak at ~529.6 eV is assigned to the bulk lattice oxygen of CuO. Since (i) the relative area of the peak at ~531.4 eV with the peak at ~529.6 eV could be used for quantitative analysis; (ii) the O_2 molecule adsorbs most strongly on the surface Cu_3 site (peak at ~531.4 eV) and hence the quantitative amount of it reflects the amount of surface Cu_3 site and (iii) the quantitative amount of bulk lattice oxygen (peak at ~529.6 eV) also reflects the quantitative amount of bulk lattice copper due to the stoichiometric ratio of CuO, the area of the peak at ~531.5 eV (S1, highlighted by blue peak) relative to the area of the peaks at ~529.6 eV (S2, highlighted by red peak) could correlate with the ratio of surface Cu sites to the bulk Cu sites.

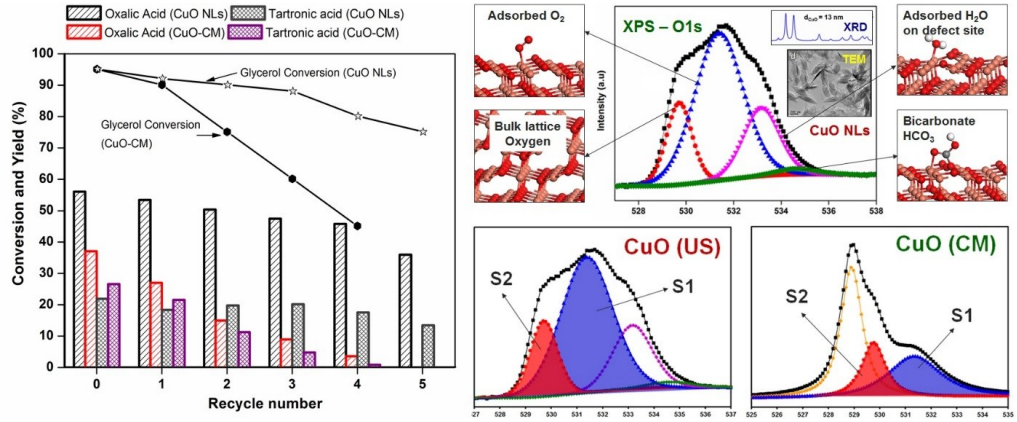


Fig. 1.3: The recycle experiments, assignment of different peaks in the O1s XPS spectra for different structures on CuO and comparison between O1s XPS spectra of CuO (US) and CuO (CM).

Dr TRINH (RF, NTU)

By comparing the O1s XPS spectra between the CuO prepared by ultrasound method (CuO-US) and the CuO prepared via the conventional method (CuO-CM), it could be seen that the ratio S1/S2 for the CuO-US is much larger than the corresponding value for the CuO-CM, which means that the amount of surface Cu site on CuO-CM is much smaller than the amount of surface Cu site on CuO-US and hence Cu vacancies are presented on the surface of CuO-CM. Due to the fewer active Cu_3 sites on CuO-CM versus CuO-US, the activity and selectivity of CuO-CM is poorer than CuO-US as was observed from experiments. Furthermore, the easier reducibility of CuO when Cu vacancies exist on the surface, as investigated by DFT calculations, is also consistent with the faster reducing in activity of CuO-CM, as was observed. Therefore, it can also be deduced that the ultrasound irradiation method not only provides a faster and more convenient preparation method but also produces CuO catalyst with higher quality in terms of both activity and stability.

Chunmiao JIA (PhD student, NTU) completed the manuscript "The fluidised bed modeling over NiMgW catalyst for CO_2 methanation". She reported that a real fluidised bed was designed and has been produced, in order to do the experiments to validate the modelling results. A new catalyst Ni/TiO_2/SiO_2 was designed and manufactured for the CO_2 methanation, and will be used in a fluidised bed.

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

Dr Polina YASENEVA's (RF, CAM) research focuses on identifying optimal routes from a biowaste feedstock to functional molecules. This is a challenging problem with multiple options, including the structure of the supply chain, optimal mass and energy flows, the environmental impact and economics. There is an additional complexity which comes from the fact that different feedstock treatments may give different compositions of the mixtures from which the starting compound is obtained. Therefore, there are likely to be different optimal routes that are dependent on the feedstock pre-treatment technology as well. It is often possible to obtain the same molecule from different feedstocks and, again, identifying which feedstock is optimal is not straightforward.

In the case of terpenes Dr YASENEVA reported that the team is considering crude sulfate terpentine (CST) and pressate, both wastes from paper processing. The target molecule 1 is nopinone, which can be obtained from both feedstocks via different treatments and then converted to other higher value functional molecules (Fig. 1.4).

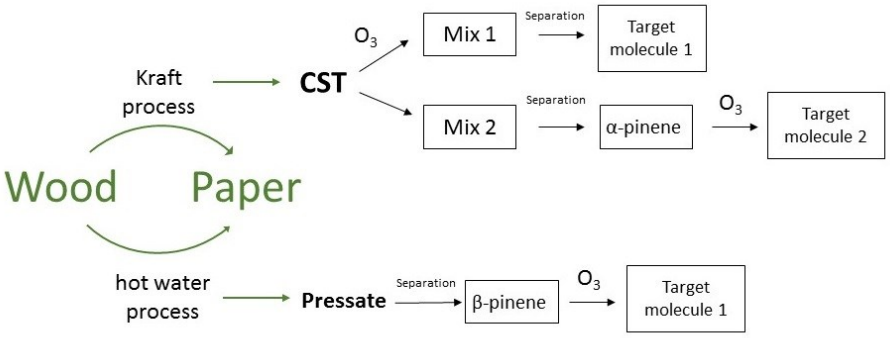


Fig. 1.4: Schematic showing the two main processes for the manufacture of cellulose fibre for paper production.

Dr YASENEVA (RF, CAM)

There are two processes for the manufacture of cellulose fibre for paper production: the Kraft process and the pressurised hot water process. The main by-product of the Kraft process, CST, contains pinenes and limonene, among other molecules. The pinenes of interest must be separated from CST. Dr YASENEVA considered two possible separation routes: hydrodesulphurisation followed by distillation, and direct ozonation of CST. These treatment processes give different distributions of the product terpenes. The second main source of terpenes from paper manufacturing is the aqueous solution waste from the hot water process. In this case the concentration of β-pinene is much higher, which opens the possibility of a very different sequence of processing and conversion steps.

The aim of this work is to identify the most environmentally and economically viable route towards platform molecules based on terpene sources from paper industry waste (Aspen and Umberto models are being built) and demonstrate the generic methodology of assessment of chemical processes within a circular economy.

WP 1.3: New materials and MOFs

Nicholas Antonio JOSE's (PhD student, CAM) recent work has explored the synthesis of two dimensional metal organic frameworks in the high shear microreactor developed previously. It was found that these materials could be fabricated at much higher rates than reported in previous studies. It was also found that new structures could be fabricated with adjustments in chemistry, synthesis parameters and post processing. The application of these materials in adsorption and gas membrane separation technologies are being explored.

He also reported that layered double hydroxides synthesised previously are being explored as methane reforming catalysts in collaboration with other researchers in IRP1.

Future work will include the study of perovskites and calcium carbonate nanomaterials synthesis.

Dr Ping LI (RF, NUS) has been working on CO_2 methanation, an efficient approach to recycling exhausted CO_2 to give a useful fuel. The noble metals are found to be the most efficient catalysts for CO_2 methanation under relatively mild reaction conditions, while their high cost greatly limits their widespread applications. In this study, via engineering a new type of graphene-supported Ni-organic complex precursor with a hierarchical sandwich-like architecture, a series of highly dispersed ultrafine Ni nanoparticles (NPs) wrapped with a few layers of graphitic carbon, have been successfully prepared by a simple controlled heat-treatment. With the high dispersion of the Ni NPs and the stabilisation by the few-layer graphitic carbon coating, the resulting nanocomposites are expected to hold great potential in the CO_2 catalytic methanation. The CO_2 methanation performance study of the materials is currently in progress (Fig. 1.5).

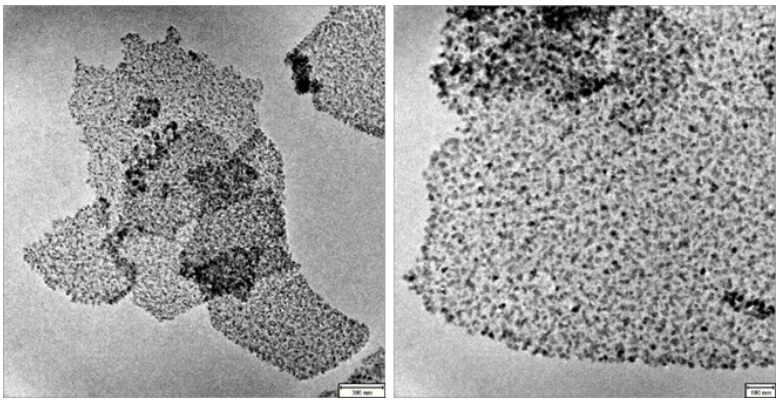


Fig. 1.5: Representative TEM images of the rGO supported Ni NPs.

Dr LI
(RF, NUS)

Dr Guowu ZHAN (RF, NUS) reports that different M@CSN nanoreactors (M = metal, and CSN = cobalt silicate nanocubes) with a maze-like 3D configuration were prepared, and then their performance in CO_2 hydrogenation was examined. First, for comparison, a blank experiment was carried out by using the pristine CSN as a catalyst. As presented in Figure 1.6a, the conversion of CO_2 was negligible (0.8% at 320 °C/30 bar) with the CSN alone, even though Co element in the CSN phase could be partially reduced under reducing conditions (being evident from the colour change of CSN). Much higher activities were obtained for samples containing metal nanoparticles under similar reaction conditions (320 °C, 30 bar, and gas flow rate of 12 mL/min). It was found that the conversion of CO_2 depends strongly on the nature of the metallic phase employed. Among the catalysts tested, a supported Pt catalyst was the most active component with the highest CO_2 conversion. The CO_2 conversion decreased in the order of Pt (41.8%) > $Pt_{0.5}Cu_{0.5}$ (27.6%) > $Au_{0.5}Cu_{0.5}$ (16.0%) > Cu (8.5%) > Au (6.0%) > Ag (4.4%). Regarding product distribution, under all the tested conditions CO and CH_4 were the only two products found (no other higher molecular hydrocarbons (C_2–C_4) were detected); it appears that more CH_4 formed at higher conversion of CO_2. The temperature-dependent performance of different catalysts was investigated over 260–320 °C (at 1 bar). Arrhenius-type expressions were employed for calculation of apparent activation energies. The linear Arrhenius-type plots of different catalysts are given in Figure 1.6b, which gives the following order of apparent activation energies for CO_2 hydrogenation: Au (62.6 kJ/mol) < Pt (71.8 kJ/mol) < $Au_{0.5}Cu_{0.5}$ (76.2 kJ/mol) < Cu (81.4 kJ/mol) < Ag (84.8 kJ/mol) < $Pt_{0.5}Cu_{0.5}$ (90.4 kJ/mol). These values are all close to those reported from RWGS reaction over noble metal catalysts (in the range of 50–110 kJ/mol), indicating that the formation of CO is the initial step (conversion rate < 10%) during hydrogenation of CO_2 over the M phase of these M@CSN nanoreactors.

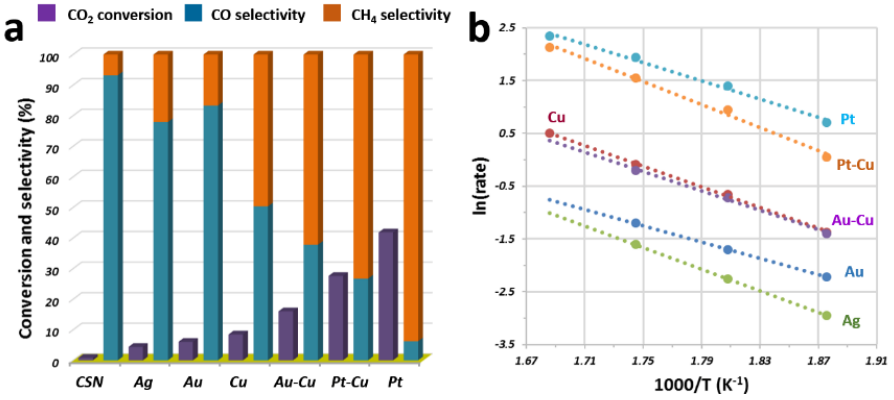


Fig. 1.6: CO_2 hydrogenation performance of the studied catalysts. (a) Activity and product distribution of a series of CSN supported metal catalysts, temperature of 320°C, pressure of 30 bar, and gas flow rate of 12 mL/min. (b) Arrhenius plots of ln(r) versus 1000/T for the CO_2 hydrogenation over different catalysts, pressure of 1 bar and gas flow rate of 12 mL/min.

Dr ZHAN
(RF, NUS)

Bowen LI (PhD student, NUS)

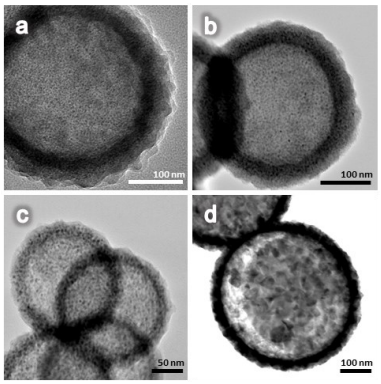


Fig. 1.7: Representative TEM images of (a) double mesoporous silica intercalated Ni/SiO_2 structure without dopant and (b) double mesoporous silica intercalated Ni/SiO_2 structure doped with 8 mol % Co; (c) a representative TEM image of Ni/SiO_2@MOF-74 structure; (d) a representative TEM image of organosilica@Co_3O_4 yolk-shell structure.

Bowen LI
(PhD student, NUS)

A double mesoporous silica intercalated Ni/SiO_2 structure has been synthesised and tested towards various liquid and gas phase reactions. When subjected to dry reforming of methane, reaction activity and stability of such catalysts could be adjusted by introducing transition metal dopants, forming bimetallic alloys with Ni nanoparticles.

Using nickel silicate hollow spheres as a starting point, a sandwich-like Ni/SiO_2@MOF-74 structure has been prepared while the MOF-74 coating shell was amorphous in nature. This amorphous MOF-74 has shown to be thermally stable over 200 °C based on our TGA study, making this overall structure applicable to hydrogenation of carbon dioxide. The influence of MOF coating shell for such hydrogenation reactions will be further explored.

In addition, the yolk-shell structure of organosilica@Co_3O_4 has been synthesised. Various approaches to further deposition of noble metal NPs such as Pd and Pt have been explored and evaluated. For example, the noble metal Pt is well known as a catalyst for CO_2 hydrogenation towards CO. This on-site generated CO could then undergo the Fischer-Tropsch reaction in the presence of a Co catalyst. A tandem reaction converting CO_2 to more valuable hydrocarbons is currently under investigation.

Runze QIN (PhD student, NUS)

Despite being investigated intensively, the stability of supported nanocatalysts with active components ranging from several to tens of nanometers is susceptible to extreme conditions such as high temperatures and extreme pH values. For example, sintering active nanoparticles would be detrimental to catalyst activity and results in deactivation of catalysts. Herein, we utilise a metal-organic framework (MOF) as a precursor to construct a micro-/meso-nanostructure with confined ultrasmall nanoparticles; the sintering effect was significantly reduced. Firstly, UiO-66, a commonly used MOF, was encapsulated within a mesoporous silica shell. Then calcination of the UiO-66@*m*SiO_2 structure produces porous metal oxide inside mesoporous silica shell and thus noble metals can be moored in channels in porous metal oxides. Carbon dioxide hydrogenation as well as a cascade reaction were used as model reactions for our catalyst and superior performances were demonstrated. Over the past six months, further characterisations were conducted and a mechanism for CO_2 hydrogenation was also studied. Furthermore, different active components (Pd and Ru, for example) can be loaded in our nanostructure, enabling this particular structure to become a general platform for a variety of chemical reactions.

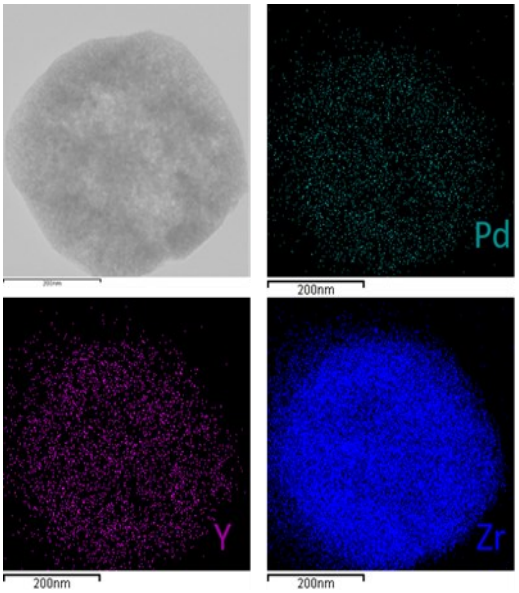


Fig. 1.8: EDX mapping of porous yttrium stabilised zirconium.

Runze QIN
(PhD student, NUS)

Jingjing WANG (PhD student, NUS)

Electrochemical splitting of water to produce hydrogen and oxygen is an important process for many energy storage and conversion devices. Therefore, developing efficient, durable, low-cost and earth-abundant electrocatalysts for the oxygen evolution reaction (OER) is of great urgency. For the first project, we are going to investigate the new synthesis, new materials and catalytic mechanism for two-dimensional (2D) ultrathin materials. In the first project, we successfully prepared 2D ultrathin cobalt hydrogen phosphate (CoHPi) through the chemical conversion of α-$Co(OH)_2$ precursor at room temperature. The CoHPi is used as electrocatalysts and the mechanism study is carried out to illustrate its enhanced performance. In the second project, a facile two-step strategy using an anionic surfactant (SDBS) to assist the recombination of monometal hydroxide nanoplates to hierarchical multimetal (Ni, Fe, Co) LDH nanoflakes has been developed. The role of anionic SDBS has been examined and the electrocatalytical performances of the CoNiFe-LDH and its derived oxide are currently under evaluation.

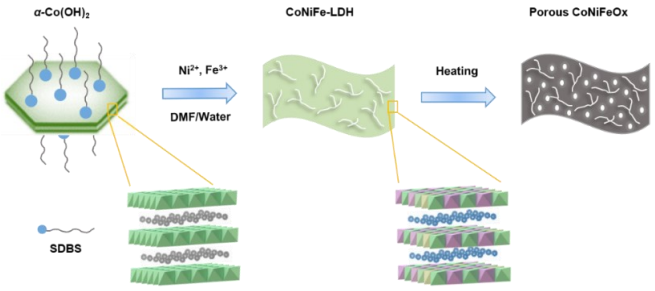


Fig. 1.9: Schematic illustration of the recombination of cobalt hydroxide platelets to hierarchical CoNiFe-LDH.

Jingjing WANG (PhD student, NUS)

Jun Wen YEO (PhD student, NUS)

Perovskite oxides hollow spheres (POHS) ABO_3 are synthesised from core-shell coordination polymers (CP) precursors, where metal B resides in the core region while metal A resides in the shell region. It is postulated that the hollow structure is achieved by calcining at high temperatures to encourage the outward diffusion of metal B and subsequent solid-state reaction with metal A to form the resultant perovskite oxide. To verify this proposed mechanism, none core-shell CPs are synthesised and calcined under the same conditions. To demonstrate the general applicability of the method, a series of perovskite oxides are synthesised in this work for a combination of A (La, Eu, Gd) and B (Al, Cr, Ni) metals. Further catalytic functionality can be imparted to the POHS by doping the precursor CP with transition metals, which upon subsequent reduction yields the evolution of active metal nanoparticles (MNPs). To demonstrate this, $LaAlO_3$ – Ni POHS is synthesised and used to carry out the dry reforming of methane reaction with good stability.

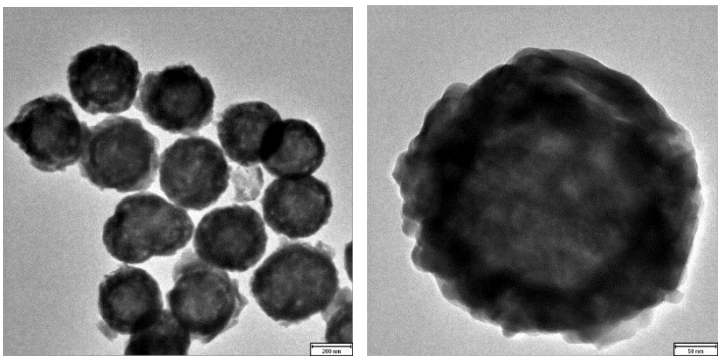


Fig. 1.10: TEM images of perovskite oxides hollow spheres (POHS) ABO_3 synthesised in this project.

Jun Wen YEO (PhD student, NUS)

The following work has been completed since the last reporting period:

- $LaAlO_3$ POHS synthesis, XRD, TEM characterisation and EDX mapping
- $LaNiO_3$ POHS synthesis, TEM characterisation and EDX mapping
- $LaCrO_3$ POHS synthesis, TEM characterisation and EDX mapping
- $LaAlO_3$-Ni synthesis, XRD, TEM characterisation and EDX mapping. Preliminary catalytic testing for dry reforming of methane reaction for mol%(Ni) = 10% and 20%.

Key improvements to be made:

• Morphology refinement through calcination temperature variation

• Dry reforming (DRM) catalytic performance benchmarking and optimisation through varying Ni loading and support doping

• Further characterisation to understand Ni bonding environment (XPS, FTIR)

WP 1.4: Multi-scale modelling

Dr Shiliang YANG's (RF, NTU) main research interest lies in the DEM study of chemical process modelling and optimisation. Granular materials are mostly polydisperse, which gives rise to phenomena such as segregation that has no monodisperse counterpart. Recently, he has been focusing on exploring the effect of particle size distribution on the granular segregation in the chemical reactors. The discrete element method (DEM) is applied to simulate lognormal particle size distribution (PSD) with the same arithmetic mean particle diameter but different PSD widths in a three-dimensional rotating drum operating in the rolling regime. Despite having the same mean particle diameter, as the PSD width of the lognormal PSDs increases, (i) the steady-state mixing index, the total kinetic energy, the fraction of the active region depth with respect to the total bed depth, the mass fraction in the active region, the steady-state active-passive mass-based exchanging rate and the mean SRT of solid phase in the active region increases, while (ii) the steady-state gyration radius, the streamwise velocity and the SRT in the passive region decreases. Collectively, these highlight the need for more understanding on such systems.

