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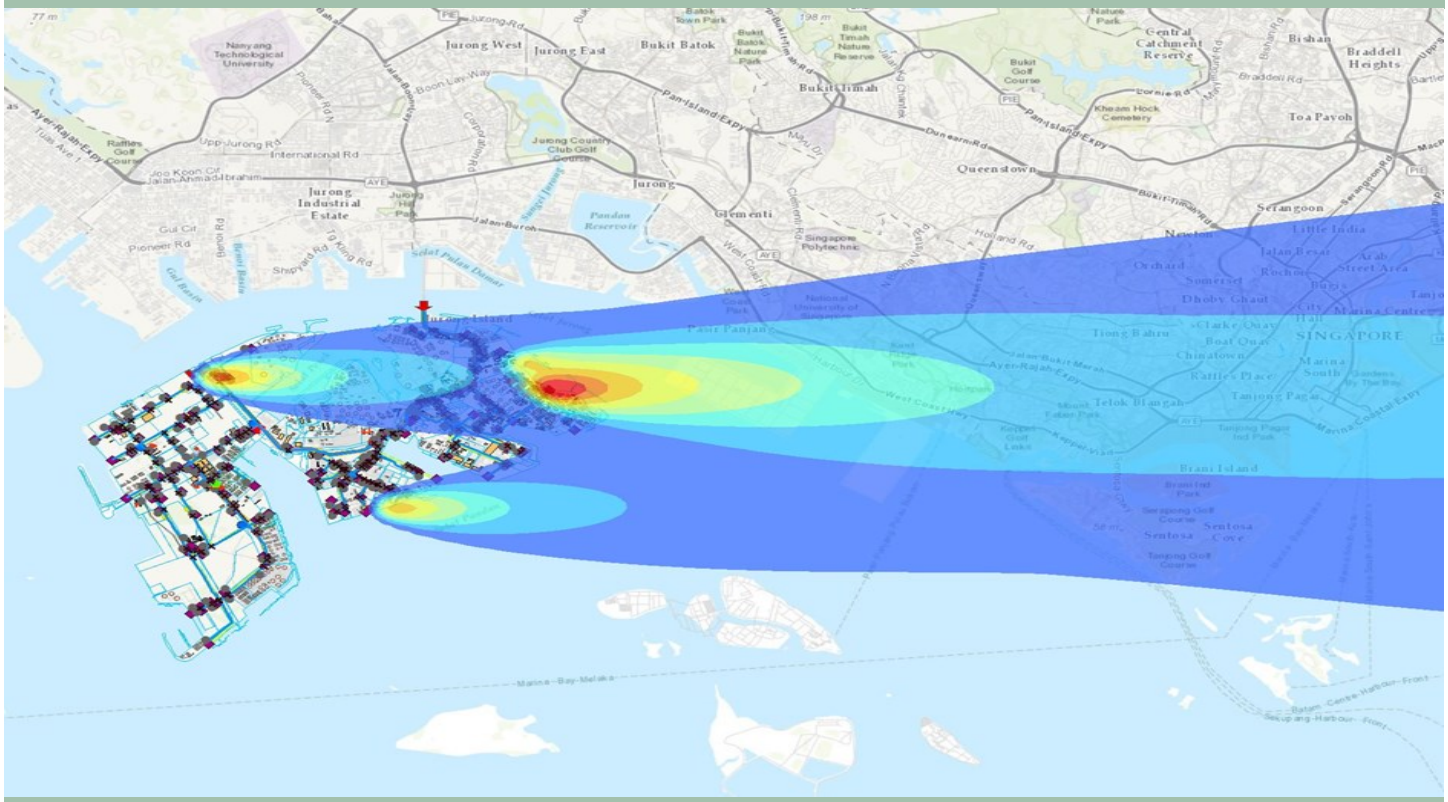
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH AND EDUCATION IN SINGAPORE LTD.

Biannual Research Report

November 2016 — April 2017

CAM.CREATE C4T

Cambridge Centre for Carbon Reduction in Chemical Technology



CREATE

Centre for Reseach Excellence and Technological Enterprise

University of Cambridge

Nanyang Technological University

National University of Singapore

Cover figure: Concentration of CO_2 released by the power plants on Jurong Island and covering the southern districts of Singapore including the Central Business District (CBD), as simulated by ADMS

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3 Foreword

Prof. Markus Kraft,

CARES Director.

April 2017

I am pleased to present the 6th Biannual Research Report of the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T), the first programme managed by the Cambridge Centre for Advanced Research and Education in Singapore (CARES).

As ever, the first part of 2017 has been a busy time for C4T. Following on from the successful six month residency in 2016 of Prof Gehan AMARATUNGA (PI, IRP4, Cambridge), we have been delighted to welcome two further Cambridge colleagues for an extended stay in Singapore in 2017. Prof Jan MACIEJOWSKI (PI, IRP4, Cambridge) and Dr Adrian FISHER (PI, IRP2, Cambridge) both arrived in early 2017 and will stay until mid-year. It is a pleasure to have them with us and they certainly have been busy! Prof MACIEJOWSKI, along with Prof LING Keck Voon (PI, IRP4, NTU), was instrumental in organising the wonderfully productive visit (under the CARES C4T Visiting Scientist Scheme) of Prof Karl ÅSTRÖM, the notable control theorist and winner of the IEEE Medal of Honour. Prof ÅSTRÖM's visit was highly generative for both the C4T members and the wider Singapore research community due, in no small part, to the generosity shown by Prof ÅSTRÖM with his time and expertise. We hope to quickly capitalise on the burst of energy and new ideas catalysed by the visit. Our Visiting Scientists Scheme has also been able to bring a number of other excellent researchers (both from academia and industry) to Singapore – Dr Peter BISHOP (Johnson Matthey), Dr Oliver INDERWILDI (ESSEC Business School) and Prof Zdenek SOFER (University of Chemistry and Technology Prague). We are already looking forward to continuing this exciting programme through the rest of the year.

Continuing the theme of collaboration, the last six months have presented some great opportunities for the CREATE programme research groups to come together and identify synergies in our areas of interest via the platform of the Intra CREATE grant calls released by NRF. I must admit it was an absolute pleasure to be able to form collaborations with colleagues from around the globe (the universities in the programme have home bases from countries as diverse as America, Israel, Germany and Switzerland; the individuals themselves are, of course, from an even broader range of nations) simply by getting in an elevator rather than on a plane! Under the two Intra-CREATE funding instruments released by NRF, CARES submitted more than ten proposals on topics as diverse as the production of value added chemicals from waste, flexible electronics, nanomachines, bio-batteries, processing of big data from smart grids, smart building materials and many more. It was particularly satisfying to see the energy and imagination that our more junior researchers applied to the seed funding grant call and witness some of the promising collaborations that emerged from the process. We look forward to the outcome of the assessment process later in the year and hopefully to starting work on some of the proposed projects soon after.

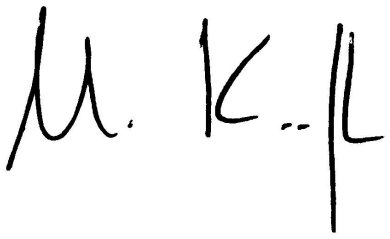
In addition to the many Intra-CREATE proposal ideas our researchers (both in Singapore and Cambridge) have been developing, the C4T team have also been hard at work on the proposal for the second phase of C4T (hoped to run from 2018 to 2023). As anyone who has tried to co-ordinate a research proposal involving over thirty senior scientists from across the disciplines will know, there is necessarily a process of focussing and refining to be gone through to identify the absolutely best and most promising ideas to attack our overall research problem of reducing the carbon footprint of the chemical industry. I am pleased to report that our team (both the senior leadership and the junior researchers) have approached that process with energy and drive. Particular mention should go to the task force of Research Fellows and students from across all areas of the programme who undertook a techno-economic assessment of our current work and proposed ideas to help us understand much better our potential impact; we are hoping to publish a position paper based on this

work in the near future. We are now nearing a final version of our proposal, which will be submitted to NRF very soon.

However, we have not only been thinking and researching on carbon footprint reduction. We have also been putting the ethos of the programme into action in other ways. In March 2017, following significant effort by Dr Derrick TAN (who worked with us previously as Laboratory Outfitting Manager) and Dr Hugo SCHMIDT (Laboratory Manager), we were delighted to be awarded the Building and Construction Authority Green Mark Platinum Award for our laboratory in the CREATE Tower. The assessment process for the award looked not only at the green technologies and infrastructure of our laboratory (for which credit should be given to the design work of Sembcorp Architects and Engineers and the construction efforts of Gennal), but also to the work practices and procedures in the laboratory. The award is testament to the efforts of a very large team, including our own researchers and support staff, the National Research Foundation Infrastructure and CREATE teams, the designers (SCAE) and construction project managers (Gennal). I am proud of everyone involved in getting this superb laboratory not only operational, but operating in line with the environmental values we espouse in the programme. The BCA Green Mark Award is a much-appreciated commendation of that large effort.