WP 1.5: Fundamentals of adsorption and PSA

Prerna GOYAL's (PhD student, NUS) research project aims to study the capture and concentration of CO_2 from power plant flue gas by using Vacuum Swing Adsorption (VSA) processes using process simulation and pilot plant experiments. She reported that MATLAB simulations of dynamic column breakthrough (DCB) and VSA processes have been extended to wet flue gas using a single adsorbent configuration. In addition, DCB simulations were performed for pure CO_2 and N_2 and a 15:85% CO_2:N_2 binary gas adsorption on silica gel using gas velocities up to 5cm/s at near ambient pressure and temperatures. Prerna reported that she has gained experience in performing numerous blank and silica gel DCB experiments over a range of gas flowrates and compositions with the pilot plant and analysis of data files in Excel. This analysis has contributed to an understanding of extra column volume effects on gas breakthrough profiles. Her future work will focus on extending process simulations to dual column adsorption processes (guard bed and carbon capture VSA columns), executing a range of DCB experiments with dry flue gas to investigate equilibrium and kinetic parameters and compare results with simulated DCB profiles.

Dr Mark John PURDUE (RF, NUS) reported that an investigation of multicomponent adsorption isotherm models using previously published adsorption loading data was completed for both dry and wet flue gas adsorption on Zeolite 13X. The selected model shall be incorporated into process simulations. A handover of Labview software for the CARES pilot plant was completed, which incorporates logging of fixed step times for VSA cycling. He reported that a reference manual "Pilot Plant for Dynamic Column Breakthrough & Capture of CO_2 from Wet Flue Gas using Dual Column Vacuum Swing Adsorption" is being drafted to enable future researchers to work with the pilot plant and is due for release after concluding the following activities.

Furthermore, Dr PURDUE reported that an assessment of the significance of extra column volume (ECV) effects on the measurement of gas flow and concentrations during dynamic column breakthrough experiments is underway, with efforts to customise experiments accordingly. ECV corrections have been explored using established point-by-point and Tank-In-Series computational approaches. For the latter, experimental data from the pilot plant in Excel was migrated to MATLAB

for further computational analysis. MATLAB code is also being developed to automate processing of all planned experimental pilot plant data. Additional ongoing work includes (i) determination of equilibrium and kinetic parameters for flue gas adsorption on silica gel in the pilot plant columns and comparison of the measured process response to computer simulations, (ii) testing of a second adsorbent in situ regeneration approach (pending delivery of some laboratory items) which can raise the productivity for repeated experiments with the pilot plant, (iii) multiple fast response relative humidity sensors were recently calibrated in CARES equipment by the sensor supplier and are due to be tested in the pilot plant.

Other Activities and Achievements

- Dr Polina YASENEVA reported that the abstract for a lecture at the 3rd Green and Sustainable Chemistry Conference, Berlin, 13-16 May, 2018, "Identification of optimal routes for valorisation of bio-waste terpenes", P. Yaseneva, P. Heer, A. Lapkin, has been accepted.
- Dr Quang Thang (Victor) TRINH (RF, NTU) attended the 2017 Annual Meeting of the American Institute of Chemical Engineers (AIChE), in Minneapolis, Minnesota from 29 October to 3 November and presented an oral talk with the title: "Novel Copper (II) Oxide Nanoleaf Catalyst for the Hydrogen Peroxide Assisted Oxidation of Glycerol to Dicarboxylic Acids: A Combined Theoretical and Experimental Study".
- Dr Jithin John VARGHESE (RF, NTU) presented his research work at the 2017 Annual Meeting of AIChE, in Minneapolis, Minnesota, USA from 29 October to 3 November.
- Dr VARGHESE and Prof. Samir H. MUSHRIF (PI, NTU) presented "The contribution of nickel and oxygen vacancies and of low valent dopants in altering the surface reactivity of NiO" at the 2017 Annual Meeting of AIChE, in Minneapolis, Minnesota, USA from 29 October to 3 November.
- Jithin John VARGHESE, Liwei CAO, Alexei LAPKIN, Yanhui YANG and Samir H. MUSHRIF presented "First principles insights into the selective conversion of glycerol to 1,3-propanediol: The synergistic effect of metal and metal oxide" at the 2017 Annual Meeting of AIChE, in Minneapolis, Minnesota, USA from 29 October to 3 November.

Prof. MUSHRIF with his group members Dr TRINH and Dr VARGHESE at the 2017 AIChE Annual Meeting.

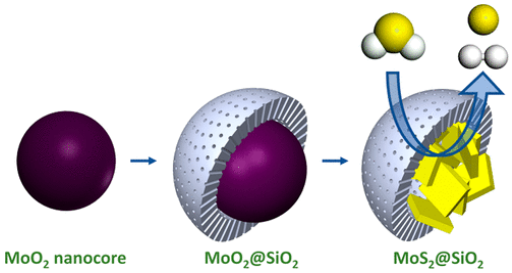
3.1.3 Scientific Output of IRP1

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.

Constrained Growth of MoS_2 Nanosheets within a Mesoporous Silica Shell and Its Effects on Defect Sites and Catalyst Stability for H_2S Decomposition

Kelvin Mingyao Kwok, Sze Wei Daniel Ong, Luwei Chen and Hua Chun Zeng

DOI: 10.1021/acscatal.7b03123



Abstract:

Molybdenum disulfide (MoS_2) is a two-dimensional transition-metal dichalcogenide that can form layered nanosheets with catalytically active sites present at edge or defect sites. The density of such active sites can be further tuned by modifying the length, layer number, strain and surface defects of the sheets. Herein, a synthetic approach has been developed to encapsulate nanoscale MoS_2 nanosheets inside a mesoporous silica shell. Small molybdenum(IV) oxide (MoO_2) cores were synthesised and coated with a mesoporous silica phase, followed by a conversion to MoS_2@SiO_2. The space constraint on the inner cores resulted in short, few-layered, highly curved MoS_2 nanosheets with circular or flowerlike morphology. The MoS_2@SiO_2 was evaluated as a catalyst for decomposition of hydrogen sulfide (H_2S), which shows high catalytic turnover frequency and superior thermal stability in comparison to unconstrained MoS_2 catalysts.

A Synthetic Protocol for Preparation of Binary Multi-shelled Hollow Spheres and Their Enhanced Oxidation Application

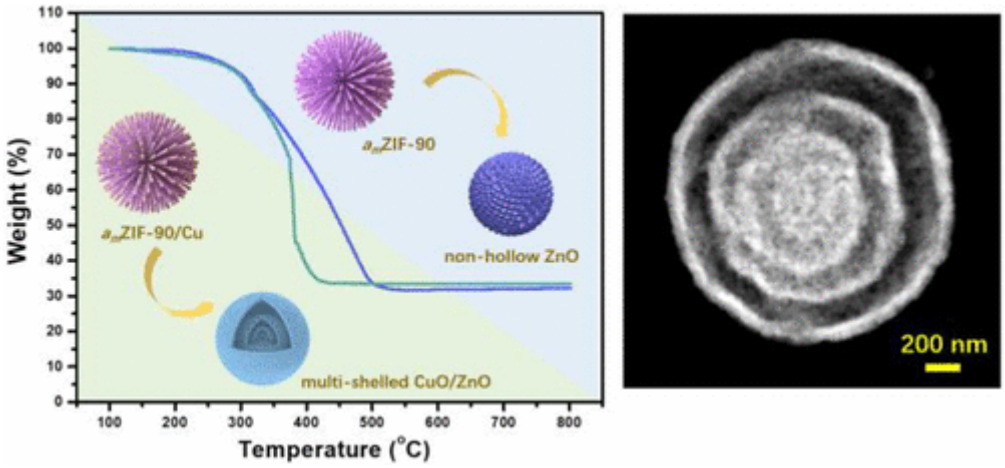
Guowu Zhan and Hua Chun Zeng

DOI: 10.1021/acs.chemmater.7b03875

Abstract:

Multi-shelled hollow materials (MSHMs) with multifunctional compositions and multilevel interiors have received great attention by virtue of their hierarchical hollow structures and diverse applications. In this contribution, we present a new synthetic protocol to fabricate binary MSHMs with up to quadruple shells through a rapid thermal process. The binary MSHMs contain hexagonal ZnO (the primary phase) and monoclinic CuO (the secondary phase), wherein, the ZnO phase was derived from the straightforward degradation of a coordination polymer (for example, dandelion-like amorphous ZIF-90 (amZIF-90)), and the CuO phase was derived from the preloaded copper nanoparticles on amZIF-90 which appear to enhance the oxidative degradation of amZIF-90. This protocol relies on

the metal nanoparticle aided degradation of amZIF-90 in which the catalytic reactivity of metal was found in the order of Au < Co < Pt < Cu. Therefore, calcining amZIF-90/Au or amZIF-90 alone only led to the formation of non-hollow products. The number of layers in binary CuO/ZnO could be controlled by adjusting copper loading, annealing temperature, or heating ramp rate. Furthermore, the resultant binary CuO/ZnO MSHMs exhibited pronounced catalytic activity on the advanced oxidation process (AOP) toward dye wastewater treatment. This synthetic protocol may be employed for fabrication of other binary MSHMs from the enhanced oxidative degradation of ZIFs or their analogues.



Defect Creation in HKUST-1 via Molecular Imprinting: Attaining Anionic Framework Property and Mesoporosity for Cation Exchange Applications

Ying Chuan Tan and Hua Chun Zeng

DOI: 10.1002/adfm.201703765

Abstract:

Discovering new methods to tailor the physical and chemical properties of metal–organic frameworks (MOFs) for their numerous potential applications is highly desired. In this work, engineering defects in MOFs via a molecular imprinting approach is developed to endow HKUST-1, a well-studied classical MOF, with hierarchical structure, mesoporosity and anionic framework property. Ringlike anionic HKUST-1 (HKUST-1-R) and a wide variety of metal-doped isostructural analogues (M/HKUST-1-R, M = Ca, Cd, Ce, Co, Li, Mn, Na, Ni, or Zn) are obtained. The benefits of transforming imprinted HKUST-1-R to M/HKUST-1-R are further demonstrated for various applications. This synthetic strategy is therefore suitable for rational design and functionalisation of MOFs in addition to their morphological control in nanoscale.

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

EMSET is led by PIs:

Dr Adrian FISHER (CAM)

Prof. Xin WANG (NTU)

Prof. Jim Yang LEE (NUS)

Dr Adrian Fisher

University of Cambridge

PI, IRP2

April 2018

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 CO_2 emissions for chemical production in the areas of commodity or speciality chemicals. There are three main thrusts to IRP2, 1) the development of high resolution electrochemical methods using big data approaches which can be exploited to gain quantitative understanding of the physical and chemical processes that limit efficient electrical conversion, 2) the investigation and discovery of advanced catalysts, electrode architectures and the wiring of these complex structures to ensure optimal conversion rates, and 3) the development of integrated advanced reactor systems.

In the latest reporting period, significant advances in our core research areas have been achieved. In collaboration with Prof. Erik BIRGERSSON (Co-PI, NUS), Dr ASHOKE Raman Kuppa (RF, NUS) explored the development of numerical models of electrochemical reduction of CO_2 into useful hydrocarbons. The design of the electrochemical reactors that modulate the transport phenomenon is under investigation, and was explored to elucidate the underlying physics leading to CO_2 conversion, which in turn will facilitate in-design optimisation.

Vishvak KANNAN (PhD student, NUS) has continued his work on modelling of advanced protocols for electrochemical control and analysis. In his latest activities the influence of voltage waveform protocols are under investigation to explore highly non-linear i/V parameters linked to electrolytic reaction. Work has also begun on scaling characteristics.

In collaboration with Prof. Xu ZHICHUAN (Co-PI, NTU) Dr Chencheng DAI (RF, NTU) has developed further efficient strategies for the electrochemical production of lactic acid by oxidation of glycerol on AuPt electrode architectures in alkaline environments. In this reporting period, understanding of the mechanistic aspects of the conversion have begun to assist the prediction of the most efficient reactor design and transport characteristics of the reaction. In addition, work has begun on the development of a test flow loop to allow integration of novel electrolytic reactors into a test station to explore lactic acid production as a function of feedstock, electrode geometry and transport characteristics.

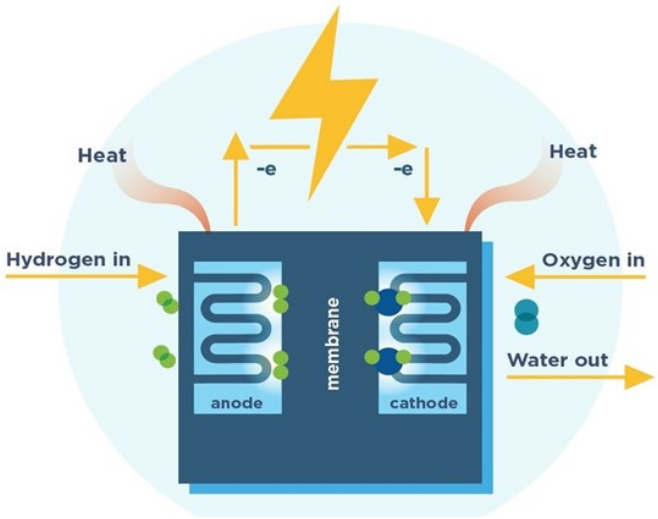
The development of the IRP2 international outreach programme has expanded significantly within the current reporting period. October 2017 saw the launch of an advanced electrochemical techniques masterclass in UK in collaboration with Zimmer and Peacock. This new masterclass programme highlights IRP2 developments in the area of electrochemical analysis. Delegates from local Cambridge companies and as far as the US attended the two-day programme. As a result of its success, a further masterclass was arranged with Zimmer and Peacock in Norway (February 2018), with attendees from local industry and academia as well as international visitors, including from Saudi Arabia. Our collaboration with Metrohm also extended with masterclass activities in Australia (December 2017) and Singapore (March 2018) in the field of advanced electrochemical techniques. In each case the programmes comprised keynote lectures from IRP2 PI Dr Adrian Fisher and hands-on training in the use of state-of-the-art analysis techniques. We were kindly supported in the Singapore programme by the Singapore section of ISE.

3.2.2 Update on Work Packages

WP 2.1: Numerical multi-scale electrochemical modelling and analysis

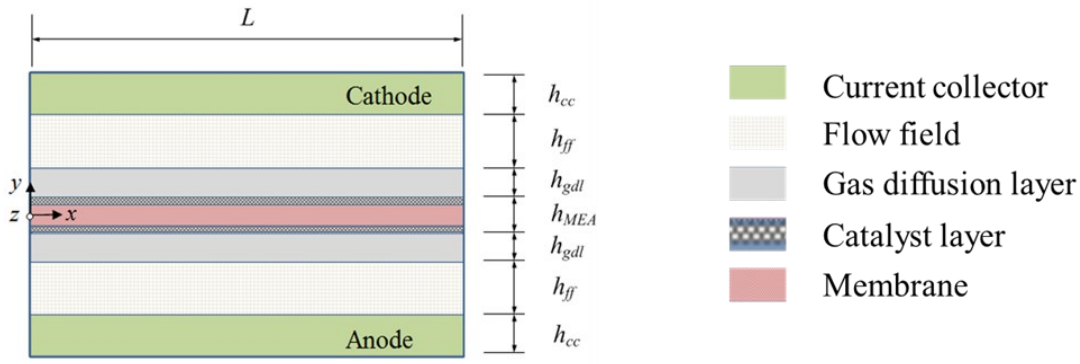
Vishvak KANNAN's (PhD student, NUS) research is focused on the mathematical modelling of an electrochemical reactor. An electrochemical reactor (ECR) is a device through which electrochemical reactions are carried out in a controlled manner. Electrochemical reactions are chemical reactions that are either caused or accompanied by a passage of electric current, mostly due to the transfer of electrons. Therefore, an ECR can be operated in two modes viz: *electrolytic* – electrical energy to chemical energy, or *galvanic* – chemical energy to electrical energy. Vishvak reported that these galvanic ECRs can be employed as an on-demand, distributed and clean source of electrical energy. A continuous, uninterrupted supply of electric current can be obtained from galvanic ECRs by the continuous supply of reactants for the chemical reaction. A galvanic ECR produces electric current as a consequence of the reaction between hydrogen and oxygen producing water. Thus, the emission from this system is just water vapour, instead of carbon emissions or other harmful emissions like NO_x and SO_x from similar systems.

Fig. 2.1: Schematic representation of the ECR working principle.



Vishvak has reported the analysis of current at the surface of a hydrodynamically modulated disc electrode in the earlier reports. After gaining experience in mathematical modelling of electrochemical systems from this project, a two-dimensional (2D), steady-state, one-phase mathematical model of the galvanic ECR was developed. A schematic of the model considered for the simulations is presented below.

Fig. 2.2: Galvanic ECR model.

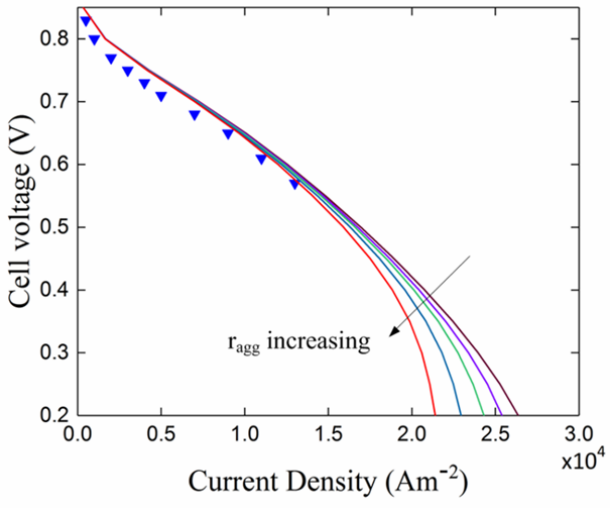


The model accounted for the effect of temperature and the radius of the agglomerates on the performance of the reactor as well. Fig 2.3 presents the polarisation curve from the 2D model of the galvanic ECR adopting parameters and the governing equations from literature. The symbols represent the experimental polarisation curve measured in previous literature and the lines represent the

Fig. 2.3: Polarisation curve for the 2D agglomerate model with experimental data ▼ and model predictions (lines).

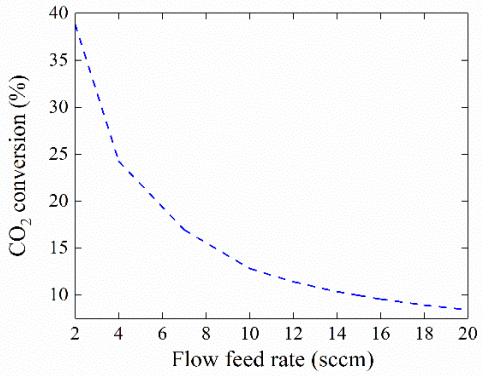
Figs. 2.1-2.3 Vishvak KANNAN (PhD student, NUS)

simulation of the mathematical model with different agglomerate radii, r_{agg} viz 0.8E-7 m, 0.9E-7 m, 1.0E-7 m, 1.1E-7 m and 1.2E-7 m. As r_{agg} increases, the current density decreases at lower potentials. This suggests that as the mass-transfer limited regime is approached, r_{agg} has a leading-order effect on the mass transport within the agglomerates. Based on this model, a transient model is being developed and a controlled current short-circuit will be implemented subsequently.



Dr Kuppa Ashoke RAMAN (RF, NUS) reported that the electrochemical reduction of CO_2 into useful hydrocarbons with the help of a low-carbon or carbon-neutral power source is a promising technique to reduce global CO_2 emissions. While the conversion of CO_2 depends on the nature of the reacting catalyst and electrode characteristics, the interplay between the flow/reactant transport with the underlying electrochemistry is essential to improvise the performance the electrochemical flow reactor. The design of the electrochemical reactor modulates the transport phenomenon. Numerical modelling of such electrochemical reactors would elucidate the flow physics leading to CO_2 conversion, which in turn will facilitate in-design optimisation. To begin with, he performed simulations on electrochemical reduction of CO_2 into CO in a microfluidic cell.

Fig. 2.4: CO_2 conversion and Faradaic efficiency as a function of volumetric flow rate.



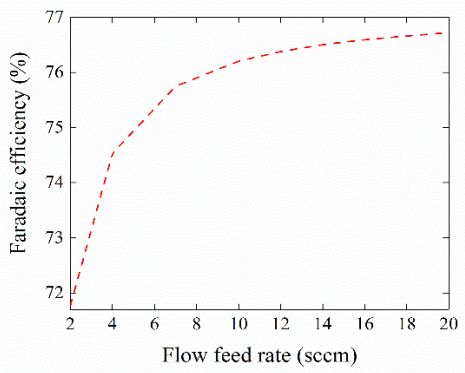


Fig. 2.4a illustrates the effects of gas feed rate at a given CO_2 concentration on the cell performance. As the feed rate is increased, we observe that the % conversion of CO_2 decreases. In particular, we notice that the rate of change of % CO_2 conversion is negligible after a feed rate of 15 sccm. This is attributed to the fact that at higher feed rates, the reaction reaches its limit due to electron transfer and is not governed by mass diffusion. Moreover, due to the high momentum of the incoming fluid, the residence time for the reactants is decreased. The Faradaic efficiency shown in Fig. 2.4b complements the observations illustrated in the % CO_2 conversion. As the gas feed rate is increased, the overall concentration of CO_2 inside the cathode gas flow channel is increased. This results in higher CO_2 concentration in the catalyst layer leading to an increase in Faradaic efficiency.

Dr RAMAN reported that previous work on electrochemical reduction of CO_2 into value-added products involved an electrolytic cell with a separator. CO_2 is bubbled into the cathode side and reduced to chemicals such as formic acid, methane, carbon monoxide and alcohols. However, the low solubility of CO_2 in water limits the overall conversion. To circumvent this issue and improve the cell

performance, a couple of modifications were made. In this work the research team employed the gas diffusion electrodes for CO_2 transfer. This allows direct contact of CO_2 with the catalyst layer, which enhances the mass transfer. The presence of a porous gas diffusion layer homogenises the reactant gas leading to efficient transport of CO_2 to the catalyst. The second modification is the use of a solid electrolyte (membrane) instead of a liquid electrolyte. Employing a membrane as an electrolyte reduces the distance between the anode and cathode, thereby improving ionic transfer as the internal resistance is decreased. The ionic conductivity of the Nafion membrane is higher than water. Owing to these advantages, we are currently working on setting up a numerical model with a proton exchange membrane as the electrolyte. This model is similar to the existing fuel cell model. The available information on electrodes and cell configurations of fuel cells would be useful to apply to the development of reactors for CO_2 electrolysis, which is the objective of the current work to convert CO_2 into propanol and ethylene.

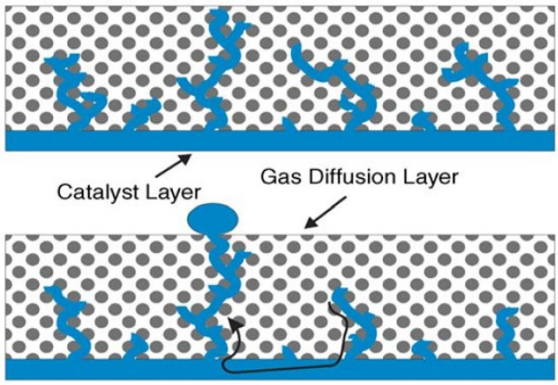


Fig. 2.5: Schematic representation of water flooding inside the gas diffusion layer of an electrochemical reactor.

In addition, Dr RAMAN reported on the **Modelling of water flooding in gas diffusion electrodes**. While gas diffusion electrodes alleviate the problem of CO_2 solubility as discussed above, it is characterised by the problem of water flooding. After reacting with the catalyst, facilitated by the momentum of the gas feed, the products diffuse out of the porous layers. However, liquid products may saturate the porous region as shown in Fig. 2.5.

This would lead to the reduction of effective diffusivity on the reactants and impede the performance of the electrochemical reactor. A fundamental understanding of the interaction between the flow transport and porous media would enable improvisation and optimisation of the cell performance. To investigate this transport phenomenon, we have developed a two dimensional phase field based lattice Boltzmann solver. The solver captures high density and viscosity ratios. To model the moving three phase contact line, both the energy based and geometry based contact angle formulations have been incorporated inside the solver. As a first step to model porosity, the solver was tested with droplet deposition on a textured surface. Fig. 2.6 shows the interface profiles of the droplet on textured surfaces with different roughness geometries. Depending on the contact area of the interface with the solid boundary and volume of air pockets between the pillars, the interface profiles and hence the subtended contact angle differs. The pillar geometry and their distribution significantly influences the droplet dynamics. Dr RAMAN reported that work on the dynamic behaviour of droplets on textured surfaces subjected to shear flow is ongoing. This model approximates the behaviour of droplets moving on top of the gas diffusion layer, as gas is fed into the flow channel. To enhance mass transfer, the usage of pulsating flow inside the gas flow channels is already known. However, the effect of such flow behaviour on two-phase flow distribution on the gas diffusion layer needs to be investigated. This investigation will be carried out firstly on smooth surfaces and then on textured surfaces.

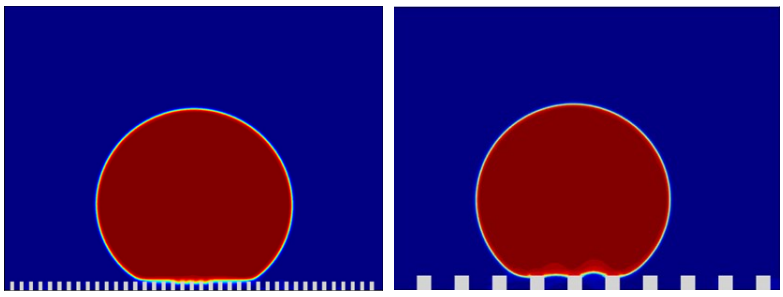


Fig. 2.6: Interface profiles of droplet resting on textured surfaces with different pillar geometries.

Figs. 2.4-2-6
Dr RAMAN
(RF, NUS)

Yian WANG's (PhD student, CAM) main research area lies in the investigation of conventional electrochemical reactions and development of the numerical models to quantify energy storage systems. He has been focusing on studying one realistic electrocatalytic process for redox systems that cannot be achieved by conventional techniques. Yian reported that he and Dr Kamal ELOUARZAKI (RF, NTU) have been working on simulations to compare the experimental data and proposed a catalytic model to depict the so-called activation and inactivation process. The understanding of the process offers a deep insight into the characteristics of some novel synthetic catalysts which are believed to be greatly useful in the reduction of carbon dioxide. They plan to submit a comprehensive paper including all the experiments and calculations on this specific phenomenon, which establishes a framework for an electrocatalytic EC'CE mechanism. Recently, Yian has used Fast Fourier Transform (FFT) voltammetry to study the EC' mechanism, and he will keep working on numerical modelling applications and computer-aided design.

WP 2.2: Electrode development and testing

Naziah Binte MOHAMAD LATIFF (PhD student, NTU) has been studying the toxicological effects of nanomaterials that show great promise for energy conversion/storage applications. Examples include graphene, metal chalcogenides and black phosphorus. These studies are important as the materials' health hazards are not yet well understood despite their likely future commercialisation. In addition she has investigated the toxicological effects of black phosphorus and metal phosphorus chalcogenides. These materials have been reported for hydrogen storage and water splitting. She has found that the metal element present as well as the material's extent of oxidation can influence the toxicological behaviour of these nanomaterials. She has currently two manuscripts in preparation.

Dr Kamal ELOUARZAKI's (RF, NTU) main research area lies in the study of chemical and electrochemical process modelling and optimisation. Recently, he has been focusing on the development of bioinspired catalysts that represent a promising class of electrochemical systems with fascinating challenges for the design of biomaterials for energy conversion. Enzymes, which allow energy conversion and electron transfer (ET) in many biological processes, are good candidates for such biomaterials. Strategies to enhance ET between redox enzymes and electrodes include the oriented immobilisation of enzymes onto an electroactive surface as well as the electron mediation. Here, he has developed a strategy for simultaneously achieving a controlled orientation and redox mediation on carbon nanotube-based electrodes. He has developed the design, synthesis, and electropolymerisation of a redox mediator based on the association of an enzyme orientation site (pyrene), an electron carrier redox mediator 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS), and an electropolymerisable monomer (pyrrole). The coupling of enzymatic orientation and mediated electron shuttling in the same chemical structure (pyrrole-ABTS-pyrene) provides high current density and long-term stability for the enzyme electrocatalysis. According to quartz crystal microbalance and electrochemical measurements, the enzymatic electrocatalysis is consistent with electron shuttling between the favourably orientated enzymatic redox centres and the electrode through the redox mediator. The ability of this tailored home-made redox mediator to connect enzymes to external circuits setup has been demonstrated using two different fuel cell configurations: a membraneless fuel cell (MlFC) and a proton exchange membrane hydrogen/air fuel cell (PEMFC). When integrated to two different setups, MlFC and PEMFC, the biocathode provides a power density of 1.07 mW cm^{-2} and 7.9 mW cm^{-2}

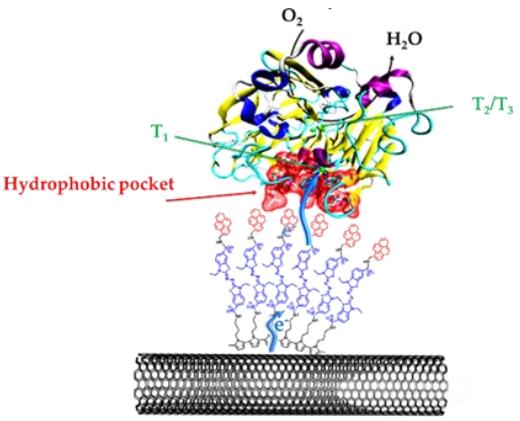


Fig. 2.7: A carbon nanotube-based electrode.

Dr ELOUARZAKI (RF, NTU)

respectively. This new principle of coupling an aromatic site for enzyme orientation and a redox mediator allows a great variety of mediators to be engineered, opening vast possibilities for the development of bioelectronics and biosensors.

Nur Farhanah Bte ROSLI (PhD student, NTU) focuses on electrode development and testing. She investigates the toxicity of new materials which are used in the development of electrodes with enhanced performance. New materials with superior electrocatalytic properties are promising materials as catalysts in clean energy generation, such as in fuel cells. Catalytic dependent reactions such as hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) occur. However, the toxicity of these new emerging materials is yet to be known and they may pose a health hazard if indeed they are proven toxic. Therefore, investigating the toxicity of new materials in such applications prior to large scale commercialisation is vital.

During the reporting period, she investigated oxygen reduction reaction (ORR) capabilities of Pt dichalcogenides as compared to the well-known platinum on carbon (Pt/C). Results obtained from her studies suggest that $PtTe_2$, as compared to the other two Pt dichalcogenides (namely PtS_2 and $PtSe_2$), possesses superior electrocatalytic properties for ORR. $PtTe_2$ possesses similar ORR performance to that of the best-reported electrocatalyst, Pt/C. Hence, from these studies, we can conclude that $PtTe_2$ can potentially replace Pt/C as a safer material for catalysts.

THAM Guo Xiong (PhD student, NTU) has been working on the development of a conducting polymer (CP) film with the use of electrochemical polymerisation (ECP) in the cathode or anode. The use of ECP allows for a simple, rapid, stable and selective preparation of certain CP films to be electropolymerised and considered further in applications such as secondary batteries and supercapacitors. A few classes of monomers such as aniline, thiophenes, quinones and phenylenediamines have been tested, and certain synthetic routes have also been explored to obtain the corresponding synthetic compound for electrochemical testing of this project. Factors that can affect electropolymerisation were also controlled accordingly for the tested compounds in order to achieve a proper CP film.

Dr Libo SUN (RF, NTU) reported on electrochemical carbon dioxide reduction in aqueous solution. The system relied on an in situ on-line system, with the traditional three-electrode system employing an H-cell separated with Nafion 117 membrane as the reaction container. The possible gas phase products such as H_2, CO and hydrocarbons like C1-C2 (CH_4, C_2H_4, C_2H_6 etc.) could be analysed through on-line gas chromatography (GC), whilst the liquid phase products like acids, alcohols and aldehydes were detected with high performance liquid phase chromatography (HPLC). The catalysts used here were transition metals (M = Fe, Co, Ni, Cu), which were embedded into a nitrogen-doped carbon based materials matrix to form single atom catalysts M-N-C. With such catalysts prepared, the electrochemical CO= reduction could be performed with above -mentioned setup. The reduction through different potential ranges was tested, and CO emerged as the main product. The highest CO faradaic efficiency, *ca.* 100%, can be achieved by judicious selection and design of such catalysts with different metals. Further results are being characterised and summarised.

Dr Chencheng DAI (RF, NTU) reported on his research focused on the production of lactic acid by electrochemical oxidation of glycerol using AuPt nanoparticle catalysts. In this work, lactic acid was prepared by the one-pot electrochemical oxidation of glycerol catalysed by AuPt nanoparticles in alkaline solution at room temperature and pressure. AuPt nanoparticles with different surface compositions were prepared by heat treatment, and the performance of the AuPt catalysts were optimised by tuning parameters, including AuPt surface composition, applied potential, electrolyte pH and glycerol concentration. The resulting electrolyte was analysed by nuclear magnetic resonance (NMR) and high performance liquid chromatography (HPLC). 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 efficient, energy-saving, environmentally friendly and commercial production of lactic acid. In addition, metal nanoparti-

cles embedded with a metal organic framework (MOF) or mesoporous carbon also have been investigated for glycerol electro-oxidation. This work could potentially link WP 2.3 (electrochemical reactor engineering) in future research.

Dr DAI also reported on the work done on **Tailoring the Co 3d-O 2p covalency in $LaCoO_3$ by Fe substitution to promote oxygen evolution reaction.** In this work, Fe substitution has been introduced in $LaCoO_3$ to boost its OER performance. Density function theory (DFT) calculations verified that the enhanced performance originates from the enhanced Co 3d-O 2p covalency with 10 at% Fe substitution in $LaCoO_3$. Both DFT calculations and Superconducting Quantum Design (SQUID) magnetometer (MPMS-XL) showed a Co^{3+} spin state transition from generally low spin state (LS: $t_{2g}^6 e_g^0$, S = 0) to a higher spin state with the effect of 10 at% Fe substitution. X-ray absorption near-edge structure (XANES) supports DFT calculations on an insulator to half-metal transition with 10 at% Fe substitution, induced by spin state transition. The half-metallic $LaCo_{0.9}Fe_{0.1}O_3$ possesses increased overlap between Co 3d and O 2p states, which results in enhanced covalency and promoted OER performance. This finding enlightens a new way of tuning the metal–oxygen covalency in oxide catalysts for OER.

Dr DAI also conducted a systematic study on the composition dependence of ORR in $ZnCo_xMn_{2-x}O_4$ (x = 0.0–2.0) spinel, presented here with special attention to the role of edge sharing $[Co_xMn_{1-x}O_6]$ octahedra in the spinel structure. The ORR specific activity of $ZnCo_xMn_{2-xO4}$ spans across a potential window of 200 mV, indicating an activity difference of ≈3 orders of magnitude. The curve of composition-dependent ORR specific activity as a function of Co substitution exhibits a volcano shape with an optimum Mn/Co ratio of 0.43. It is revealed that the modulated e_g occupancy of active Mn cations (0.3–0.9), as a consequence of the superexchange effect between edge sharing $[CoO_6]$ and $[MnO_6]$, reflects the ORR activity of edge sharing $[Co_xMn_{1-x}O_6]$ octahedra in the $ZnCo_xMn_{2-x}O_4$ spinel oxide. These findings offer crucial insights in designing spinel oxide catalysts with fine-tuned e_g occupancy for efficient catalysis.

Revealing the dominant chemistry for oxygen reduction reaction on small oxide nanoparticles has also been a focus. Here, Dr DAI reports a systematic study on Mn-substituted ferrite $Mn_xFe_{3-x}O_4$ (x = 0.5–2.5) nanoparticles and the roles of surface Mn in determining their ORR activities. Gradual Mn substitution induced changes in Mn valence and crystal structure. However, there is no remarkable correlation that can be found between their bulk chemistry and ORR activities. Instead, the surface Mn density and valency were found to play dominant roles in determining the ORR. This work shows that, at a small particle size, the bulk chemistry of oxides may not be the descriptor for their electrochemical properties. Due to the significantly high surface/bulk ratio, the surface chemistry has to be carefully characterised to interpret the activities of oxide nanoparticles.

Finally, some work has been done on spinel manganese ferrites for oxygen electrocatalysis: effect of Mn valency and occupation site. Here, an investigation is reported on the ORR and OER performance of intermediate spinel $MnFe_2O_4$. The modulation of cation oxidation state and inversion degree of spinel $MnFe_2O_4$ were achieved by a simple annealing process. X-ray absorption spectroscopy analysis reveals that the Mn occupancy in octahedral sites varied from 0.25 ~ 0.41 and Mn cations were oxidised from 2+ to 3+ with increasing temperature treatment. Convinced by the leading role of the octahedral-geometric, we further reveal the role of Mn oxidation state through normalising the activity to active $Mn_{[Oh]}$ site number. Our findings clearly indicate that Mn^{3+} was more catalytically active than Mn^{2+} in catalysing ORR and OER.

WP 2.3 Electrochemical reactor engineering: cogeneration and electrosynthesis

Dr WANG Jiong (RF, NTU) reported on a recent discovery; that Ni^{2+} ions can be incorporated into a graphene interface under mild conditions to form heterogeneous and molecularly well-defined Ni sites for oxygen evolution in alkaline aqueous solutions. The molecular Ni sites on graphene were intrinsically not OER-active. However, they could interact with Fe species in KOH solutions to form Ni-Fe sites. This structural variation resulted in a significant enhancement on OER activity. The structure of Ni-Fe sites was investigated by various techniques. The results showed that they maintained molecular dispersion on graphene, and the Ni-Fe distance was revealed to be 2.7 Å. The research team also proposed that the adsorption configuration with HO− ions was tuned from pristine Ni sites to Ni-Fe sites. HO− ions were bridged with the Ni-Fe sites before OER. These results demonstrate a novel, molecularly well-defined and heterogeneous structure catalyst for OER, and might also serve as a platform to gain further insights into the OER mechanism.

Dr Tianran ZHANG (RF, NUS) focuses on developing manganese dioxide-based electrocatalysts as the alternative to noble metal oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalysts. While manganese oxides are the current favourite, their native activity must still be substantially improved before they can realistically be considered as the substitute of noble metals. Recently, he Dr ZHANG discovered phosphate modification to be an effective strategy to increase the bifunctional oxygen electrocatalytic activity of MnO_2. Specifically, the half-wave potential of phosphate-promoted α-MnO_2 (PMO) for ORR is 0.85V vs. RHE, ~70 mV, more positive than α-MnO_2 and the same as the benchmark 20wt% Pt/C catalyst. The OER potential to maintain 10 mA cm^{-2} of current density is 1.63V, ~40 mV, more negative than α-MnO_2 and about the same as the benchmark 20wt% Ir/C catalyst (1.60 V). The potential difference between ORR (at -3 mA cm^{-2}) and OER (at 10 mA cm^{-2}) is 0.79 V, a standard measure of bifunctional oxygen activity, significantly surpasses the performance of α-MnO_2 (0.91 V) and the noble metals (0.95V for Pt/C and 0.93V for Ir/C). Additional electrochemical measurements and density functional theory calculations suggest that the promoted bifunctional activity of PMO is due to the dual-affinity of phosphate for O and H atoms, which facilitates the O_2 adsorption in ORR and H_2O deprotonation in OER. The results have provided a new insight for the improvement of the activity beyond the influence of chemical valence, crystal structure and morphology.

ZHANG Shengliang (PhD student, NUS) is interested in the design and preparation of nanocrystals for spectrally-selective electrochromic smart windows. His recent work focused on the study of oxygen-deficient tungsten oxide nanowires for electrochromic applications. He has successfully demonstrated that dynamic and independent control of near-infrared (NIR) and visible (VIS) light transmittance can be accomplished in a single-component material — monoclinic oxygen-deficient tungsten oxide nanowires (m-WO_{3-x} NWs) — without the need for compositing with other active electrochromic components (the common approach in use today). The cast films of m-WO_{3-x} NWs not only deliver the desired dual-band response, but also provide a high optical modulation of the full solar spectrum (91.7%, 92.7%, 94.6%, 87.3% at 633, 800, 1200, 1600 nm respectively), a high colouration efficiency (101.7 and 184.3 cm^2 C^{-1} at 633 and 1200 nm respectively) and good cycle stability (8.3% of optical loss at 633 nm after 1000 cycles). In addition, he also examined the mechanism of dual-band optical modulation in m-WO_{3-x} NWs. He has published this work in *Materials Horizons* (IF: 10.7).

Dr CAO Sheng (RF, NUS) is interested in dual band electrochromic materials and devices based on metal-doped TiO_2 nanocrystals (NCs) for the selective and dynamic control of the intensity of incident thermal radiation without affecting visible light transmission. His current work involves the synthesis of doped TiO_2 NCs and tailoring their plasmonic features across the near-infrared region by varying the dopant concentrations. He reports here the discovery of metal-doped colloidal TiO_2 NCs with broadly tunable plasmon resonance absorption and their synthesis by a facile and scalable one-pot method. Strong localised surface plasmon resonance (LSPR) absorption oc-

curs in the as-synthesised Mo, W, and Nb-doped TiO_2 NCs in the visible, near-infrared (NIR) and mid-infrared regions respectively. Density functional theory calculations indicate the dopant perturbation of the TiO_2 electronic structure and the resultant increase in the electron density at the Fermi level as the likely cause for the strong LSPR effect. The W-doped TiO_2 NCs are the most versatile since their LSPR absorption in the NIR region can be tuned from 980 to 1700 nm by the dopant concentration and NC morphology. The method of synthesis can also be scaled for gram-level productions in batch reactors. Tunable LSPR properties and the ease and scalability of synthesis are the strong features of these metal-doped TiO_2 NCs for plasmonic applications. His ongoing work will focus on the fabrication of transparent flexible electrochromic devices based on these doped TiO_2 NCs and the characterisation of their optical performance.

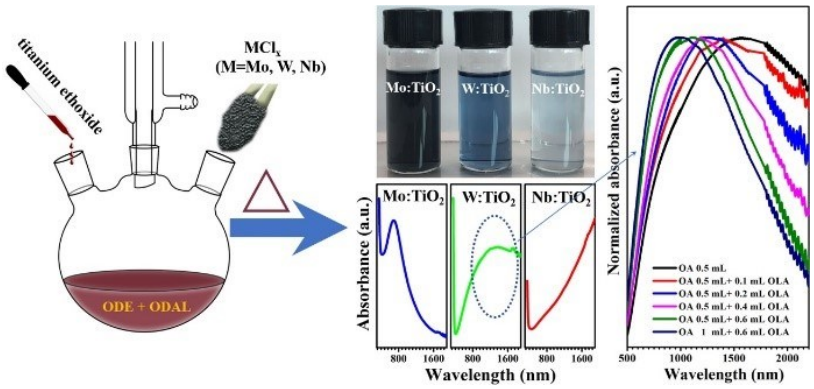


Fig. 2.8: A series of metal-doped TiO_2 nanocrystals with broad LSPR absorption tunability was produced by a facile and scalable one-pot method.

Dr CAO
(RF, NUS)

Other Activities and Achievements

- Dr Kamal ELOUARZAKI (RF, NTU) reported that a ground-breaking UK-Malaysia British Council Institutional Links project that generates sustainable electricity from effluent waste processing has been awarded the Newton Prize. This Newton-funded project, spearheaded by lead researchers from the UK and Malaysia, paves the way for greater access to energy supply, particularly for the rural population in Malaysia. British High Commissioner to Malaysia, Her Excellency Vicki Treadell, and Malaysia's Science Advisor to the Prime Minister, Prof. Emeritus Tan Sri Zakri Abdul Hamid, presented the award to the winning project's lead researcher, Prof. Phang Siew Moi from University of Malaya and Dr Adrian Fisher from IRP2.
- Vishvak KANNAN (PhD student, NUS) presented a poster at the COMSOL conference Singapore in November 2017, entitled "Analysis of current at the surface of a rocking disk electrode". In addition, he presented a poster at the CREATE@10 Symposium, 2017, which was displayed in the VIP section, entitled, "Better molecules, better electrodes and better reactors".