Finally, I would like to draw your attention to a new section of our Biannual Research Report that I hope you will enjoy. Regular readers will be pleased to know that our 'Focus on Impact' feature continues in this edition with a contribution from Dr LI Ping (RF, IRP1, NUS) looking at how nanostructures contribute to efficient CO_2 capture. However, this time we add a new feature, 'Focus on Fundamental Science', the purpose of which is to explain the important underlying scientific concepts of our programme to an interested layman. In this first edition of the column, WANG Jing Jing (PhD student. IRP1, NUS) explains what layered double hydroxides are and how they can be applied.

I am certain you will find plenty of interest in our current outputs; I warmly encourage you to contact us for further details of any of our workstreams.



Prof. Markus Kraft, CARES Director

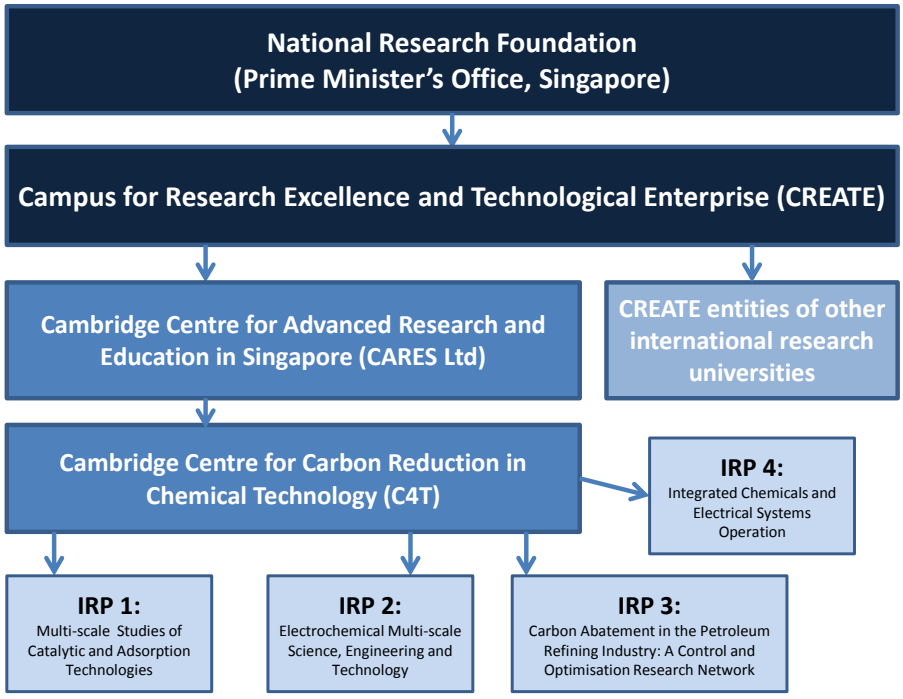
April 2017

1.1 Structure and Organisation

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

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

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



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

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

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

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

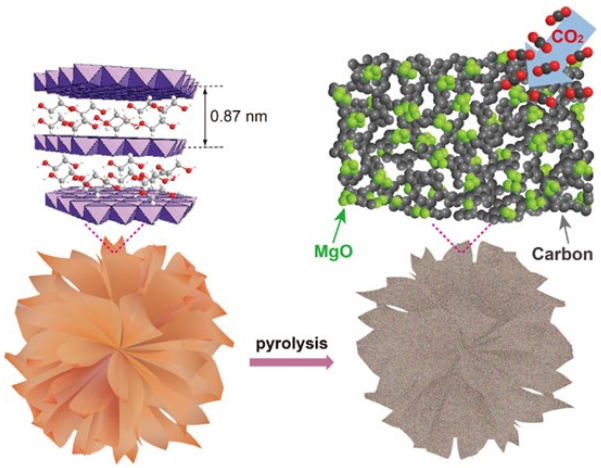
2.1 IRP1: 'Synthetic Architecture of MgO/C Nanocomposite from Hierarchical-Structured Coordination Polymer towards Enhanced CO_2 Capture'

P. Li, W. Liu, J.S. Dennis and H.C. Zeng

DOI: 10.1021/acsami.6b14960

Abstract:

Highly efficient, durable and earth-abundant solid sorbents are of paramount importance for practical carbon capture, storage, and utilization. Here we report a novel and facile two-step strategy to synthesize a group of hierarchically structured porous MgO/C nanocomposites using flowerlike Mg-containing coordination polymer as a precursor. The new nanocomposites exhibit superb CO_2 capture performance with sorption capacity up to 30.9 wt% (at 27 °C, 1 bar CO_2), fast sorption kinetics and long cycling life. Importantly, the achieved capacity is > 14 times higher than that of commercial MgO, and favorably exceeds the highest value recorded to date for MgO-based sorbents under similar operating conditions. On the basis of the morphological and textural property analysis, together with CO_2 sorption mechanism study using CO_2-TPD and DRIFT techniques, the outstanding performance in CO_2 uptake originates from unique features of this type of sorbent materials, which include hierarchical architecture, porous building blocks of nanosheets, high specific surface area (*ca.* 300 m^2/g), evenly dispersed MgO nanocrystallites (*ca.* 3 nm) providing abundant active sites, and the *in situ* generated carbon matrix that acts as a stabilizer to prevent the growth and agglomeration of MgO crystallites. The nanocomposite system developed in this work shows good potential for future low-cost CO_2 abatement and utilization.



Synthesis procedure for flowerlike MgO/C nanocomposites. In Mg-EG complex (*i.e.*, coordination polymer), for illustrative purpose, Mg^{2+} ion is located inside octahedrons formed by six oxygen atoms of EG ligands, and the edges of octahedron then connect into metal-oxygen sheets.

'A novel W-doped Ni-Mg mixed oxide catalyst for CO_2 methanation'

Yan Yong, Dai Yihu, He Hong, Yu Yunbo, Yang Yanhui

doi.org/10.1016/j.apcatb.2016.05.016

Highlights:

- $NiWMgO_x$ catalysts showed excellent CO_2 methanation activity.
- Adding W improved the catalyst stability and anti-CO-poisoning ability.
- Tungsten also facilitated the formation of more active monodentate formate.

Abstract:

Novel Ni-W-Mg mixed oxide catalysts ($NiWMgO_x$) were prepared by homogeneous precipitation and attempted for the methanation of CO_2. Adding W remarkably promoted the activity with improved stability, anti-CO-poisoning ability and resistance against coke formation compared to the undoped $NiMgO_x$ catalyst. The superior reactivity of monodentate formate towards hydrogenation than that

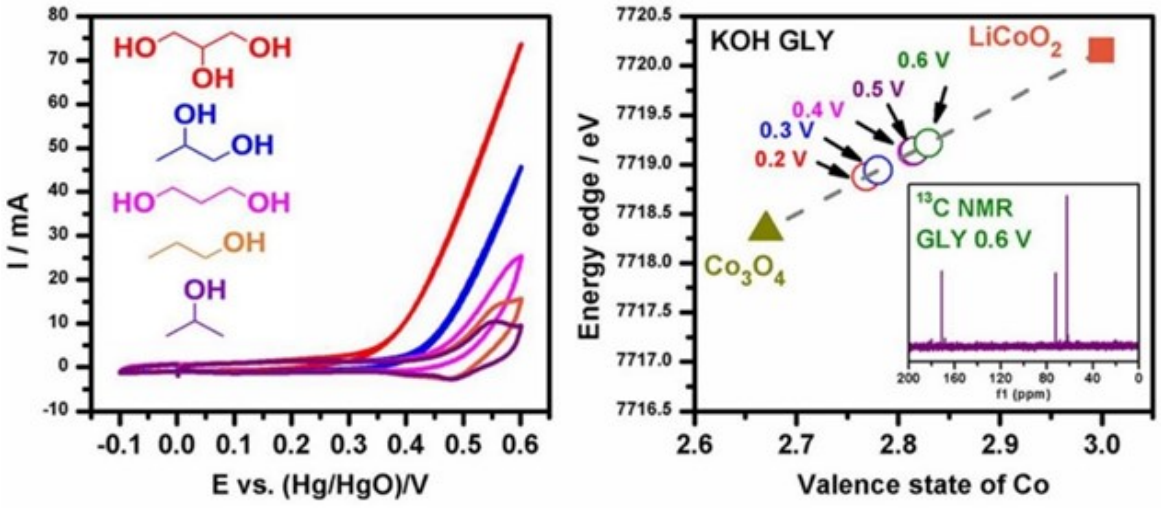
of bidentate formate species was identified by DRIFTS analysis and the formation of more active monodentate formate species was indisputably facilitated by W additives, leading to the greatly enhanced catalytic activity. H_2-TPR and CO_2-TPD characterization showed that doping W increased the number of stable CO_2 adsorption sites and helped in anchoring the Ni sites as a result of strengthened Ni-Mg interaction, both of which were responsible for the enhanced CO_2 methanation activity and the improved resistance against sintering.