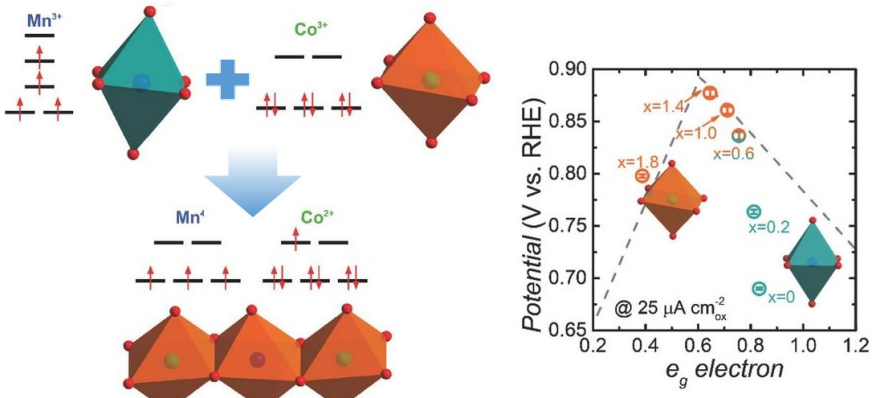
3.2.3 Scientific Output of IRP2

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.

Superexchange Effects on Oxygen Reduction Activity of Edge-Sharing $[Co_xMn_{1-x}O_6]$ Octahedra in Spinel Oxide

Ye Zhou, Shengnan Sun, Shibo Xi, Yan Duan, Thirumany Sritharan, Yonghua Du and Zhichuan J. Xu

DOI: 10.1002/adma.201705407



Abstract:

Mn–Co containing spinel oxides are promising, low-cost electrocatalysts for the oxygen reduction reaction (ORR). Most studies are devoted to the design of porous Mn–Co spinels or to strongly coupled hybrids (e.g. $MnCo_2O_4$/N-doped-rmGO) to maximise the mass efficiency. The lack of analyses by metal oxide intrinsic activity (activity normalised to catalysts' surface area) hinders the development of fundamental understanding of the physicochemical principles behind the catalytic activities. A systematic study on the composition dependence of ORR in $ZnCo_xMn_{2-x}O_4$ (x = 0.0–2.0) spinel is presented here with special attention to the role of edge sharing $[Co_xMn_{1-x}O_6]$ octahedra in the spinel structure. The ORR specific activity of $ZnCo_xMn_{2-xO4}$ spans across a potential window of 200 mV, indicating an activity difference of ≈3 orders of magnitude. The curve of composition-dependent ORR specific activity as a function of Co substitution exhibits a volcano shape with an optimum Mn/Co ratio of 0.43. It is revealed that the modulated e_g occupancy of active Mn cations (0.3–0.9), as a consequence of the superexchange effect between edge sharing $[CoO_6]$ and $[MnO_6]$, reflects the ORR activity of edge sharing $[Co_xMn_{1-x}O_6]$ octahedra in the $ZnCo_xMn_{2-x}O_4$ spinel oxide. These findings offer crucial insights in designing spinel oxide catalysts with fine-tuned e_g occupancy for efficient catalysis.

Spinel Manganese Ferrites for Oxygen Electrocatalysis: Effect of Mn Valency and Occupation Site

Ye Zhou, Yonghua Du, Shibo Xi and Zhichuan J. Xu

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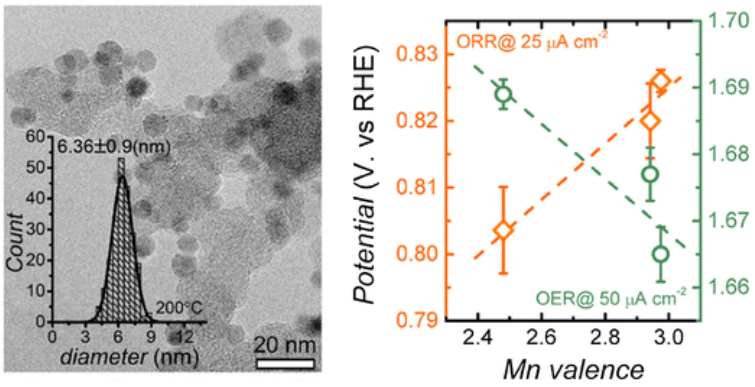


Abstract:

Spinel catalysts have been widely explored for the electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). To consolidate the understanding on electrocatalysis by spinel family, intermediate spinels should be deliberately examined because most spinel oxides are of intermediate structure. Here, we report an investigation on the ORR and OER performance of intermediate spinel $MnFe_2O_4$. The modulation of cation oxidation state and inversion degree of spinel $MnFe_2O_4$ were achieved by a simple annealing process. X-ray absorption spectroscopy analysis reveals that the Mn occupancy in octahedral sites varied from 0.25 ~ 0.41 and Mn cations were oxidised from 2+ to 3+ with increasing temperature treatment. Convinced by the leading role of octahedral-geometric, we further reveal the role of Mn oxidation state through normalising the activity to active $Mn_{[Oh]}$ site number. Our findings clearly indicate that Mn^{3+} was more catalytically active than Mn^{2+} in catalysing ORR and OER.

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

CAPRICORN 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

April 2018

3.3.1 IRP3 Research Overview

Over the past six months, we have continued to add new functionalities to the J-Park Simulator (JPS), thus further enhancing its range of applications as a tool to simulate and optimise networks of industrial operations using machine learning and big data technologies. For instance, we are now able to employ three-dimensional representations of buildings, and hence cities, which we have coupled with commercial software for atmospheric pollutant dispersion. Together, they allow more accurate and relevant predictions of the distribution of pollutants in the atmosphere in Singapore. Secondly, we have refined a trading scheme for CO_2 emissions based on blockchain technology such that it can autonomously trade emissions permits for plants in the JPS. This is now conducted in a fashion that maximises cost savings for the participants and enables responding to changes in market conditions or plant data, which represents another step in realising machine-to-machine communication using real-time information.

In the laboratory, this reporting period has seen exciting progress in the synthesis of nanomaterials for catalytic applications. In particular, the flame-synthesis of nanocatalysts, being a continuous process with high throughput and yielding a product with large specific surface area, is promising sustainable ways to produce renewable energy, for example by utilising solar energy to catalytically convert CO_2 into fuels such as methanol or ethanol, or other valuable products.

Furthermore, we have added a number of quantitative characterisation capabilities to our portfolio, namely laser-induced fluorescence, laser-induced incandescence, and 2- and 3-colour pyrometry to measure a variety of quantities in hydrocarbon flames such as species concentrations, and soot temperature and volume fraction. Additionally, using a range of techniques including mass spectrometry, high-resolution transmission electron microscopy and Raman spectroscopy, we have analysed charcoal (image below) on the nano-level. This revealed that there are significant amounts of curved closed carbonaceous structures present, which has important implications for the use of charcoal for carbon capture as it sheds light on the origin of its resistance to oxidation.

In addition to these experimental achievements, we have managed to gain insights into the nanostructure of various carbon materials using computational chemistry tools. For example, we have calculated the optical band gap of several classes of polycyclic aromatic hydrocarbons (PAHs) by means of density functional theory methods. This will help identify which PAHs are involved in the formation of the very first soot particles and thus help solve the mystery of soot inception, which is still poorly understood.

Charcoal forming in a gasifier.

Jacob MARTIN (PhD student, IRP3)

3.3.2 Update on Work Packages

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

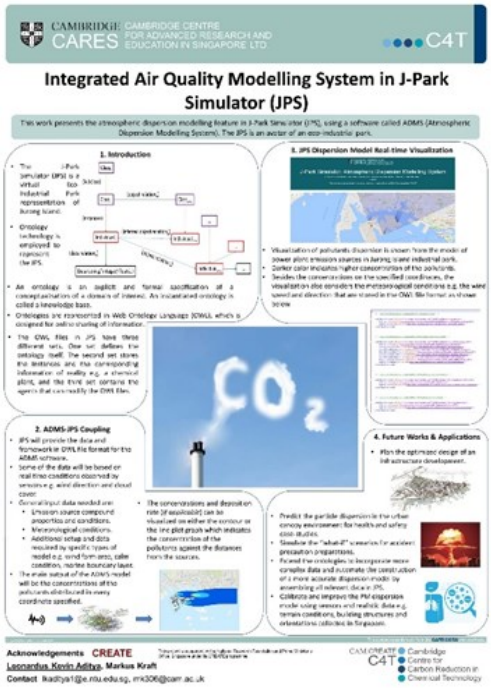


Fig. 3.1: Poster describing modelling pollutant dispersion in the atmosphere using the J-Park Simulator.

Leonardus Kevin ADITYA (Project Officer, NTU)

Leonardus Kevin ADITYA (Project Officer, NTU) has been extending the J-Park Simulator with several new feature models. One of them is a model predicting the dispersion phenomenon of some pollutants in the atmosphere considering meteorological, source, and site factors by using a software called ADMS (Atmospheric Dispersion Modelling System). Furthermore, he created the ontology, the knowledge bases, and codes related to it for integration into the J-Park Simulator, which uses ontologies as containers for data and models. He has joined the NEA-NERI Air Quality Workshop as a poster presenter about the J-Park Simulator, especially focusing on the dispersion model created (see Fig. 3.1). In addition, he also started to work on exploiting the CityGML format, which can be used to represent 3D models of objects, in particular buildings and terrains, and thus to create 3D models of entire cities. He has created an ontology for CityGML so that it can be integrated into the J-Park Simulator. The plan is to implement this into the ADMS dispersion model for more advanced modelling and also for visualisation purposes.

Khamila Nurul KHAQQI (PhD student, NTU) has been working on creating a trading algorithm for an autonomous blockchain-enabled emissions trading scheme (ETS), which also includes the participants' reputation as polluters. Conventional ETSs largely fail in stimulating abatement investment, with firms being decidedly reluctant to invest in energy-saving equipment or devices even when there is cost saving to be gained. The developed algorithm is able to manage a firm's trading of emission permits so that it can be performed autonomously and be based on current emissions data and the state of production of the firm. The objective of the algorithm is to optimise the firm's ownership of emission permits. Accordingly, the algorithm will try to ensure that firms will have sufficient permits to cover their CO_2-production whilst simultaneously minimising the amount of excess permits. This trading algorithm is applied within the J-Park Simulator by connecting the trading algorithm to chemical plants in the JPS. In this way, the algorithm can initiate a trade as a response to a change in the plant's state of production. The result is a system that can run securely and autonomously whilst simultaneously introducing a measure to lower the energy-efficiency gap. She also performed an analysis of her algorithm to ascertain its performance and robustness, as well as to optimise the design of the system. The objectives are to observe the behaviour of the system under different market conditions and to optimise the system parameters so that the incentives and deterrents which are distributed based on firms' reputation as polluters are reaching the proper target and do not cause unnecessary or unforeseeable harm.

ZHANG Chuan (PhD student, NTU) has begun the third and final year of his PhD and is working on the design and optimisation of the energy and material network on Jurong Island. His research interests include energy system environmental assessment, sustainable heating and cooling and waste heat recovery. Chuan's current focus is a feasibility analysis of power plant decarbonisation for the Jurong Island industrial network, which will be added as a functionality to the J-Park Simulator.

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

Dr Maria BOTERO (RF, NUS) has been studying the morphology and nanostructure of soot particles formed in a reference co-flow diffusion flame. The aim of this investigation is to improve the understanding of the underlying processes involved in the formation of soot particles during the combustion of different fuels. The evolution of primary soot particles as they form, grow and finally oxidise in the flame (Fig. 3.2) was studied using a fast-insertion thermophoretic sampling technique and Transmission Electron Microscopy (TEM). The experimental results suggest that after inception, the nascent soot particles coagulate and fully sinter to form larger primary particles. As these primary particles travel along the flame, they grow mainly due to coagulation and condensation and a layer of amorphous hydrocarbons (as revealed by high-resolution TEM) forms on their surface. This amorphous layer appears to glue together the primary particles and promote their aggregation to form fractal structures. Fast graphitisation of the amorphous layer leads to a graphitic-like shell around the particles and compacts them, resulting in a decrease of their size. Towards the flame tip the primary particles decrease in size due to rapid oxidation. In addition, a detailed population balance model has been used to investigate the mechanisms that are important for prediction of primary particle size distributions. Simulation results indicate that the primary particle size distributions are very sensitive to the parameterisation of the sintering and particle rounding processes. By contrast, the average primary particle size is less sensitive to these parameters. This demonstrates that achieving good predictions for the average primary particle size does not necessarily mean that the distribution has been accurately predicted. The results from this experimental and numerical investigation have been submitted to the 37th International Symposium on Combustion.

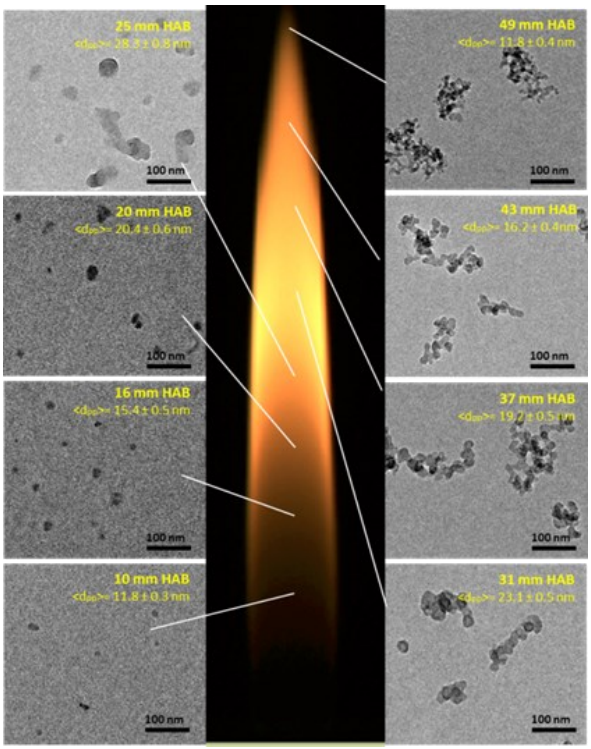


Fig. 3.2: Transmission Electron Microscope (TEM) images of soot particles sampled in a co-flow diffusion flame.

Dr BOTERO (RF, NUS)

Dr TAN Yong Ren (RF, NUS) has been studying the sooting propensity of fuels (oxygenated and non-oxygenated) blended in commercial diesel fuel, employing the standardised ASTM D1322 smoke point method. The oxygenated fuels studied were polyoxymethylene dimethyl ethers ($PODE_1$-$PODE_4$), methyl butyrate (ester), dimethyl carbonate (carbonate) and n-butanol (alcohol), while the non-oxygenated fuels were hexane and hexadecane). The main objective of this investigation is to elucidate the influence of different fuel additives on the sooting propensity of additive-diesel blends. The sooting propensity of each fuel blend was represented using the Oxygenated Extended Sooting Index (OESI) because of their linear relationship to fuel composition which facilitates the analysis of fuel mixtures. When looking at non-oxygenated fuel additives and oxygenated fuel additives (Fig. 3.3), it can be seen that the dilution of the aromatics in diesel plays the most prominent role in soot suppression, amounting to 44-72% of the soot reduction. The hydrocarbon chain length effect (shortening of the chain length of the aliphatic component from C16 to C7 in current study) was found to have the lesser effect. Lastly, the oxygen content effect from oxygenated fuels has the least effect with 18-26% on the overall soot suppression to diesel fuel combustion. The results of the investigation have important implications for engine applications as in terms of volumetric addition of oxygenates, there is no noticeable difference in using one oxygenated additive or another.

Besides that, it was found that the chain length effect of $PODE_1$-$PODE_4$ has no clear difference in soot suppression ability. The results from this experimental investigation have been submitted to the FUEL journal and are currently under review. Following the results from the current study, he is going to further investigate the oxygenated fuel additives in the areas of Particle Size Distribution and combustion chemical species identification.

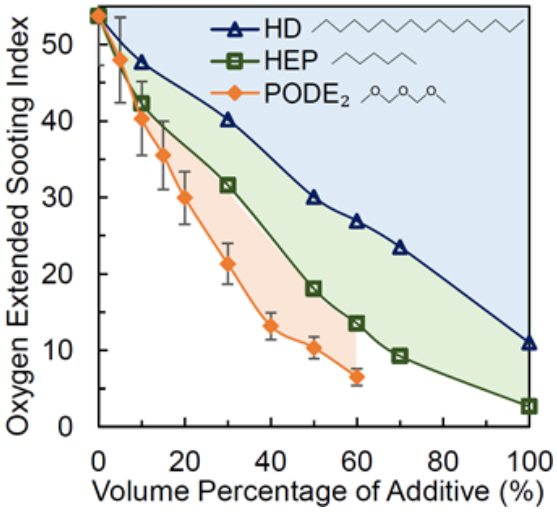


Fig. 3.3: OESI values for PODE2-Diesel and Heptane-Diesel blends versus volume percentage of fuel additive in the fuel mixture. The colour-shaded regions represent:

Dilution effect

Hydrocarbon chain effect

Oxygen content effect

Abbreviations:
HD = Hexadecane
HEP = Heptane
PODE = polyoxymethylene dimethyl ether.

Dr TAN
(RF, NUS)

Dr ZONG Yichen (RF, NUS) has been studying ultrafine particles (<100 nm) and fuel emissions in Singapore. Based on the results from the measurement campaign during the southwest monsoon in 2017, a database of particle number concentration and size distribution (PNSD) from emissions in Singapore has been successfully established. The particle size distribution is recorded at 1 Hz in the range from 5 nm to 1000 nm by a fast-response differential mobility spectrometer (DMS). The meteorological data including atmospheric pressure, air temperature, relative humidity (RH), rainfall, solar irradiance, wind speed, and wind direction have also been merged in the database. From the observation, the source apportionment on PNSD is performed for the first time in the region. Major emission sources have been detected as traffic exhausts, power plants and industry, and local nucleation events. The conditional probability function (CPF) analysis further indicates that the cross-border airborne pollutants could be significant during the monsoon season. Reports on diurnal variation and new particle formation of PM emissions in Singapore are being prepared at the moment. On the other hand, the lab-scale emission research based on laser diagnostics system has also been established during the reporting period. A comprehensive test has been performed on both new pump laser and dye laser. Diagnostic techniques like laser induced fluorescence (LIF), laser induced incandescence (LII), Rayleigh scattering and 2-colour pyrometry have also been performed on a well-defined burner. Fig. 3.4 shows the OH radical distribution in a xylene flame which reveals the location where radical reactions occur during the combustion process.

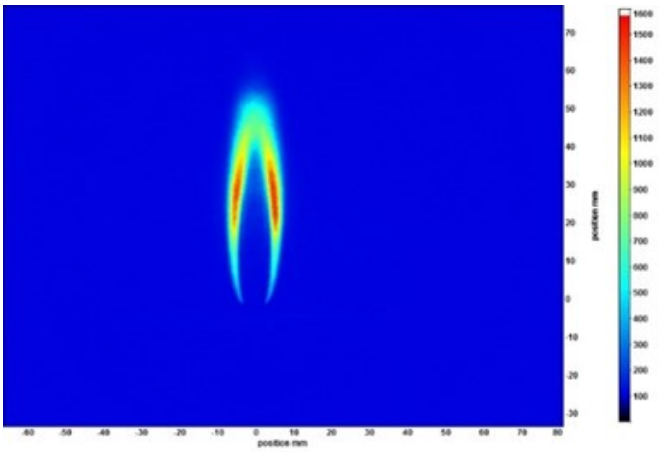


Fig. 3.4: OH radical distribution in a xylene flame from LIF diagnostics.

Drs ZONG and BOTERO
(RF, NUS)

Dr Jochen DREYER's (RF, CAM) work aims at elucidating the fundamental processes leading to soot formation during hydrocarbon combustion in flames and also other flame-made nanoparticles for applications in catalysis and sensing. He recently studied the influence of aromatic fuels (toluene) on the soot particle size distribution and number density inside a co-flow diffusion flame. Toluene is shown to increase the amount of soot precursor species and leads to earlier soot nucleation (see yellow luminescent zone in Fig. 3.5). The earlier nucleation increases the time for soot particle growth prior oxidation and elongates the visible flame height. This study has been submitted for publication. Besides the ongoing flame characterisation, new experimental techniques were developed. One example is a thermophoretic particle collector to deposit soot on different substrates. Another one is a flame pyrometry method to optically determine soot temperatures and volume fractions. This is achieved by taking digital images of the flame, splitting the red, green and blue colour channels (Fig. 3.6a) and reconstructing the cross-section of the cylindrical flame from its projection using the inverse Abel transform. The colour ratios of the flame cross-section (e.g., red/blue, R/B in Fig. 3.6b) is characteristic of the soot temperature. It is also possible to image the CH• radicals present in the flame using special filter optics (Fig. 6b). Dr Maurin SALAMANCA (RF, CAM) recently joined to support these ongoing experimental efforts.

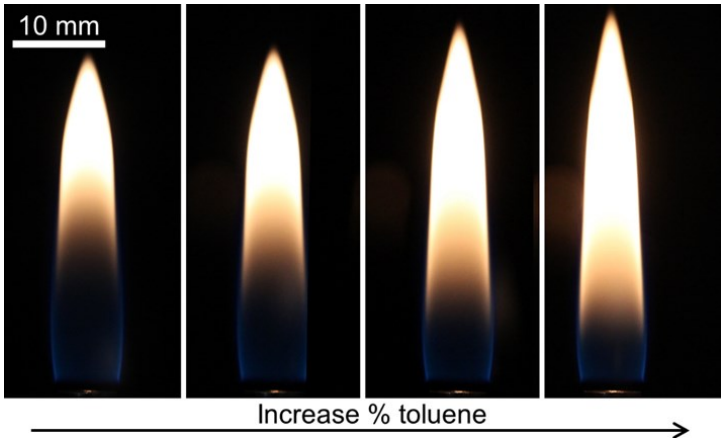


Fig. 3.5: Images of co-flow diffusion flames containing increasing concentrations of toluene. The luminescent zone moves closer towards the burner outlet with increasing toluene content, indicating earlier soot nucleation. The particles grow to larger sizes and take longer to oxidise, causing the visible flame height to increase.