2.2 IRP2: 'Electrochemical oxidation of C3 saturated alcohols on Co_3O_4 in alkaline'

Sun, S.; Sun, L.; Xi, S.; Du, Y.; Prathap, M. U. A.; Wang, Z.; Zhang, Q.; Fisher, A. C.; Xu, Z. J.

DOI: 10.1016/j.electacta.2017.01.086

Highlights:



- A systematic study on the electrochemical oxidation of C3 saturated alcohols on Co3O4 in alkaline.
- Activity trend: propanetriol > 1,2-propanediol > 1,3-propanediol > 1-propanol > 2-propanol in 1.0 M KOH.
- The C-C bond cleavage occurred faster in alcohols having adjacent hydroxyl groups.
- The KOH concentration influenced electro-oxidation of those alcohols bearing secondary hydroxyl group more dramatically than that of those primary alcohols

Abstract: In this work, we present a systematic study on the electrochemical oxidation of C3 saturated alcohols (propanetriol, 1,2-propanediol, 1,3-propanediol, 1-propanol, and 2-propanol) on Co_3O_4 in alkaline. Co3O4 electrode was prepared by electrodeposition of Co(OH)2 on graphite paper followed with a calcination step. The electro-oxidation of C3 saturated alcohols were investigated by a combination of cyclic voltammetry, multi-step chronoamperometry, and electrochemical impedance spectroscopy techniques in KOH solution. The electro-oxidation studies at Co_3O_4 electrode followed an activity trend in the following order: propanetriol (GLY) > 1,2-propanediol (1,2-P) > 1,3-propanediol (1,3-P) > 1-propanol (1-P) > 2-propanol (2-P). The NMR analysis of the oxidized products showed that C-C bond cleavage occurred faster in alcohols having adjacent hydroxyl groups. X-ray absorption near-edge structure (XANES) spectroscopy study showed that there was no significant difference in Co oxidation state in the absence and the presence of glycerol. It was also found that the KOH concentration influenced electro-oxidation of those alcohols bearing secondary hydroxyl group (GLY, 1,2-P, and 2-P) more dramatically than that of those primary alcohols (1.3-P and 1-P).

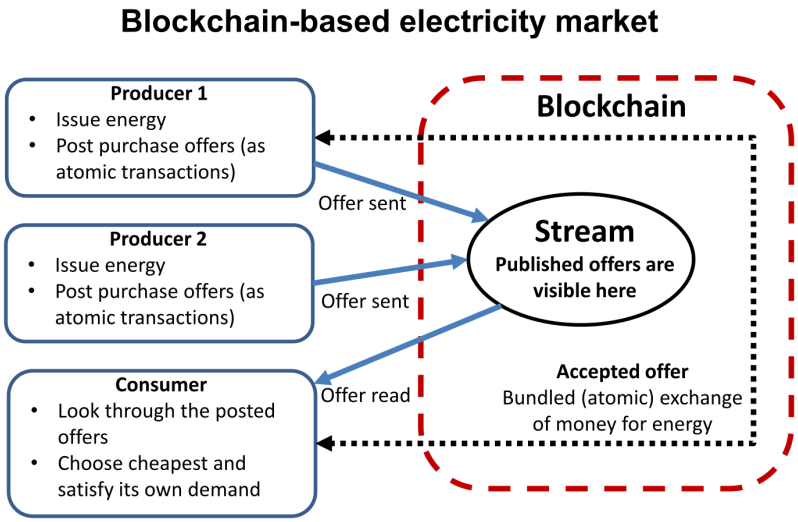
2.3 IRP3: 'Blockchain technology in the chemical industry: machine-to-machine electricity market'

Janusz Sikorski, Joy Haughton, Markus Kraft

dx.doi.org/10.1016/j.apenergy.2017.03.039

Highlights:

- It is demonstrated that it is possible to successfully employ blockchain technology to facilitate machine-to-machine (M2M) interactions and establish a M2M electricity market in the context of the chemical industry via the Internet of Things.
- The presented scenario includes two electricity producers and one electricity consumer trading with each other over a blockchain.
- This paper describes and discusses the research and application landscape of blockchain technology in relation to Industry 4.0.