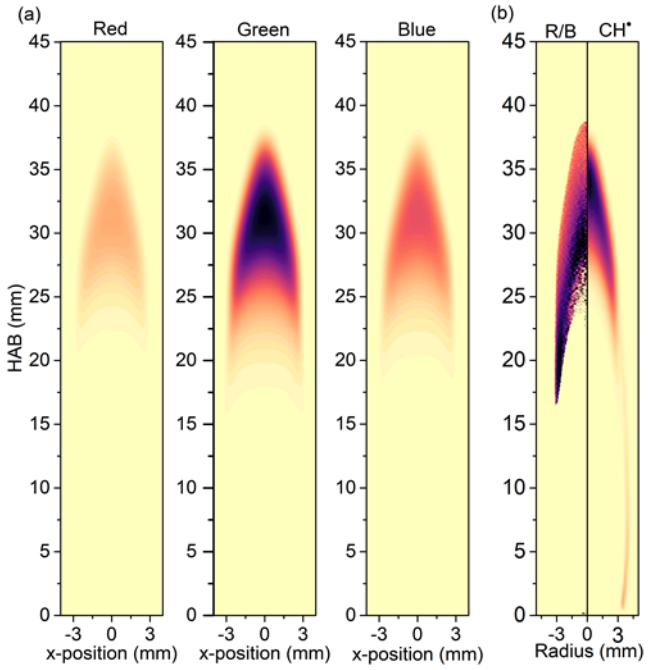


Fig. 3.6: (a) Red green, and blue channels of a digital colour image taken from a co-flow diffusion flame. (b) Reconstructing the cross section of the flame using the inverse Abel transform and taking the red/blue colour ratio enables the calculation of the soot temperature. Special optical filters can be used to image CH• radicals inside the flame.

Figs. 3.5 and 3.6
Dr DREYER
(RF, CAM)

WU Shaohua (PhD student, NUS) has continued his work on developing a mathematical tool to help better understand the soot formation and oxidation process in flames so that better combustion strategies can be proposed to reduce the emission of soot. His research is based on using the method of moments to solve the population balance equations, which describe the soot particle dynamics. Previously, he developed an approximation method called the Moment Projection Method (MPM) to close the moment equations. This method has been implemented into a diesel engine code and flame code to help predict the soot emissions from diesel engines and flames, respectively. Recently, Shaohua has extended his moment projection method into a bivariate one to allow two -variable particle descriptions. A paper on this has been written and will be submitted shortly. In addition, a maximum entropy method has been adopted to generate the soot particle size distribution based on the obtained moments. Furthermore, a new fragmentation kernel function has been proposed to better predict the soot oxidation process and this has been evaluated on a two-stage premixed flame burner system. This new soot model predicts well the soot mass and number along the flame height. A paper based on this has been submitted to the Combustion Symposium.

Angiras MENON's (PhD student, CAM) research project involves using computational chemistry tools, particularly density functional theory, to study the formation and nanostructure of carbonaceous nanoparticles, mainly soot, formed in flames and engines. He is also interested in reaction kinetics, molecular dynamics, and optimisation techniques as applied to combustion. Development has continued on new techniques to characterise the physiochemical properties of soot and probe the internal structure of these carbonaceous nanoparticles. In this project, accurate time-dependent density functional theory (TD-DFT) calculations have been used to compute the optical band gap (OBG) of several small polycyclic aromatic hydrocarbons (PAHs), molecules which are widely accepted to be the precursors of soot formation. The optical band gaps of a range of PAHs of different size and shape have been computed using accurate methods (Fig. 3.7). The aim of these calculations is to provide some new information on what PAHs are present during the formation of nascent soot, a crucial question in the combustion community. This work gave rise to more questions on the role of cross-linked (Fig. 3.8) and curved (Fig. 3.9) PAHs in soot formation and their properties. Work is ongoing on computing the rates of cross-linking reactions between different PAHs, as well as computing the spectral properties of these molecules. The computed OBGs were then compared to experimental UV-Visible spectroscopy measurements performed in collaboration with Dr Jochen DREYER (RF, CAM) to calibrate the calculations. Further calculations have been performed to accurately determine trends in OBGs for larger PAHs, as well as PAHs with more complex geometries, such as those which exhibit curvature

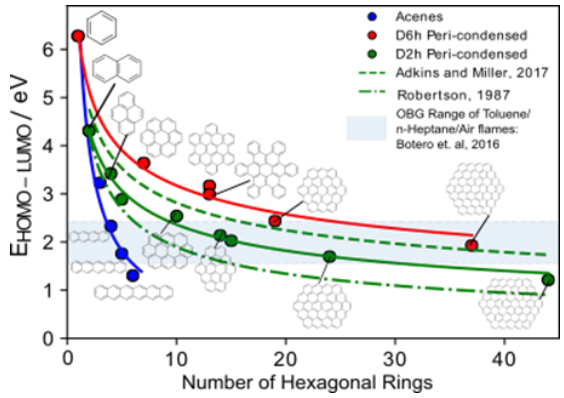


Fig. 3.7: Optical Band Gap (OBG) of various polycyclic Aromatic Hydrocarbons (PAHs) as function of shape and number of rings .

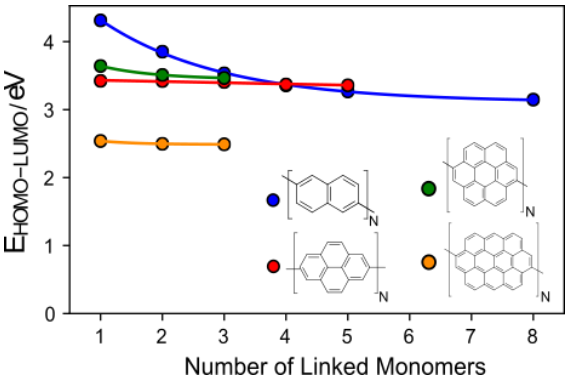


Fig. 3.8: Optical Band Gap (OBG) of various cross-linked Polycyclic Aromatic Hydrocarbons (PAHs) as function of monomer type and number of monomers.

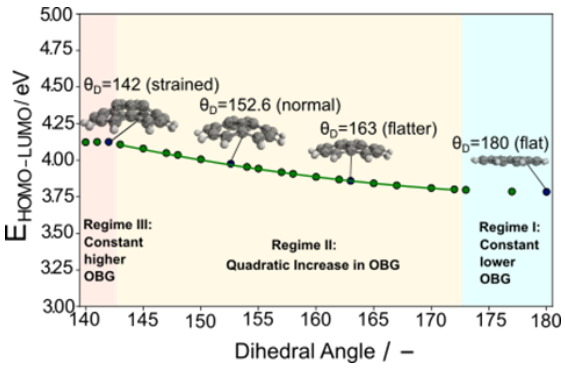
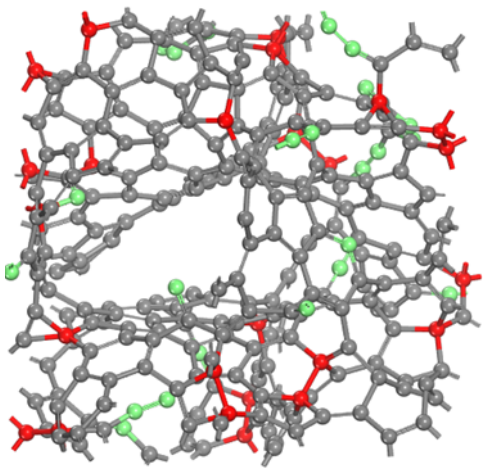


Fig. 3.9: Optical Band Gap (OBG) of corannulene – a curved Polycyclic Aromatic Hydrocarbon (PAH) – as function of curvature.

Figs. 3.7-3.9
Angiras MENON
(PhD student, CAM)

and cross-linking features. This work has been submitted for publication and future work will include comparison to experimentally measured OBGs in real flames. In another project, the dipole-dipole and quadrupole-quadrupole polarisabilities of PAHs are being investigated using DFT. These calculations will enable the prediction of the spectral properties of PAHs, such as the Stokes Shift and other scattering properties. These will help interpret measurements on soot formation in both engines and flames.

Prof. John ROBERTSON (Co-PI, CAM) has constructed a network model of amorphous graphitic carbon nitride. Graphitic carbon nitride (g-C_3N_4) or g-CN_x is of interest as a catalyst for solar water splitting because of its suitable band gap and electron affinity values. However, g-CN_x can suffer from low carrier mobilities due to the localisation of its band edge states by disorder. To test this possibility, we have built a random network model of g-CN_x. Our first attempts to do this using density functional (DF) molecular dynamics (MD) produced a 90 atom model for a density of 1.5 g/cm^3. However, it had too much disorder with too many badly coordinated atoms. The locally graphitic structure could not complete its local curvature to tie up bonding. A much larger network was needed. A 300 atom network was created by DF MD, as shown in Fig. 3.10. It has mainly sp^2 bonding, consistent with its low density, and mostly 6-fold bond rings. But it does have many non 6-fold rings. This network was first converted into a network of sp^2 a-BN by replacing alternate C atoms by B or N. The objective was to minimise the number of B-B or N-N bonds, by favouring 6-fold rings. The final stage was to convert this a-BN network into a g-C_3N_4 model with local melan groups by converting the B atoms into C, and deleting 25% of the C atoms to give the correct composition, as shown in Fig. 3.11. Next steps include calculating its electronic structure.



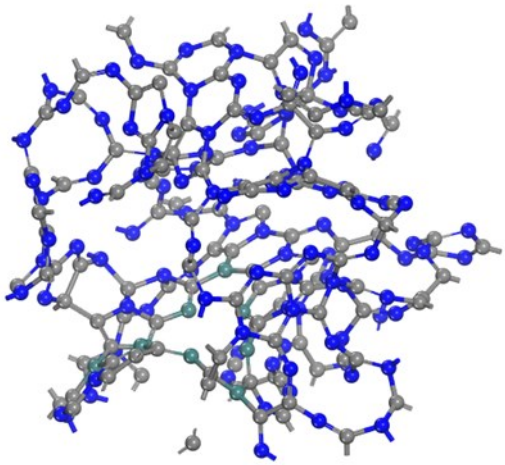


Fig. 3.10 (left): Network model of graphitic carbon nitride of density 1.5g/cm^3. Grey = sp^2, green = sp^1, red = sp^3 .

Fig. 3.11 (right): Network model of amorphous graphitic carbon nitride (a-CN_x). Blue = N, grey = C.

Figs. 3.10 and 3.11 Prof. ROBERTSON (Co-PI, CAM)

Jacob MARTIN (PhD student, CAM) has been performing calculations on the self-assembly of soot nanoparticles and other carbon materials in flames using quantum chemistry and molecular dynamics. In particular, he has been looking at the impact of curved aromatic molecules. A paper was published on the electric polarisation due to curvature in graphene molecules in the Journal of Physical Chemistry C. The magnitude of the electric field and origin of the molecular dipole was determined. He is currently collaborating with researchers in the UK and France to integrate the molecular dipoles into a force-field that will allow molecular dynamics simulations to be performed to discover how curved aromatics self-assemble into soot nanoparticles. He has submitted a follow-up paper that considers how curvature is integrated into graphitic molecules as they grow. Binding energies of curved aromatics were compared with planar molecules and a similar binding energy was found for 1-3 pentagonal rings integrated with greater curvature leading to a significant decrease in binding energy. Reactive molecular dynamics simulations have been performed on planar aromatic molecules to determine the mechanical properties of soot particles. Comparison with nanoindentation indicates that each aromatic is cross-linked with at least one or two other molecules which has im-

portant implications for how easily they are broken down with oxygen. In addition, a paper has been submitted on the nanoscale structure of a possible carbon sink – charcoal. Extending the work previously done on the carbonisation of fullerenes, charcoal, formed from the heat treatment of wood, was analysed using mass spectrometry, high-resolution electron microscopy and Raman spectroscopy (Fig. 12). We were able to show a similar nanostructure to that of heat-treated fullerene soot and that there are significant amounts of curved closed graphene structures in charcoal. This nanoscale model has important implications for the use of charcoal as a carbon capture technology as it reveals the origin of the oxidation resistance of charcoal and potentially how to improve it.

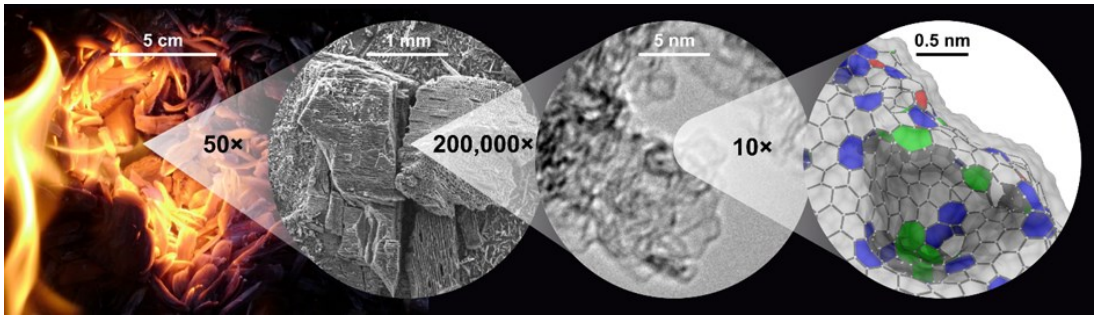


Fig. 3.12: The structure of charcoal at various length scales — from the macroscale to the nanoscale.

Jacob MARTIN (PhD student, CAM)

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

Dr SHENG Yuan's (RF, NTU) research in the past six months has been focused mainly on the applications of flame-synthesised transition metal oxides in water splitting and CO_2-utilisation. In his previous work about flame-synthesised Co_3O_4 and $Fe_xCo_{3-x}O_4$ nanoparticles and films for water splitting, now published on ACS Applied Energy Materials, it was found that poor electrical conductivity of the metal oxides limits their performance in the oxygen evolution reaction (OER). Therefore more efforts have been directed to the synthesis of Co/Fe oxide-carbon nanocomposites for enhanced conductivity which was achieved in rich flames where soot forms concurrently with metal oxides. Increased metal dispersion due to co-formation of soot has been observed, with the size of metal oxide particles reduced from about 5 nm to 2-3 nm. However, these nanocomposites did not present an advantage over the pure $Co_3O_4/Fe_xCo_{3-x}O_4$ in terms of OER performance, most likely due to blocking of exposed metal oxide surface and/or low electrical conductivity of soot. On the other hand, a few cobalt oxide-soot nanocomposites have exhibited significant activity in the oxygen reduction reaction (ORR), with a half-wave potential of 675 mV versus reversible hydrogen electrode and a four-electron ORR mechanism (0.1 M KOH, 1600 rpm, 0.15 mg/cm^2 catalyst loading). Further research is ongoing on the tuning of flame condition and the use of post-synthesis heat treatment to improve the accessibility of active sites in the nanocomposites. Dr Sheng is also involved in the CARES-BEARS intra-CREATE project on electrochemical reduction of CO_2. For this he has synthesised pure CuO nanoparticles using the current flame-synthesis apparatus and carried out preliminary experiments on their CO_2 reduction activity. To realise the production of more complex nanocatalysts by flame synthesis, he has been working with Drs Jochen DREYER (RF, CAM) and Maria BOTERO (RF, NUS) on the design of new burners that would allow accurate control of the composition of multi-metal oxides and sequential deposition of different catalyst films. In addition, he has published a review article on the applications of flame-synthesised nanocatalysts where photocatalysis and electrocatalysis were identified as fields with great unexplored opportunities.

WU Shuyang (PhD student, NTU) has been working on the flame-synthesis of nanoparticles for energy applications – as a sustainable way to produce renewable energy to substitute traditional fossil fuels, for example to utilise solar energy to convert CO_2 to CO, methanol or ethanol. Flame synthesis of nanoparticles is a continuous one-step synthesis process with high throughput and less waste compared to traditional wet chemistry methods. It can produce uniform, small-sized nanoparticles with high specific surface area at a fast rate (up to several g/h in a lab-scale burner). The particles require no further processing and can be directly used as photocatalyst after synthesis. Due to these

favourable properties, flame synthesis is a promising method for industrial production of nanoparticles. Over the last six months, Shuyang's research was mainly focussed on the flame synthesis of carbon materials for electrochemical production of hydrogen peroxide. The flame-made carbon materials are considered efficient electrocatalysts for H_2O_2 production. Hydrogen peroxide is one of the 100 most important chemicals in the world. It has wide applications in our life and industry. Therefore, continuous research on improving the electrochemical synthesis of hydrogen peroxide is carried out, but electrocatalysts still suffer from high costs, limited selectivity or low activity. In our experiment, the mesoporous N-doped carbon catalyst is produced by a facile one-step combustion method. The catalyst was prepared by burning pyridine through our wick burner at CREATE. Around 15ml pyridine was injected into the burner. Pyridine was driven to the top of the wick by capillarity and then ignited. Due to the insufficient combustion, carbon was formed and collected by a coverslip which was placed at 5 cm above the flame.

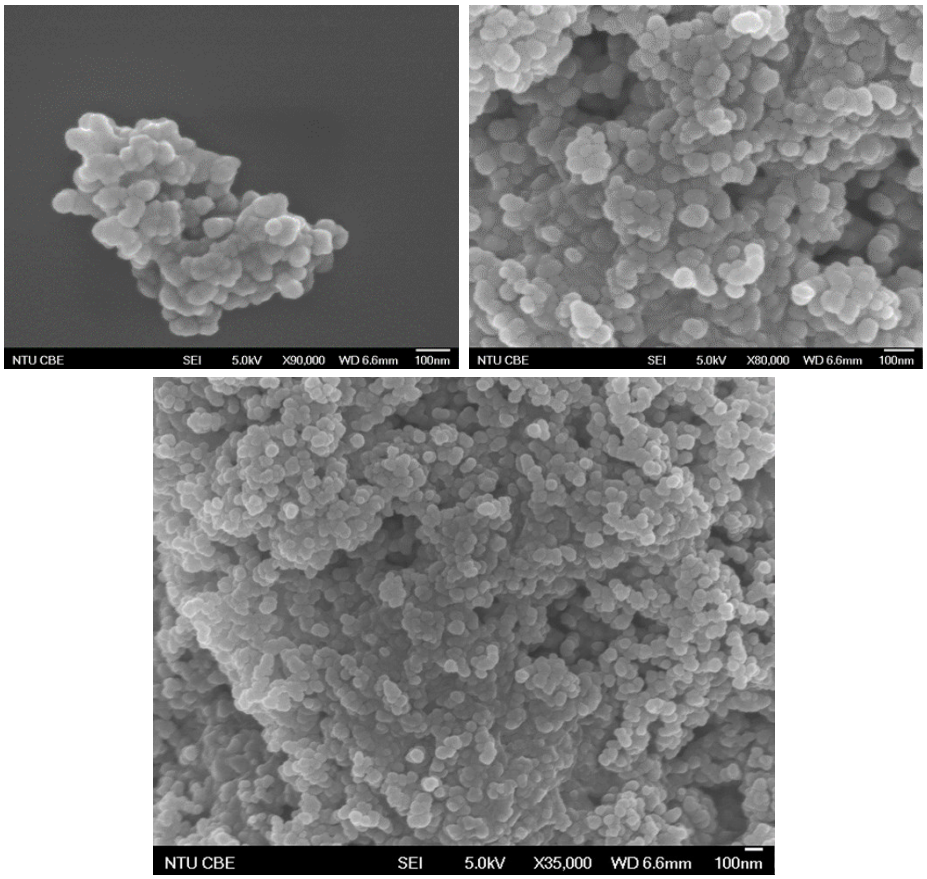


Fig. 3.13: FESEM images of N-doped carbon. The average diameter of N-doped carbon is around 40-50 nm. The particle size is small and uniform. Large specific surface area can promote the electrochemical reaction.

The produced nanoparticles are then characterised using various techniques. Measured data includes photoelectrochemical properties such as photocurrent and EIS spectra, TEM analysis of Pt nanoparticles loaded on different kinds of samples and transient PL spectra to investigate the separation efficiency of electron-hole pairs. FESEM and TEM images are shown in Figs. 3.13 and 3.14. A Raman spectrum, confirming successful nitrogen-doping, is shown in Fig. 15. The electrocatalytic activity of the catalyst in the oxygen reduction reaction was evaluated by means of rotating disc electrode (RDE) linear sweep voltammetry (LSV). The goal of this experiment is to obtain the electrocatalyst that has high selectivity toward the 2-electron reduction of O_2 to H_2O_2 and to avoid further electrochemical reduction of H_2O_2 to H_2O by another 2-electron reduction. This is different from the process when using Pt/C, which is a 4-electron transfer process.

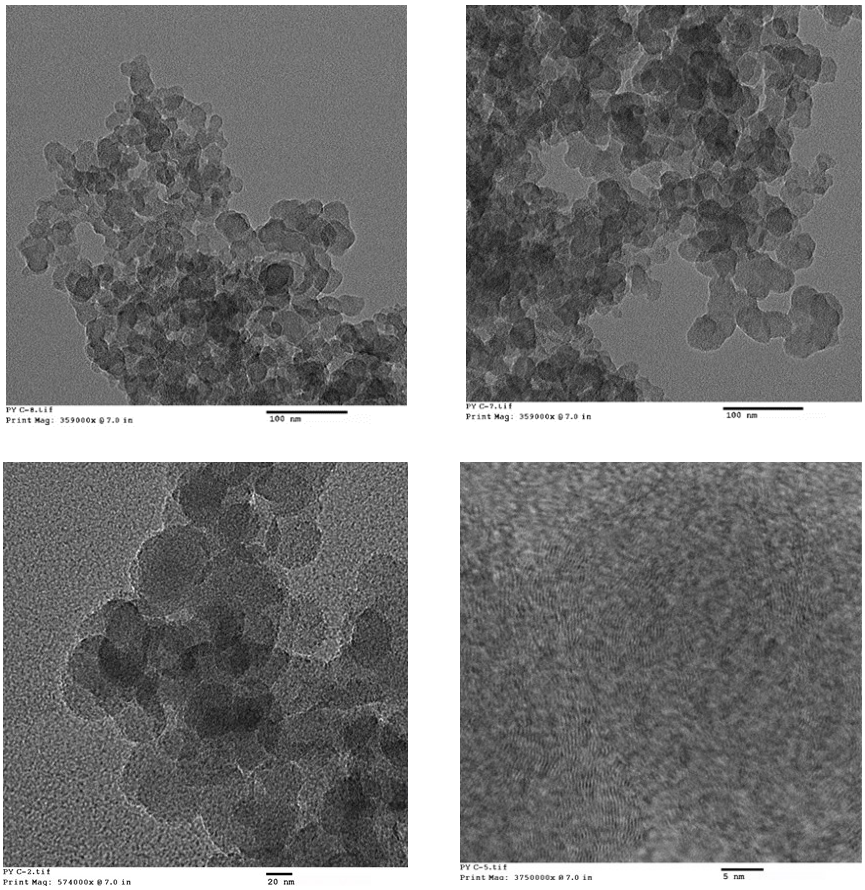


Fig. 3.14: TEM images of N-doped carbon.

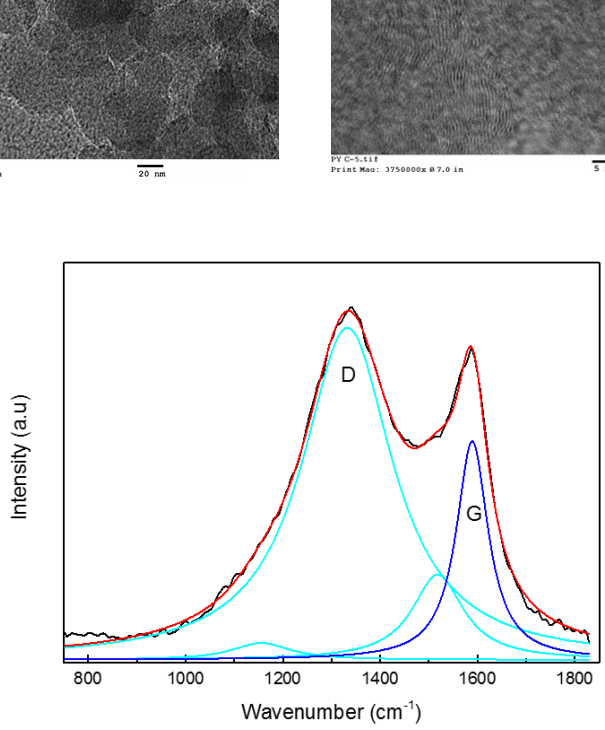


Fig. 3.15: Raman spectrometry. The G band peak at 1580/cm is the signal for high ordered graphite. For disordered carbons, additional bands induced by the defects in the microcrystalline lattices will appear. The D band at 1350/cm is due to in-plane defects and heteroatoms doped. This is caused by the doping of nitrogen.

Results of such measurements for an alkaline environment are shown in Fig. 16. The first platform between 0.3V and 0.6V corresponds to two-electron transfer, of which the product is H_2O_2. When the potential is increased further, the reaction will move to four-electron transfer. To investigate the kinetic reaction mechanism of the electron process, we use the Koutecky–Levich (KL) plot which was obtained from the polarisation curves at various rotation speeds to determine the number of electron transferred. The number of the electron transferred is measured to be 2.3-2.4, which belongs to two-electron transfer. The product of this reaction in 0.1M KOH is H_2O_2. This result is comparable to the literature.

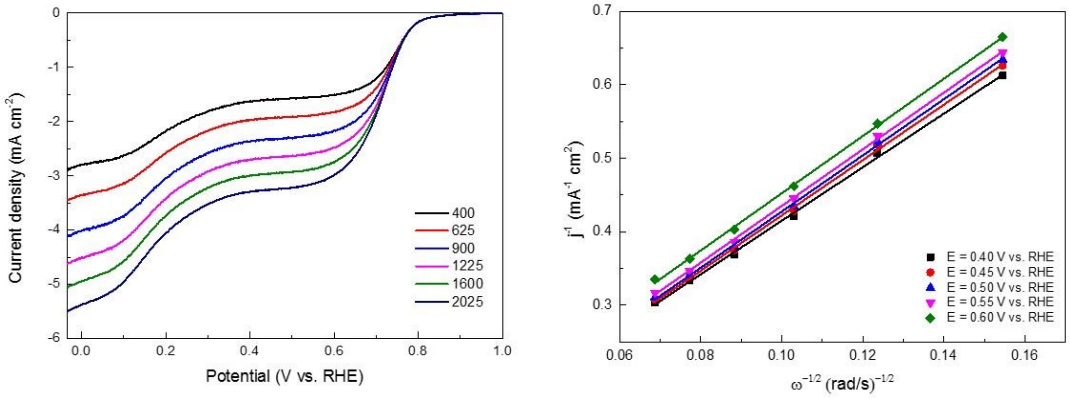


Fig. 3.16: ORR in O_2-saturated 0.1 M KOH solution. Left: LSV on rotating disk electrode at different rotation speeds from 400 to 2025 rpm and a scan rate of 5 mV/s. Right: Koutecky–Levich (KL) plot to determine the number of electrons transferred.

Analogously, in an acidic environment (Fig. 3.17), the number of the electron transferred is measured to be around 3.0. This process may be the combination of two-electron transfer and four-electron transfer. The selectivity for this reaction in acidic conditions is not as good as in basic solution. H_2O_2 production in acidic solution is more challenging than in alkaline solution.

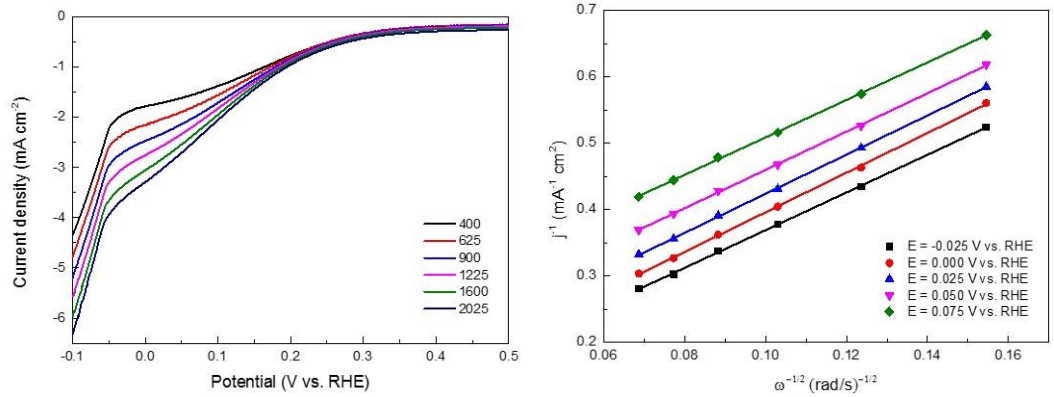


Fig. 3.17: ORR in O_2-saturated 0.1 M $HClO_4$ solution. Left: LSV on rotating disk electrode at different rotation speeds from 400 to 2025 rpm at a scan rate of 5 mV/s. Right: Koutecky–Levich (KL) plot to determine the number of electrons transferred.

Figs. 3.13-3.17
WU Shuyang
(PhD student, NTU)

In summary, the results in alkaline environments are promising. The size of the nanoparticles is small and uniform, which ensures a large specific surface area and a sufficient density of active sites. The number of electrons transferred is measured to be 2.3-2.4 in alkaline solution, which indicates two-electron transfer, leading to the production of hydrogen peroxide rather than water. The current results suggest that an alkaline environment is more beneficial for H_2O_2 production. The carbon nanoparticles exhibit excellent performance and selectivity on the synthesis of H_2O_2 in the alkaline environment.

Astrid BOJE's (PhD student, CAM) research is focused on modelling industrial titanium dioxide (titania) synthesis using detailed population balance models. She has developed a model for reactor and cooler units used for industrial titania synthesis, using a network of ideal reactors to simplify treatment of the flow behaviour and a detailed population balance model to focus on the shape and structure of the pigmentary product. She has presented this to our industrial sponsors Venator (formerly Huntsman) on several occasions. She has recently been working on resolving numerical issues encountered when using particle population balance modelling techniques to study industrial synthesis conditions, such as high concentrations and temperature, and ways to mitigate these using statistically weighted particle methods.

Casper LINDBERG (PhD student, CAM) is developing a detailed population balance model for flame synthesised nanoparticles to simulate the complex aggregate morphology and crystal phase of titanium dioxide. In collaboration with Manoel MANUPUTTY (PhD student, CAM), he has developed a two-step simulation methodology for modelling the stagnation flame synthesis of titanium dioxide nanoparticles from titanium tetraisopropoxide (TTIP) precursor. In the first step, the method combines a detailed kinetic decomposition mechanism for TTIP with a one-dimensional stagnation flow

model and method of moments with interpolative closure. The resulting gas-phase profile is post-processed using a detailed stochastic population balance model to resolve the aggregate morphology. This methodology facilitates simulation of quantities that are directly comparable to experimental observations; for example, primary particle size distributions and aggregate projected area distributions obtained from Transmission Electron Microscopy (TEM) images. The method is currently being used to model experiments performed in the CARES laboratory. His research is focused on investigating the flame synthesis of titanium dioxide nanoparticles using detailed population balance models. He is interested in developing a particle model that captures detailed morphological information of particles.

Manoel MANUPUTTY's (PhD student, CAM) research focuses on modelling and experimental characterisation of titania (TiO_2) particles synthesised in flames. Previously he has worked on developing a moment-based model of TiO_2 formation in a one-dimensional flame simulation. Recently this model has been post-processed with a detailed population balance model in collaboration with Casper LINDBERG (PhD student, CAM) to simulate the complex particle morphology and produce TEM-like images. The TEM-like images have been compared against experimental TEM images collected in the CARES laboratory to provide unprecedented insights into the early-stage nanoparticle formation. The work was submitted to the Proceedings of the Combustion Institute. Further experimental work includes, jointly with Dr Maria BOTERO (RF, NUS), developing characterisation techniques for TiO_2 nanoparticles prepared in flame synthesis, namely measuring particle mobility size distributions with a Differential Mobility Spectrometer (DMS), as well as investigating morphology and nanostructure using X-Ray Diffraction (XRD). Studies employing the latter have revealed the presence of a previously unreported polymorph, TiO_2-II. These experimental studies will be accompanied by development of particle models which include a phase transformation model to improve our understanding of the complex processes involved in TiO_2 nanoparticle formation.

WP 3.4: Modelling and optimisation of unit operations

Aravind DEVANAND (PhD student, NUS) has extended our world power plant database, that is, an ontological knowledge base containing information about the power generation facilities in the world. The knowledge base can be visualised on Google maps and is now available online on the J-Park Simulator website. He also has implemented a nuclear power plant model into the JPS. He applied an algorithm capable of finding optimal locations for modular nuclear power plants within the JPS. It requests input from the user, solves an optimisation problem in the background, and visualises the results on the JPS website. Furthermore, he has published a paper on some of the methodologies behind the JPS. It explains how the ontology-based cyber-infrastructure is used to store this information in a structured and machine-readable form, and how the knowledge bases are then utilised to conduct case studies. Currently, he is working on implementing an ontology-based market model into the JPS. The framework utilises a multi-agent system for the trading of commodities within an eco-industrial park.

VO Chi Hung (PhD student, NUS) has continued his work on the construction and utilisation of metabolic models for the methanogen *M. maripaludis S2*, an organism which can capture CO_2 and produce methane. He is currently working on the cultivation of this methanogen before analysing metabolic data. Since the organism is an anaerobe, he has spent the last six months setting up and refining a gas system to facilitate the removal of oxygen gas from the system. Several parameters were investigated, including gas flow, temperature and chemical concentrations. Knowledge gained from the study of this organism will allow genetic modification to enhance its capabilities for CO_2 capture. A promising application is the use of a bioreactor to convert CO_2 into useful fuels or other organic products.

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

Sushant GARUD's (PhD student, NUS) has continued his research on the design and analysis of computer experiments for the parameterisation of complex systems. He has published his third paper on an evaluation of a smart sampling algorithm (SSA) for multidimensional surrogate modelling in Computers & Chemical Engineering. He also made significant progress investigating a surrogate guidance scheme – a learning-based evolutionary paradigm for surrogate selection, which will be published later this year. Additionally, as part of ongoing development of the J-Park Simulator, he has created time-series models for various sensors in a Building Management System (BMS). He also worked on an industrial project where he developed a model for a reverse osmosis (RO) membrane used for water purification.

Other Activities and Achievements

- Dr LIM Mei Qi (Project Officer, NTU) prepared and coordinated presentations of the J-Park Simulator to Shell's Projects & Technology Director and to the Singapore Public Utilities Board.
- Astrid BOJE (PhD student, CAM) presented progress on her titania work to our industrial partner Venator (formerly Huntsman), which funds part of her PhD, on 26 January 2018 in Cambridge.
- Pulkit CHHABRA (PhD student, NTU) will give an oral presentation of his work at the 28th European Symposium on Computer-Aided Process Engineering (ESCAPE) in Graz, Austria in June 2018.
- Aravind DEVANAND (PhD student, NUS) will give an oral presentation on his research at the Process Systems Engineering (PSE 2018) conference to be held in San Diego, USA in July 2018.
- Sushant GARUD (PhD student, NUS) presented his work to broad audiences from the chemical engineering community at the WCCE-10 conference in Barcelona, Spain in October 2017 and the ESMOC-2017 conference in Durgapur, India in December 2017.
- Jacob MARTIN (PhD student, CAM) visited International Community School, Singapore, to give a science demonstration. Jacob inspired the primary school children about science, the states of matter and mitigating climate change.

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.

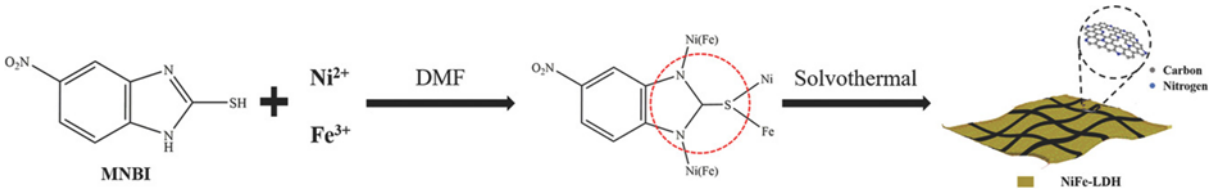
A Highly Efficient Oxygen Evolution Catalyst Consisting of Interconnected Nickel–Iron-Layered Double Hydroxide and Carbon Nanodomains

Shengming Yin, Wenguang Tu, Yuan Sheng, Yonghua Du, Markus Kraft, Armando Borgna and Rong Xu

DOI: 10.1002/adma.201705106

Abstract:

In this work, a one-pot solution method for direct synthesis of interconnected ultrafine amorphous NiFe-layered double hydroxide (NiFe-LDH) (<5 nm) and nanocarbon using the molecular precursor of metal and carbon sources is presented for the first time. During the solvothermal synthesis of NiFe-LDH, the organic ligand decomposes and transforms to amorphous carbon with graphitic nanodomains by catalytic effect of Fe. The confined growth of both NiFe-LDH and carbon in one single sheet results in fully integrated amorphous NiFe-LDH/C nanohybrid, allowing the harness of the high intrinsic activity of NiFe-LDH due to (i) amorphous and distorted LDH structure, (ii) enhanced active surface area, and (iii) strong coupling between the active phase and carbon. As such, the resultant NiFe-LDH/C exhibits superior activity and stability. Different from postdeposition or electrostatic self-assembly process for the formation of LDH/C composite, this method offers one new opportunity to fabricate high-performance oxygen evolution reaction and possibly other catalysts.



The Polarization of Polycyclic Aromatic Hydrocarbons Curved by Pentagon Incorporation: The Role of the Flexoelectric Dipole

Jacob W. Martin, Radomir I. Slavchov, Edward K. Y. Yapp, Jethro Akroyd, Sebastian Mosbach and Markus Kraft

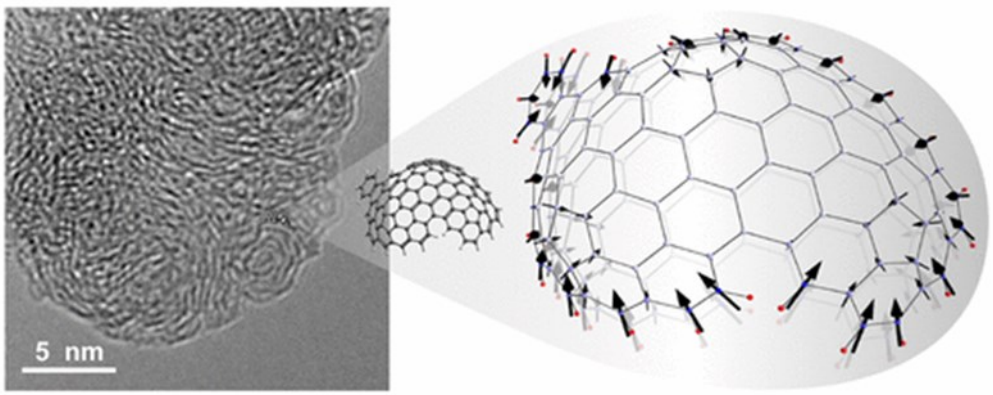
DOI: 10.1021/acs.jpcc.7b09044

Highlights:

- The dipole moment was calculated for a range of curved polycyclic aromatic hydrocarbons.
- The π-electronic flexoelectric effect is the main contributor to the dipole moment.
- Atom-centred point charge models of curved arenes are inadequate; point dipoles have to be accounted for.

Abstract:

Curvature in polyaromatic hydrocarbons (PAHs), due to pentagon integration, produces a dipole moment that contributes significantly to self-assembly processes and adsorption at the surface of carbon materials containing curved structures. This work presents electronic structure calculations of the dipole moment for 18 different curved PAH molecules for various numbers of pentagons and total number of aromatic rings. A significant dipole moment was found that depends strongly on the number of aromatic rings (4-6.5 debye for ring count 10-20). The main cause for the dipole is shown to be the π-electron flexoelectric effect. An atom-centred partial charge representation of the charge distribution in these molecules is insufficient to correctly describe their electrostatic potential; distributed multipoles were instead required.



Towards an Ontological Infrastructure for Chemical Process Simulation and Optimization in the Context of Eco-Industrial Parks

Li Zhou, Ming Pan, Janusz J. Sikorski, Sushant Garud, Leonardus K. Aditya, Martin J. Kleinelanghorst, Iftekhar A. Karimi and Markus Kraft

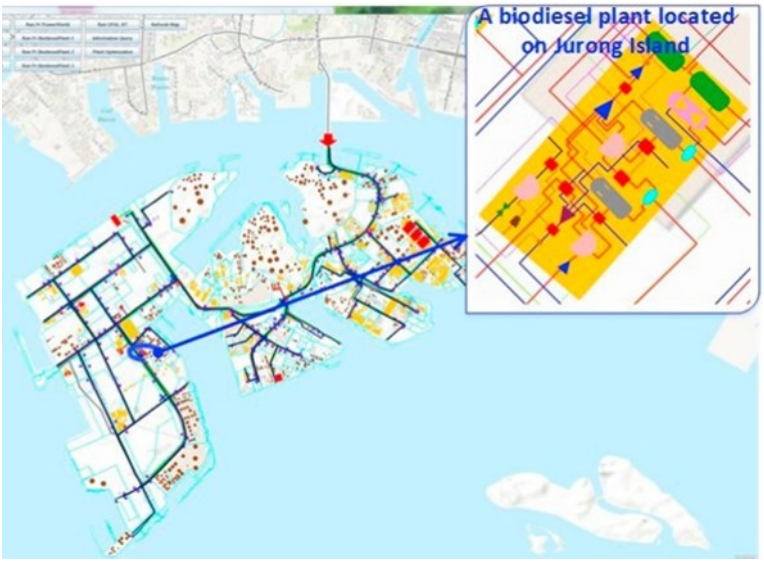
DOI: 10.1016/j.apenergy.2017.05.002

Highlights:

- The concept of constructing an expert system called JPS for EIPs is introduced.
- A biodiesel plant is implemented into the system as a first step.
- OntoCAPE is adapted to establish a knowledge base for the biodiesel plant.
- Plant-wide process simulation and optimisation can be carried out via JPS.
- Simple information query can be carried out based on the developed knowledge base.

Abstract:

In this paper, we introduce the concept of constructing an ontology-based decision support system called J-Park Simulator for the design and operation of eco-industrial parks. It is inspired by Jurong industrial park in Singapore. A biodiesel plant is implemented into the system as a first step. OntoCAPE is adapted for the purposes of the biodiesel plant to establish a knowledge base, which is employed to carry out a number of applications via J-Park Simulator. Firstly, information query can be performed. Information of the biodiesel plant can be extracted through natural language query. Secondly, J-Park Simulator can be used to carry out process simulation. New process equilibrium can be evaluated after certain operation parameters change. Thirdly, process optimisation can be realised through J-Park Simulator. Optimal operation condition under different market scenarios can be obtained for the biodiesel producing process in order to reduce the energy consumption and achieve maximal plant profit.



Incorporating Seller/Buyer Reputation-Based System in Blockchain-Enabled Emission Trading Application

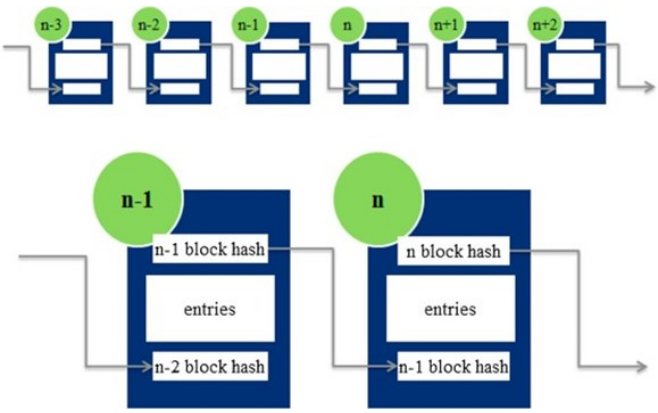
Khamila Nurul Khaqqi, Janusz J. Sikorski, Kunn Hadinoto and Markus Kraft

DOI: 10.1016/j.apenergy.2017.10.070

Highlights:

- A blockchain-enabled system is proposed for emissions trading application.
- The objective is to improve management and increase abatement investment.
- Financial incentive is used to motivate industry participants.
- Multi-criteria analysis emphasises the benefit of the system against established ETS.