Abstract:

The purpose of this paper is to explore applications of blockchain technology related to the 4th Industrial Revolution (Industry 4.0) and to present an example where blockchain is employed to facilitate machine-to-machine (M2M) interactions and establish a M2M electricity market in the context of the chemical industry. The presented scenario includes two electricity producers and one electricity consumer trading with each other over a blockchain. The producers publish exchange offers of energy (in kWh) for currency (in USD) in a data stream. The consumer reads the offers, analyses them and attempts to satisfy its energy demand at a minimum cost. When an offer is accepted it is executed as an atomic exchange (multiple simultaneous transactions). Additionally, this paper describes and discusses the research and application landscape of blockchain technology in relation to the Industry 4.0. It concludes that this technology has significant under-researched potential to support and enhance the efficiency gains of the revolution and identifies areas for future research.

2.4 IRP4: 'Economic dispatch using hybrid grey wolf optimizer'

T. Jayabarathi, T. Raghunathan, B.R. Adarsh, Ponnuthurai Nagaratnam Suganthan[b]

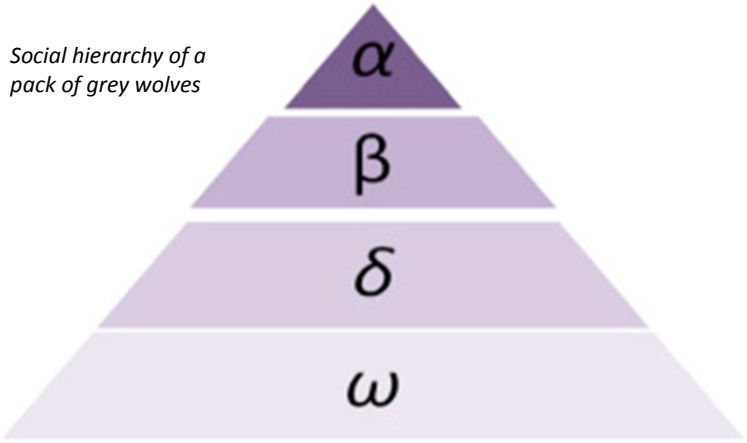
doi.org/10.1016/j.energy.2016.05.105

Highlights:

- The hybrid grey wolf optimizer, a new metaheuristic optimization algorithm has been used.
- The problem solved – the economic dispatch problem – is nonlinear, discontinuous.
- It has number of equality and inequality constraints.
- The results either outperform or compare favourably against those by other methods.

Abstract:

This paper presents the application of one of the latest swarm intelligence algorithms, the grey wolf optimizer, for solving economic dispatch problems that are nonlinear, non-convex and discontinuous in nature, with numerous equality and inequality constraints. Grey wolf optimizer is a new metaheuristic algorithm that is loosely based on the behavior of the grey wolves. The optimizer has been hybridized to include crossover and mutation for better performance. Four economic dispatch problems (6, 15, 40, and 80 generators), with prohibited operating zones, valve point loading effect and ramp rate limit constraints have been solved, with and without transmission losses. The losses are calculated using *B*-coefficients. The results obtained are compared with those reported using other methods in the literature. The comparisons show that the hybrid grey wolf optimizer used in this paper either matches or outperforms the other methods.



Social hierarchy of a pack of grey wolves

Dr. Li Ping obtained B.Sc. in Chemistry at Southwest University in 2009, and Ph.D. in Physical Chemistry at Institute of Chemistry, Chinese Academy of Sciences, China in 2014. She is currently a Research Fellow at Naional University of Singapore, supervised by Prof. Zeng Hua Chun under the CARES C4T program. Her research interests include: i) developing cost-effective micro-/nano-structured materials (e.g., CaO, MgO, porous carbon/silica, MOFs, and LDHs) with high surface area and abundant nanopores for superior CO2 capture; ii) developing advanced heterogeneous catalysts for more sustainable and green catalytic processes through rational engineering of the chemistry and structure.