Abstract:



Emission Trading Scheme (ETS) has dual aims to reduce emission production and stimulate adoption of long-term abatement technology. Whilst it has generally achieved its first aim, some issues are hindering the accomplishment of the second. Several solutions have been proposed to improve ETS's efficacy, yet none of them have considered the advancement of Industry 4.0. This paper proposes a novel ETS model customised for Industry 4.0 integration. It incorporates blockchain technology to address ETS's management and fraud issues whilst it utilises a reputation system in a new approach to improve ETS efficacy. Specific design of how the blockchain technology and reputation system are used to achieve these objectives is showed within this paper. The case study demonstrates the inner working of reputation-based trading system—in which reputation signifies participants' performance and commitment toward emission reduction efforts. Multi-criteria analysis is used to evaluate the proposed scheme against conventional ETS models. The result shows that the proposed model is a feasible scheme and that the benefits of its implementation will outweigh any drawbacks.

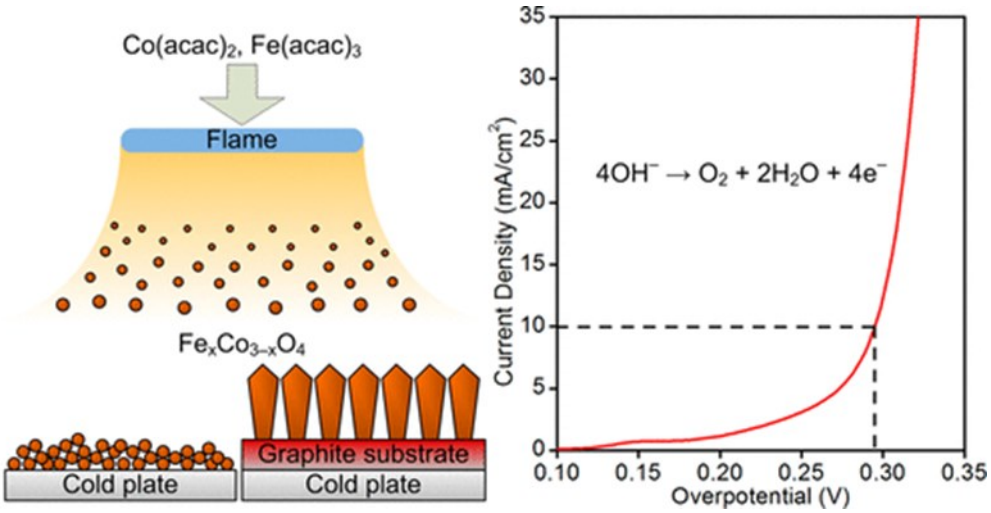
Co_3O_4 and $Fe_xCo_{3-x}O_4$ Nanoparticles/Films Synthesized in a Vapor-Fed Flame Aerosol Reactor for Oxygen Evolution

Yuan Sheng, Maria L. Botero, Manoel Y. Manuputty, Markus Kraft and Rong Xu

DOI: 10.1021/acsaem.7b00172

Abstract:

Synthesis of earth-abundant nanocatalysts for the oxygen evolution reaction (OER) has depended largely on highly diluted, batchwise wet chemical methods, leaving it a challenge to improve throughput and sustainability of the process. Herein, we demonstrate for the first time the production of Co_3O_4 and $Fe_xCo_{3-x}O_4$ nanoparticles using vapor-fed flame aerosol synthesis (VFAS), a continuous and scalable process requiring minimal waste treatment. In 1 M KOH, the catalysts exhibit stable OER overpotentials of 295 mV at 10 mA/cm^2 and Tafel slopes down to 38 mV/dec, which are comparable to the performances of wet-chemically derived benchmark (Fe-doped) Co_3O_4 catalysts. The high activity is attributed to ultrafine particle size of $\langle D_p \rangle$ = 3.1–4.4 nm and rich surface defects. Furthermore, nanostructured Co_3O_4 and $Fe_xCo_{3-x}O_4$ films can be conveniently grown on graphite substrates by VFAS and serve as OER electrodes without further treatment. Remarkably, the morphology of the films can be easily tuned from columnar to granular by varying precursor concentration in feed gas, achieving optimal utilization of catalytic materials with a hierarchical structure consisting of elongated nanoparticulate building blocks.



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

ICESO 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
Prof. Jan Maciejowski

University of Cambridge

PIs, IRP4

April 2018

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 optimisation, and in power network analysis. Resources available to IRP4 include two lab-scale microgrids (one at NTU and one at NUS), which include real and simulated renewable and traditional generators. We have also acquired a powerful real-time power system simulator.

IRP4 is addressing questions related to the 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. The heterogeneous structure of the power system, including the incorporation of microgrids as subsystems, is also 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 that 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 centralised and decentralised control structures being investigated.

The research vision is to work towards a new architecture of control, estimation and optimisation 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

Thuy VAN DANG (PhD student, NTU), supported by Prof. LING Keck Voon (PI, NTU) and Prof. Jan MACIEJOWSKI (PI, CAM), has continued his work on exploiting the structure that exists in many control problems when using the “Alternating Directions Method of Multipliers” (ADMM) to solve quadratic programming optimisation problems. This work is based on the observation that the (known) “reduced Hessian” method becomes very efficient if a banded basis of the null space of the Hessian exists. This is important for embedded implementations of model predictive controllers, especially when the hardware architecture restricts the use of floating-point arithmetic and fast solutions are required. A journal paper reporting this work is in the final stages of preparation.

It has recently been realised by Prof. LING Keck Voon (PI, NTU) that this work on exploiting the banded structure of the Hessian matrix also has a wider implication: it can be incorporated in many algorithms which need to solve the saddle-point-type system of linear equations, also known as the Karush–Kuhn–Tucker (KKT) system, which arise as first-order necessary conditions in constrained optimisation problems. Thus, in addition to its application to the ADMM algorithm, the work is also applicable to the very powerful "interior-point" methods, in which the key step is to repeatedly solve the saddle-point-type system.

Thuy and Prof. LING have also pursued work on "anytime control" algorithms for networked/embedded systems. This work has been (conditionally) accepted for journal publication.

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

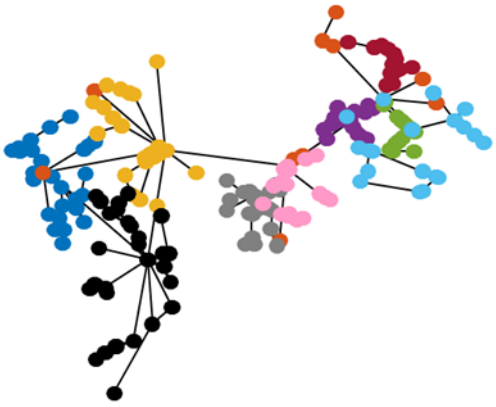
Dr Bhagyesh PATIL (RF, NTU), together with Prof. LING Keck Voon (PI, NTU) and Prof. Jan MACIEJOWSKI (PI, CAM), has continued his work on the study of efficient global optimisation algorithms and their use in Model Predictive Control applications. As previously reported, they have developed a fast Model Predictive Control approach based on Bernstein polynomials. In the last reporting period this approach was tested on the model of a power network containing highly nonlinear synchronous generators. A paper addressing the preliminary findings of this work was recently presented at the IEEE Conference on Decision and Control, Melbourne, Australia, in December 2017.

Dr PATIL is also developing a new approach, still based on Bernstein polynomials, which replaces general non-convex polynomial optimisation problems by convex quadratic-programming relaxations. Publication of this work is in preparation.

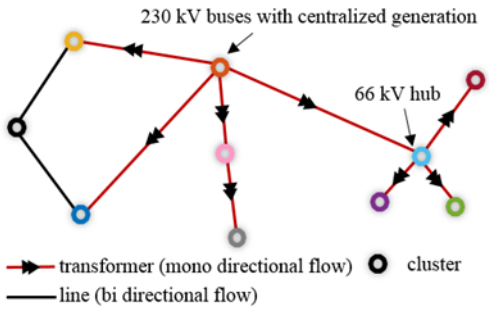
WP 4.3: Modelling and Control of heterogeneous power generation networks with chemical process loads

Dr Rémy RIGO-MARIANI (RF, NTU) reported on his investigation of optimisation methods for grid planning studies. The objective is to determine the best allocations of distributed resources in the electrical grid in order to reduce the CO_2 emissions related to power generation. Different types of assets are considered with solar generation, energy storage and small gas turbines as well as controllable loads. Several configurations in terms of sizes and sites of the resources are compared. In particular, fast computational times are allowed thanks to a linearisation of the lines losses as well as a zonal representation of the grid. Obtained results show that great CO_2 reductions are reached with the introduction of solar generation and small gas turbines. As for storage technologies, they should be mixed with other resources in order to have a significant impact. Other investigations lie on the scheduling of different co-generation units in order to supply both electrical and thermal

loads. The idea is to take advantage of those heterogeneous loads in order to operate the units closer to their maximum efficiency and while fulfilling a set of grid constraints. Dr RIGO-MARIANI has also been involved in research works to apply game theory concepts for distributed control in power systems. The objective is to implement different market mechanisms and estimate the impact of prices, taxes or incentives on the behaviours of customers and power generation companies. This work was reported in a journal paper published in *Energy Technology* (January 2018).



Jurong Island Power Grid – Nodal Representation



Jurong Island Power Grid – Zonal Representation

Fig. 4.1: Nodal and zonal representations of the Jurong Island power grid.

Dr RIGO-MARIANI (RF, NTU)

Dr Anthony TRAN (SRF, NTU) and Prof. Jan MACIEJOWSKI (PI, CAM) reported on work that has been done, together with Prof. LING Keck Voon (PI, NTU), on the use of the Quadratic Dissipation Constraint (QDC). A paper developing the underlying theoretical results has been submitted to the *International Journal of Robust and Nonlinear Control,* which is currently under review. An application of QDC to the "Automatic Generation Control" problem in a multi-area power system is currently being developed, for the case that fast communication between areas is not possible (i.e. a "decentralised" control architecture is assumed). A journal paper documenting this work is being prepared.

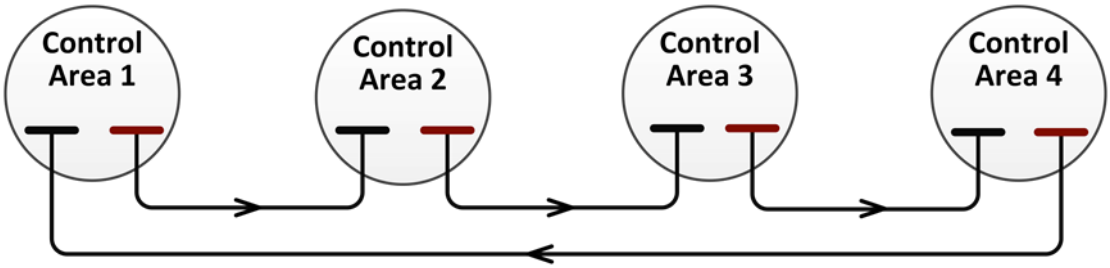


Fig. 4.2: Four loop areas.

Dr TRAN (SRF, NTU)

CHEN Tengpeng (PhD student, NTU), supported by Prof. LING Keck Voon (PI, NTU), reported that the paper "Distributed State Estimation Using Modified Partitioned Moving Horizon Strategy for Power Systems" has been published by the journal *Sensors*. In this paper, a distributed state estimation method based on the modified partitioned moving horizon estimation (mPMHE) is proposed for large-scale power system state estimation (PSSE) application. The power system is decomposed into several local areas with non-overlapping states. Instead of all measurements being sent to a control centre in a centralised approach, the measurements at each local area are sent to its local control centre so the communication load is alleviated. Under the scheme of the partitioned moving horizon estimation (PMHE) presented in literature, each local area solves a small optimisation problem to estimate its own local states by using the local measurements and the estimated results from its neighboring areas, so that the computation load becomes small. In contrast with PMHE, the error from the process model is ignored in mPMHE and the size of the optimisation problem arising from mPMHE is smaller than PMHE. Therefore, the computation time of mPMHE is less than that of PMHE. The trade-off is the estimated accuracy of mPMHE is a little lower than that of PMHE. One advantage of mPMHE is that constraints on states can still be taken into account during the optimisation process so the influence of the outliers can be further mitigated.

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

Dr Prakash Kumar RAY (RF, NTU) reported on his research which is focused on the detection and classification of power quality disturbances in microgrids and the biodiesel plant using advanced signal processing and pattern recognition techniques. For detecting power quality issues, he has applied techniques such as wavelet transform, wavelet packet and spectral kurtosis. For identifying power quality disturbances, he has used support vector machine and extreme learning machines based classifiers. These techniques are implemented and simulated in the MATLAB/Simulink environment for different operating scenarios. Further, to demonstrate the efficacy of the proposed techniques, simulations studies are carried out in real-time using the OPAL-RT simulator. He is also collaborating with Dr Eddy FOO (Co-PI, NTU) and Ashok KRISHNAN (PhD student, NTU) for simulating power quality issues in the biodiesel plant during variations in the chemical processes. In addition, he is also studying stability issues in microgrids and large bus power systems with the incorporation of power system stabiliser (PSS) and flexible AC transmission system (FACTS) such as static var compensator (SVC) and static synchronous compensator (STATCOM).

Gourab KARMAKAR (Research Intern, NTU) has been working on the detection of power quality issues in microgrids using advanced signal processing techniques under the guidance of Prof. GOOI Hoay Ben (Co-PI, NTU) and Dr Prakash Kumar RAY (RF, NTU). He has developed the electrical network model of an exemplar microgrid in MATLAB and e-MEGASIM in OPAL-RT. He is examining the transient behaviour and the power quality issues which arise when there is a load change in the microgrid. The power quality issues are detected in real time using OPAL-RT by applying signal processing techniques such as wavelet transform (WT) and dual tree complex wavelet transform (DTCWT).

Ashok Krishnan's (PhD student, NTU) main research interest lies in the optimal scheduling of multi-energy systems. Recently, he has been focusing on the coupled interactions between the electricity and heat networks in industrial parks. Specifically, he has been focusing on formulating optimisation problems for the planning and scheduling of multi-energy networks in industrial parks. In addition to heterogeneous energy generation sources, he considers electrical and heat distribution network constraints in his model. A detailed model of the combined cycle power plants is being used to integrate the heat and electricity networks in the optimisation scheduling and planning problems. He is currently exploring the possibility of integrating his model with the JPark Simulator. He has recently submitted three research manuscripts on microgrid/multi-energy system scheduling problems. Jointly with Dr Eddy FOO (Co-I, NTU) and Dr Prakash Kumar RAY (RF, NTU), he is also currently studying the power quality issues caused by production changes in the biodiesel plant. The real-time simulation capabilities of the OPAL-RT system are being used for this study. He is also currently mentoring an undergraduate final year project student in the development of an under frequency load shedding testbed utilising the OPAL-RT system.

Dr Joymala MOIRANGTHEM (RF, NUS) reported that as a local generator-based electrical network, a cluster of prosumer buildings has been considered that have facilities for their own photovoltaic generation, storage and flexible loads. Their synergistic operation to derive maximum benefit from the cluster would require a secondary control unit (SCU). The SCU would be a system containing various sub-systems to acquire or perform load forecasts, electricity price forecasts, power-flow calculations, demand side management, stability analysis, loss calculations, financial computations, environmental impact computations, and optimisations of certain objectives set by the system. It is important for the system to be fast enough to work in near real-time, serve multiple primary control units like a service, and be reliable in its computations since it would often lack the luxury to rerun the computations upon any failure or algorithms' non-convergence. Holomorphic Embedded Power Flow (HEPF) is used here for the power-flow, and its scope has increased since the electrical grid is undergoing a paradigm shift, as shown in Fig. 4.3.

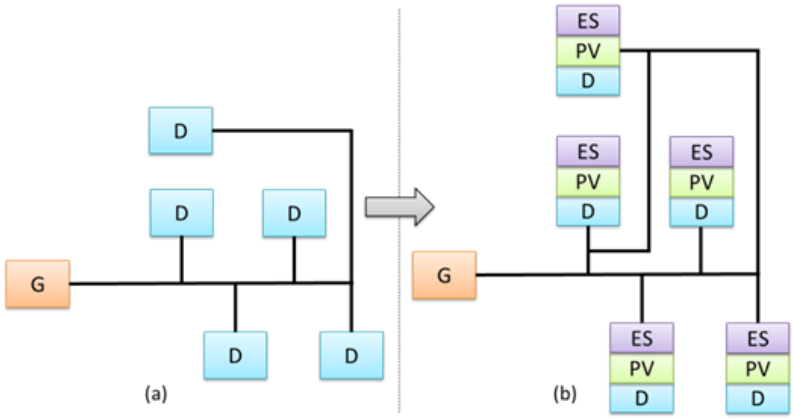


Fig. 4.3: The change in physical distribution system with centralised generation (a) G supplying demands D (b) This represents the transformed distribution system where local generation (like photovoltaic panels, PV) and energy storage ES can contribute to meeting the local load. The network is envisaged to be more meshed than radial in nature, allowing sharing of resources.

The HEPF has been proposed as a key enabler for the digitalised services that are possible in the changed paradigm. For optimising the various ad-hoc nonlinear objectives, an objective-function-agnostic design of optimisations for grid-management is used. The operation of such optimisation for the context of Optimal Power Flow (OPF) for microgrid of prosumers is performed using Differential Evolution (DE) and the results shown in Fig. 4.4 establish validity of the proposed system's operation.

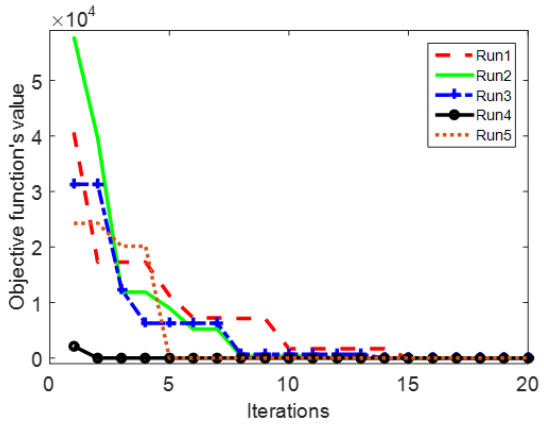


Fig. 4.4: The convergence property of the DE optimisation algorithm used in illustrated. Within a few steps a penalty-free solution is found, and a low-cost solution is achieved in a few more iterations.

A screenshot of the resultant power-flow on a geographical information system (GIS) platform is shown in Fig. 4.5.

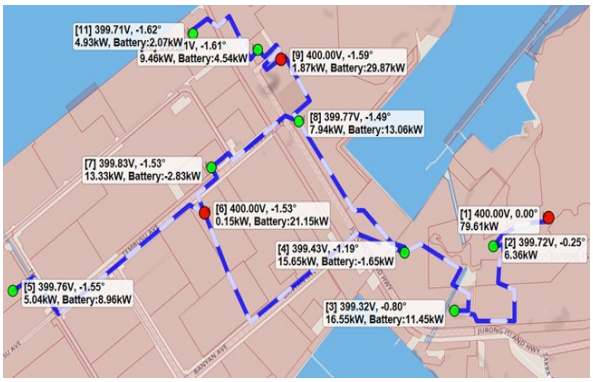


Fig. 4.5: This represents the power-flow based on the DE optimisation. It is noticeable that the nodes in the cluster which produce more than they consume for an interval are shown as red dots. The scope for adding real-time analytics and providing value for industrial applications would be significantly large.

Figs. 4.3-4.5
Dr MOIRANGTHEM
(RF, NUS)

Srinivasarao KAMALA (PhD student, NUS) reported on his study of small-signal stability analysis of a microgrid when subjected to small disturbances. He noted that if system oscillations are caused by small disturbances which can be suppressed such that the deviations of system state variables remain small for a long time, then the power system is stable. On the contrary, if the magnitude of oscillations continues to increase or is sustained indefinitely then the power system is unstable. Microgrid small-signal stability is affected by many factors, including initial operation conditions, types of sources in the system and characteristics of various loads (e.g. constant power loads). Due to lower inertia of microgrids compared to the traditional grid, it is prone to small signal instability. In the present research, impedance-based small signal stability analysis of the microgrid in the presence of constant power loads has been carried out.

- In the impedance-based stability analysis, the system is divided into source and load subsystems (as shown in Fig. 4.6) and the source, load impedances are evaluated using perturbation methods. Subsequently, the stability is checked using General Nyquist stability criteria (GNC) based on system impedance ratios.

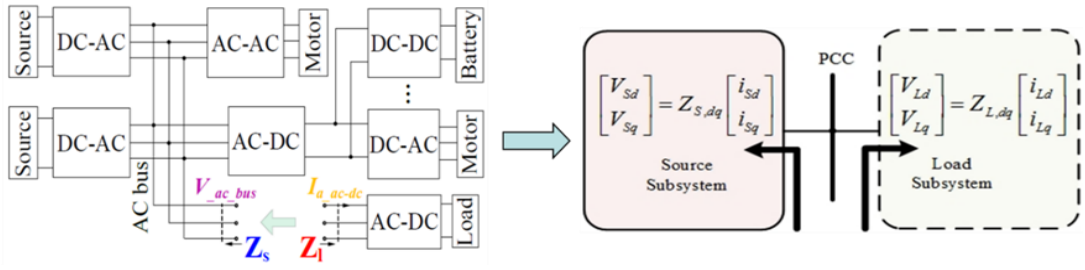


Fig. 4.6: Microgrid and its equivalent source and load sub systems.

- The system shown in Fig. 4.7 is considered for the stability study and the simulations are carried out in a MATLAB/Simulink platform. The motor drive system is connected through an active front end (AFE) rectifier (constant power load) from a 3-phase power supply. The source and load impedances are evaluated by the multi-tone shunt perturbation method.

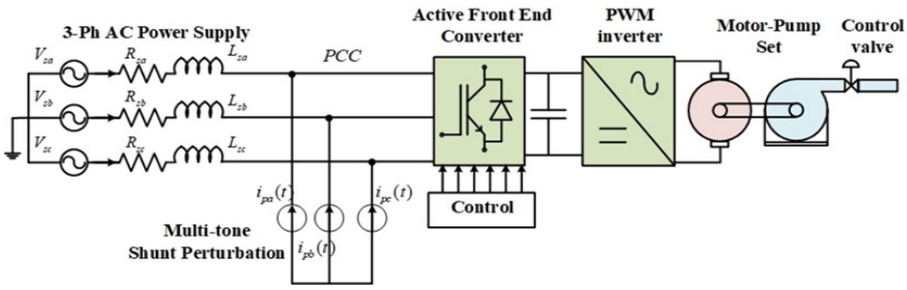


Fig. 4.7: Three phase system with motor load (CPL) and shunt perturbation at PCC.

- The simulated source and load impedances are shown in Fig. 4.8 and Fig. 4.9. The general Nyquist stability plot is given Fig. 4.10. It can be observed from Fig. 4.10 that the system is stable as the plot does not include the (-1,0) point.

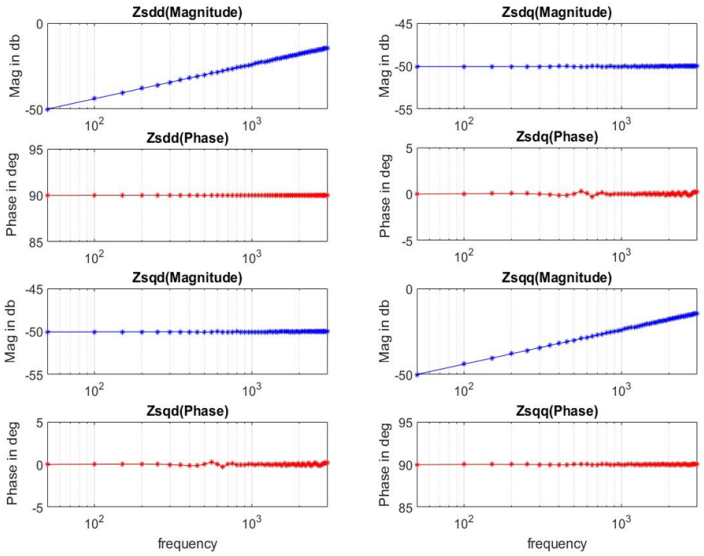


Fig. 4.8: Source impedances Zs_{dd}, Zs_{dq}, Zs_{qd} and Zs_{qq}.

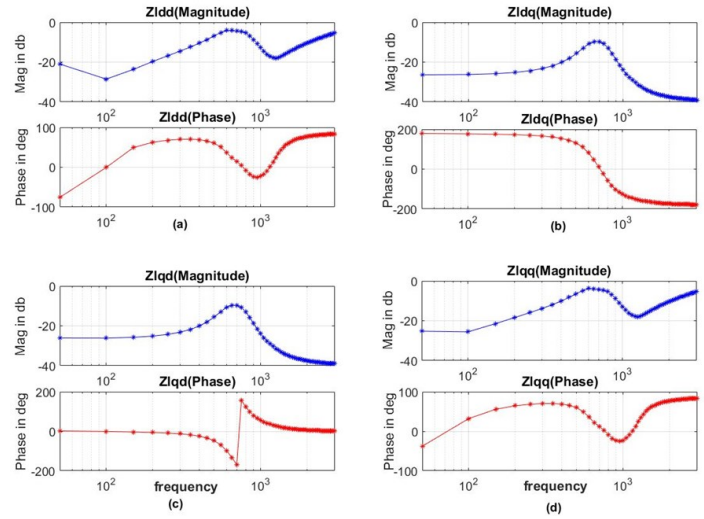


Fig. 4.9: Load impedances Zl_{dd}, Zl_{dq}, Zl_{qd} and Zl_{qq}.

- The effect of the source impedance on stability is shown in Fig. 4.11. The outer circle is with the high source impedance i.e. weak grid. As the source impedance increases, the system moves towards an unstable region.
- The experimental study is being carried out for the stability analysis of the microgrid system with multiple sources and loads.

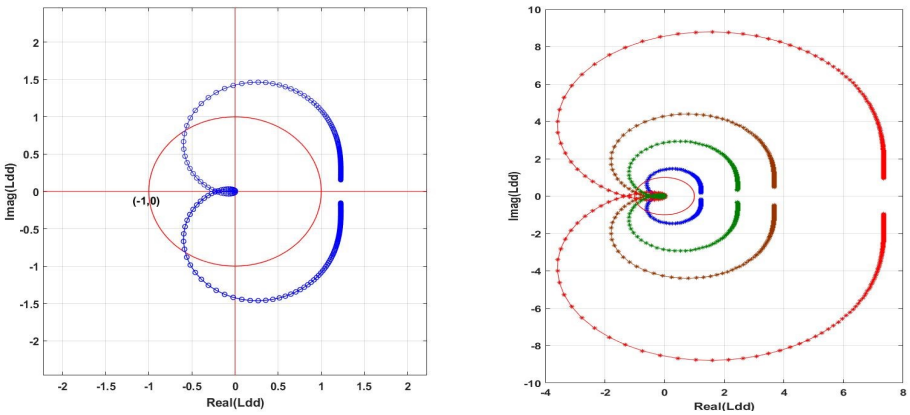


Fig. 4.10 (left): Polar plot and the stability analysis.

Fig. 4.11 (right): Effect of source impedance on stability.

Figs. 4.6-4.11
Srinivasarao KAMALA
(PhD student, NUS)

Partha Pratim BISWAS (PhD student, NTU) reported on his research is focused on power system optimisation applying evolutionary algorithms, a subset of artificial intelligence. The optimisation topics include but are not limited to planning of power transmission and distribution networks, the power flow in the network, distributed generations, integration of renewable sources, design of power quality improvement filters. He reported that most optimisation problems in power system are non-linear and constrained, and classical methods are not very effective in solving these problems. In the last couple of decades, population-based metaheuristics have gained immense popularity due to their prowess in solving non-linear, multimodal and constrained optimisation problems. Though many algorithms have been applied to power system related problems, there is ample scope to formulate new problems or work on existing problems with the implementation of newly developed evolutionary algorithms.

The topic of his PhD thesis is "Evolutionary algorithms for solving Power System Optimisation problems". Several evolutionary algorithms for single-objective and multi-objective optimisations have been developed in the field of computer science. His research is mainly focus on analyzing, improving and applying variants of differential algorithm (DE) in the field of power system. Maximising profit, minimising cost, system losses, carbon emission etc. are usually set as objectives of the optimisation problems. In last few months, state-of-the-art variants of differential evolution algorithms and a few advanced constraint handling (CH) techniques have been integrated to optimise cost, emission etc. satisfying various constraints in power system. A proper CH method has been found to be more effective in optimising constrained, non-linear power system problems. Distribution network loss minimisation with incorporation of distributed generators, optimal power flow study with stochastic wind and solar power, windfarm layout design and optimisation, power filter design etc. have been performed using evolutionary algorithms. The results and findings have been promising and most of those have already been published in reputed journals and conferences.

QIU Xue Heng (PhD student, NTU) reported that better time series forecasting models have been investigated and proposed by developing better ensemble strategies. Specially, short-term electric load forecasting plays an important role in the management of modern power systems. Improving the accuracy and efficiency of electric load forecasting can help power utilities design reasonable operational planning which will lead to the improvement of economic and social benefits of the systems. A hybrid incremental learning approach composed of Discrete Wavelet Transform (DWT), Empirical Mode Decomposition (EMD) and Random Vector Functional Link network (RVFL) is presented in this work. RVFL network is a universal approximator with good efficiency because of the randomly generated weights between input and hidden layers and the close form solution for parameter computation. By introducing incremental learning, along with ensemble approach via DWT and EMD into RVFL network, the forecasting performance can be significantly improved with respect to both efficiency and accuracy. The electric load datasets from Australian Energy Market Operator (AEMO) were used to evaluate the effectiveness of the proposed incremental DWT-EMD based RVFL network. Moreover, the attractiveness of the proposed method can be demonstrated by the comparison with eight benchmark forecasting methods.

QIU Xue Heng's project is "Ensemble Time Series Forecasting Algorithms with Applications in Power Systems and Financial Markets" and he reported that his research field is mainly focused on deep learning methods and ensemble algorithms. He has reviewed various kinds of time series forecasting algorithms, 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.

Furthermore, he investigated a randomised 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 accepted by the journal Knowledge-Based Systems recently. Moreover, an Empirical Mode Decomposition based incremental ensemble

approach is proposed for crude oil price forecasting, which has been submitted to IEEE World Congress on Computational Intelligence (IEEE WCCI 2018). For future research directions, multivariate time series forecasting models shall be constructed making using of the potential learning ability of deep learning methods. Moreover, the concept of deep learning can also be applied with RVFL to develop deep RVFL structure to make use of RVFL's advantages in computation time.

WP 4.5: Model building, integration and maintenance

Prof. Jan MACIEJOWSKI (PI, CAM) reported that work on the relationship between 'inverse response' of linear systems and the zero locations of transfer functions (already reported in the previous report) has been continued. It has been shown that zeros in the right-half plane are not necessary for inverse response to exist. This is a new result; it has generally been assumed that they are necessary. A paper reporting this work has been accepted for the 2018 European Control Conference.

WP 4.6: Demonstration of proposed algorithms on pilot scale

Dr Eddy FOO (Co-I, NTU) reported that he has completed the tendering process for purchasing a power amplifier for the OPAL-RT system in the Clean Energy Research Lab (CERL) at NTU. The power amplifier will equip researchers with the capability to perform power hardware-in-the-loop (PHIL) testing by allowing the exchange of real power flows between the OPAL-RT system and the microgrid testbed in CERL and to verify and validate the real-time simulations. Furthermore, he is working with Dr Prakash Kumar RAY (RF, NTU) and Gourab KARMAKAR (Research Intern, NTU) on power quality research. In this work, the performance of various power quality detection techniques used in identifying the types of power quality issues are validated and tested. Some preliminary findings have been documented in a conference paper, which has been accepted for the IEEE PES General Meeting 2018. This work is being extended using experimental data from the static frequency converter (SFC) located in the microgrid testbed at CERL. In future, the different types of power quality issues will be classified. Furthermore, future work will also examine ways to mitigate the problems associated with the power quality issues. The power amplifier will also permit PHIL testing which empowers researchers with the ability to inject different types of power quality disturbances in the microgrid testbed in order to assess the performance of the power quality detection techniques.

Lu SUN (PhD student, NUS), Xuebing CHEN (PhD student, NTU) and Dr Yuhao SUN (SRF, NTU), under supervision of Associate Prof. RUSLI (Co-I, NTU) and Prof. Gehan AMARATUNGA (PI, CAM), reported on the challenges of deploying mPMU sets in Singapore's medium-level grid network. This team has been working on collaborations with other entity owners to jointly deploy the mPMU sensors in their grids such as the Marina Bay Sands 22 kV voltage network. The deployment of mPMUs will bring to the project a great additional amount of exciting real and meaningful data on electrical systems.

They reported that the communication capability of micro PMU sensors has recently been upgraded from minute's level to 100 milliseconds. The new update ensures the real-time capability of the whole system. The accuracy of the data received from the grid is now jointly verified and calibrated. This sub-project is led by Astar National Metrology Centre. The efforts will ensure the monitoring system always reaches an extremely high standard of accuracy.

The researchers have been conducting a literature review on fault detection and location. Immediate detection and accurate location of a fault on a line is extremely important to restore the line in the shortest time possible. Since a fault occurrence will result in frequency characteristics change of current and voltage signals, a variety of methods have been proposed to analyse frequency characteristics of time-domain signals. S-transform is such a mathematical tool that can provide joint time-frequency representation with frequency-dependent resolution based on a moving and scalable localising Gaussian window. The fault location methods can be divided into two categories: imped-

ance-based fault location algorithms and traveling-wave based fault-location methods. Impedance based methods use bus voltage and line current data of either a single bus or two buses that are connected to the faulted line. Considering the propagation of PMU in power system, the researchers are trying to find a way to apply PMU measurements to fault detection and location.

Other Activities and Achievements

- Dr Eddy FOO (Co-I, NTU) received the NTU EEE Start-Up Grant of SGD $60,000 from Jan 2018 to Jan 2019. The proposed project is titled "Linking Waste Heat Recovery and Electrical Power Networks for Energy Efficiency in Eco-Industrial Parks with Heterogeneous Generation Sources". Dr Zhang Xinan, Lecturer, School of EEE, NTU is collaborating in this project as a Co-PI. Some collaborative research works are currently done in conjunction with Cambridge CARES IRP4. The objective of this research work will be to improve the energy efficiency of eco industrial parks (EIPs) by studying synergies between different energy streams.
- Dr Yuhao SUN (SRF, NTU) submitted a paper and attended the 12th IEEE International Conference on Power Electronics and Drive Systems (PEDS 2017) in December 2017. He was invited as a chair to host a session, Distributed Generation and Smart Grid.
- Prof. Jan MACIEJOWSKI (PI, CAM) and Dr Bhagyesh PATIL (RF, NTU) attended the IEEE Conference on Decision and Control in Melbourne, Australia, in December 2017, and presented a paper entitled 'Optimal nonlinear model predictive control based on Bernstein polynomial approach' there.
- Dr Bhagyesh PATIL (RF, NTU) is running a Special Track on Power Systems at this year's International Conference on Principles and Practice of Constraint Programming. The power system problems have unique characteristics such as fast evolving dynamics, large data sources and the need for real-time operational control. Recently, there has been a high demand for efficient algorithms that can address integration of the renewable generation, environmental issues and development of smart grid technologies. Such information processing techniques are expected to make the real-time operation of power systems more intelligent and reliable. In the last decade, with tremendous advancement in the field of constraint solving, optimisation algorithms and computer hardware technology, existing power system problems can be solved more effectively. This track intends to investigate state-of-the-art work related to all constraint solving and optimisation-based methodologies that result in efficient operation of power systems (url: http://cp2018.a4cp.org/).
- Thuy VAN DANG (PhD student, NTU) has submitted his PhD thesis for examination. He has now joined a three-month entrepreneurship course, as the result of an offer from *Entrepreneur First LLC* (a London-based company) for this course, which is being held in Singapore from January to April 2018.
- Thuy VAN DANG (PhD student, NTU) has implemented his version of the ADMM algorithm on proprietary equipment (for power distribution systems) produced by the German company A.Eberle GmbH. Hardware-in-the-loop simulation has been completed and discussions are in progress to arrange testing with real transformer hardware.
- Xueheng QIU (PhD student, NTU) attended the 2017 IEEE Symposium Series on Computational Intelligence (IEEE SSCI 2017) hosted by IEEE Computational Intelligence Society in December 2017 at Honolulu, Hawaii, USA.

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.

Optimal Reconfiguration and Distributed Generator Allocation in Distribution Network Using an Advanced Adaptive Differential Evolution

Partha Biswas, Rammohan Mallipeddi, Ponnuthurai Suganthan and Gehan Amaratunga

DOI: 10.1109/SSCI.2017.8280824

Abstract:

Power loss in an electrical network is unavoidable due to its inherent resistance. However, for economical and efficient operation, the network loss shall be minimised to the extent possible. Construction of the distribution network is usually closed loop, though operation is radial with opening of a suitable sectionalising switch that disconnects a branch in the loop. This process of reconfiguration i.e. selection of sectionalising switch is done in a way such that system loss in minimised. Another effective way of reducing power loss is addition of distributed generators (DGs) locally to the system nodes (buses). DG size and location also need to be optimised for minimisation of real power loss. This paper presents an application of a metaheuristic to simultaneously allocate DGs and perform reconfiguration of a couple of standard radial distribution networks. Both location and placement of the DG are optimised by the algorithm. As an obvious fact, the optimisation problem is a combination of discrete (location) and continuous (rating) variables. Linear population size reduction technique of success history based adaptive differential evolution (L-SHADE) is implemented to perform the optimisation task with objective of minimising network real power loss. The algorithm is tested on standard IEEE 33-bus and 69-bus radial distribution networks. The simulation results are found to be promising and highly competitive when compared with results of other equivalent algorithms.

Optimal Nonlinear Model Predictive Control Based on Bernstein Polynomial Approach

Bhagyesh V. Patil, K. V. Ling and Jan M. Maciejowski

Abstract:

In this paper, we compare the performance of Bernstein global optimisation algorithm based nonlinear model predictive control (NMPC) with a power system stabiliser and linear model predictive control (MPC) for the excitation control of a single machine infinite bus power system. The control simulation studies with Bernstein algorithm based NMPC show improvement in the system damping and settling time when compared with respect to a power system stabiliser and linear MPC scheme. Further, the efficacy of the Bernstein algorithm is also compared with global optimisation solver BMIBNB from YALMIP toolbox in terms of NMPC scheme and results are found to be satisfactory.

Micro PMU Based Monitoring System for Active Distribution Networks

Yuhao Sun, Xuebing Chen, Shiliang Yang, Rusli, King Tseng and Amaratunga Gehan

Abstract:

Distribution systems are evolving into active networks due to the high penetration of distributed generation in recent years. Micro Phasor Measurement Unit (micro-PMU) is capable of providing super-fast and accurate synchronised phasor measurements, and eligible for distribution networks applications. This paper introduces a project aiming to develop a micro-PMU based monitoring system for distribution networks. In this project, parallel computation method is proposed for big data screening, gathering and processing. This paper takes linear state estimation as an example to show the improvement of parallel computation on big data processing.

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 IRP2

- 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., (5), 1687–1695. 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

IRP1 and IRP3

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A.2 CARES C4T Visiting Scientists Programme

Through the CARES C4T Visiting Scientists Programme, expert researchers from around the world are invited to spend time at C4T in Singapore. The following researchers visited CARES C4T and hosted seminars during the reporting period:

Emeritus Professor Malcolm Mackley

December 2017

Emeritus Professor Malcolm Mackley, University of Cambridge

Unexpected outcomes from curiosity and technology driven science in the field of polymeric materials and process engineering

Abstract: Both curiosity and technology driven scientific discoveries have and continue to play a major part in all our lives and this presentation will overview areas where initial curiosity driven science and process innovation has resulted for most cases in significant technological application. The examples are drawn from direct experience and cover a period of nearly 40 years where aspects of polymer and process innovation is involved. An early example concerns the fundamental study of polymer morphology at Bristol University by the Late Prof. Andrew Keller and Sir Charles Frank where their work resulted in the eventual discovery of a key membrane element for modern batteries and also High Modulus Polyethylene (HMP) fibres and recently films. Further examples will be given where a blend of curiosity and technology driven science resulted in the invention of a continuous Oscillatory Flow Mixing technology (OFM), a Multi Pass Rheometer (MPR) and novel plastic Micro Capillary Film (MCF). Finally a fast filament stretching apparatus initially designed for ink jet printing science will be described which provides general understanding of droplet and surface tension related technologies. In all cases described the underlying theme will be that “good science”, whether curiosity or technology driven, will invariably eventually find useful application, although often not in the initially intended area.

Biography: Malcolm Mackley graduated in Physics from the University of Leicester in 1969. He then obtained his PhD at Bristol University working in the field of Flow induced Polymer crystallisation under the guidance of the late Sir Charles Frank and Andrew Keller. After a brief period as lecturer in Material Science at Sussex University he joined in 1979 the Department of Chemical Engineering at the University of Cambridge.

Malcolm is a scientist an engineer and an inventor and his Polymer Fluids Group scientific contributions involved mainly rheology and polymer processing. He is the inventor of a number of scientific apparatus and in terms of process innovation he has invented a novel chocolate extrusion process, a different way of mixing using oscillatory flow and a more recent plastic Microcapillary Film (MCF) that contains continuous arrays of 100 micron hollow capillaries. He has lectured extensively at Cambridge in the fields of polymers, process innovation and rheology and has given many conference presentations throughout the world. He is a Fellow of the Royal Academy of Engineering and an Emeritus Fellow of Robinson College Cambridge.

Professor Richard G Compton

March 2018

Professor Richard G Compton, Department of Chemistry, Oxford University

Electrochemical nano-impacts: new insights into nanoparticles

Abstract: First, the analytical need for nanoparticle detection will be introduced and electrochemical studies on suspensions of nanoparticles shown to allow the detection and characterisation of diverse nanoparticles at the single entity level. For electroactive nanoparticles such as those of silver, Ag, or iron oxide, Fe_3O_4, quantification of the charge associated with single collisional impacts allows the sizing of the particles in the range from ca 100nm down to less than 5nm. The frequency of impact events permits article concentrations to be estimated and the potential dependence indicates the chemical nature of the impact particles.

In many cases the electrochemistry reveals agglomeration or aggregation of the particles and since the monomers and agglomerated diffuse at different speeds the kinetics of de-agglomeration can be inferred in cases such as that of uncapped Bi_2O_3 particles, where the electrochemical signals are dominated by the monomer signal whilst independent evidence shows significant agglomeration in bulk solution. Models for the extent of agglomeration have been developed.

Second, the extension to the study, at the single entity, will be described in terms of the detection of bacteria and red blood cells and the doping of particles of solids and polymers and in nanodroplets will be reported. Finally, the possible nano-toxicity of silver will be discussed.

Biography: Richard G Compton is Professor of Chemistry and Aldrichian Praelector at Oxford University, United Kingdom, where he is also Tutor in Chemistry at St John's College. He received his PhD in 1980 at Imperial College, London. Professor Compton has broad interests in both fundamental and applied electrochemistry and electroanalysis including nanochemical aspects. He has published more than 1500 papers (H = 93; with more than 36,000 citations excluding self-cites) and seven books. The second edition of his graduate textbook *Understanding Voltammetry* (with C E Banks) was published in late 2010 by World Scientific Press and a third edition will appear early in 2018. He is a co-author of the scientific biography *A G Stromberg - First Class Scientist, Second Class Citizen: Letters from the GULAG and a History of Electroanalysis in the USSR* (WSP, 2011).

Patents have been filed on 25 different topics including novel pH sensors (leading to the San Francisco based spin out Senova), gas sensing (in collaboration with Honeywell) and the detection of garlic strength and chilli heat in foodstuffs. The Senova pHit Scanner based on Compton group patents - the world's first calibration-free pH meter - won the prestigious 'best new product' award at PITTCON March 2013. Professor Compton has been CAS Visiting Professor at the Institute of Physical Sciences, Hefei and is a Lifelong Honorary Professor at Sichuan University. He holds Honorary Doctorates from the Estonian Agricultural University and Kharkov National University of Radioelectronics (Ukraine) and is a Fellow of the RSC and of the ISE. He is the Founding Editor and Editor-in-Chief of the journal *Electrochemistry Communications* (current IF = ca 4.85) published by Elsevier and is the joint Editor-in-Chief of the newly launched *Current Opinion in Electrochemistry*.

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