2.5 Focus on Impact: How synthetic architecture of nanostructure contributes to efficient CO_2 capture

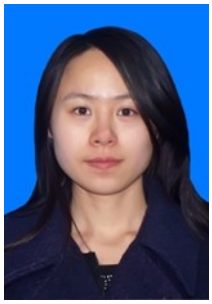
In the third of a CARES C4T series of short articles focusing on the potential real world impact of the programme's research, Dr. Ping LI (Research Fellow, IRP1, NUS), explores the benefits of the synthetic architecture of nanostructured materials for efficient CO_2 capture.

CO_2 is a typical greenhouse gas in the atmosphere, leading to serious global warming, climate change and related environmental issues. Since the beginning of the Industrial Revolution, with the large-scale combustion of the fossil fuels, the concentration of atmospheric CO_2 has showed a remarkable increase from pre-industrial level of ca. 280 ppm to the present day of ca. 400 ppm in less than 260 years. Accordingly, the CO_2 capture, storage, and utilization scheme (CCSU) has been proposed as a plausible solution, and lots of materials and technologies have been developed for CO_2 capture over the last decades. The conventional carbon capture is based on scrubbing techniques using liquid amines. Unfortunately, such processes require high energy input, and cause irreversible solvent degradation and serious equipment corrosion. As an attractive alternative, the use of regenerable solid sorbents for the CO_2 removal is regarded as a competitive approach, because of its ease to operate, wide working temperature range, and low environmental impact.

To evaluate a solid sorbent for the practical application, the important parameters including sorption capacity, kinetics, selectivity, durability, and the cost should be considered. In recent years, a wide variety of materials that include zeolites, carbonaceous materials, solid amine-based materials, organic polymers, layered double hydroxides (LDHs) and metal oxides/salts have been explored for CO_2 capture. However, they still suffer from unsatisfactory CO_2 capture performance, such as low sorption capacities, sluggish kinetics, and poor stability, *etc*. How to further improve the CO_2 capture performance of the solid sorbents remains a considerable challenge.

The recent fast-advancing nanoscience and nanotechnology enlighten a promising way to synthesize high-performance solid sorbents based on nanostructured materials. Compared with their bulk counterparts, nanostructured materials are able to expose more active sorption centers, better facilitate mass transportation, and thereby superior sorption performance. In CARES C4T, with rational materials design and architecture, a wide variety of nanostructured materials, such as flower-like MgO/carbon nanocomposite, LDH ultrathin nanosheets, porous carbon nanospindles, and nano-sized metal-organic frameworks (MOFs), are finely customized through facile and controllable syntheses (e.g., top-down and bottom-up methods). Featuring with well-controlled hierarchical architecture, large surface area, abundant nanoporous structure, and fully exposed sorption active sites with proper bonding intensity, these new functional materials present outstanding CO_2 capture performance with high uptake capacity, fast sorption kinetics and excellent stability.

Applications of the synthetic architecture of nanostructured materials can also be extended to other technological fields, for example, heterogeneous catalysis, which holds vast similar characteristics with gas sorption. By finely and careful engineering, nanostructured catalysts (or nanocatalysts) with desirable active centers and architectures can also be prepared for different chemical reactions with greatly enhanced performance. For example, nano-Pd/carbon for hydrogenation reactions; zeolites for a wide range of industrially important reactions including cracking, hydrocracking, isomerization, and reforming reactions. Thus, benefitting from the synthetic architecture of nanostructured materials for efficient CO_2 capture and catalysis, a more green and sustainable industry can be favorably expected.

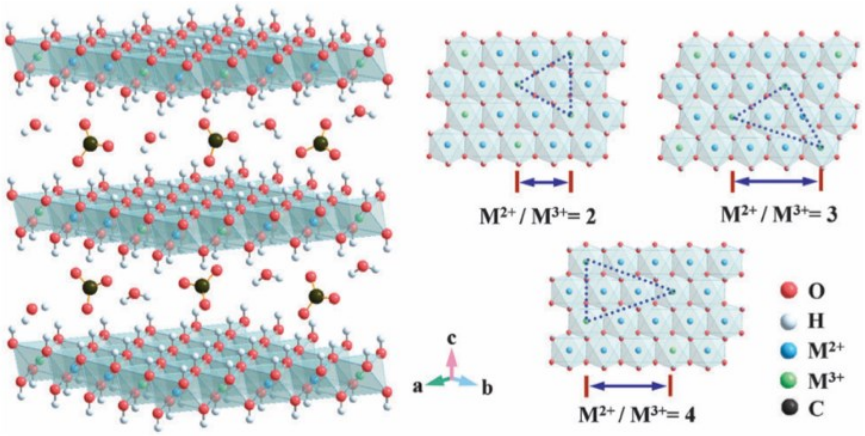


Wang Jing Jing (PhD student, NUS , IRP1) She received her bachelor's (B.E.) and master's (M.E.) degree from Tianjin University of materials science and engineering. Her research interests focus on design and fabrication of catalytic materials for OER and CO2 transformation.

2.6 Focus on Fundamental Science: What are layered double hydroxides (LDHs)?

Layered double hydroxides (LDHs) are a large family of two-dimensional (2D) inorganic solid materials which can be found not only in laboratories and man-made products but occur foremost in nature in the form of clays. They consist of positively-charged host layers and exchangeable interlayer anions, which can be expressed by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ (M^{2+} and M^{3+} are divalent and trivalent metals, respectively; A^{n-} is the interlayer anion). The value of x is equal to the molar ratio $M^{2+}/M^{2+}+M^{3+}$ and is generally in the range 0.2–0.33; water and anions are present in the interlayer galleries. Each hydroxyl group in the LDH layers is oriented toward the interlayer region and may be hydrogen bonded to the interlayer anions and water molecules, as shown in the **Figure below.**

LDHs can be seen as derived from hydroxides of divalent cations, by oxidation or cation replacement in the metal layers, so as to give them an excess positive electric charge and intercalation of extra anion layers between the hydroxide layers to neutralize that charge. LDHs can be formed with a wide variety of anions in the intercalated layers, such as Cl^-, Br^-, NO_3^-, CO_2^{2-} and SO_4^{2-}.



*The idealized structure of carbonate-intercalated LDHs with different M^{2+}/M^{3+} molar ratios showing the metal hydroxide octahedra stacked along the crystallographic **c**-axis, as well as water and anions present in the interlayer region.*[1]

Properties of layered double hydroxides

1. The M^{II} and M^{III} cations are distributed in a uniform manner in the hydroxide layers and it's easy to tune the types and ratios of these metal ions without altering the structure. The precisely-controlled chemical composition provides great potential to disperse and tune active sites at the atomic scale. [2]
2. The anions located in the interlayer regions can be replaced easily and a wide variety of anions can be incorporated, ranging from simple inorganic anions (e.g. CO_3^{2-}) through organic anions (e.g. benzoate, succinate) to complex biomolecules (e.g. DNA).
3. LDH microcrystals can be exfoliated into positively-charged 2D nanosheets, which can serve as building blocks for assembly with various catalytically active anions.
4. The LDH morphology on the micro-nanoscale can be easily manipulated by various facile syn-

thetic strategies, like in-situ growth, biological template, and electrochemical synthesis. [3]

5. The transformation of the LDHs precursors to mixed metal oxides (MMOs) or metal/metal oxide composites upon calcination in an air or hydrogen atmosphere, can further improve the structure modulation strategies and thus expand the applied range of LDH materials as catalysts and adsorbents. [4]

Applications of layered double hydroxides

Based on the inherent merits of easy tunability of chemical composition, anion exchange properties, various synthesis approaches as well as the unique topotactic transformation behavior, LDH-based materials become promising alternatives in a wide variety of fields, including water treatment, energy conversion and storage, magnetism, pharmaceutics, thin film devices, ion exchange materials, elastomer composites, and fire-retardant additives. In particular, LDHs have been widely employed in heterogeneous catalysis and adsorption.

For heterogeneous catalysis, LDH materials can serve as supports for active components such as metal nanoparticles, which prevent the sintering/aggregation of them by means of an exterior confinement effect from the LDH layers.[5] Moreover, the topological transformation of the LDH precursors containing VIII element (e.g., Fe, Co, Ni) or some noble metals (e.g., Pd) offers a facile strategy to prepare supported metal nanocatalysts.[6]

For the application to serve as adsorbents, LDH materials have various structural units, such as positive ion or basic sites, to provide specific active sites for many adsorbates with strong chemical affinity. In terms of CO_2 capture, the MMO (mixed metal oxides) materials derived from the calcination of LDHs have been identified as the most suitable one in the high temperature range. The alkaline component (e.g., MgO, CaO) in MMOs can serves as the active species for the adsorption of acidic CO_2 molecule.[7]

Conclusion

Due to the versatility and unique features, LDH-based nanomaterials have been widely applied to various fields. It is believed that with the rapid advance in synthetic and characteristic strategies of nanoscience and nanotechnology, the design and controlled synthesis of LDH-based materials would lead to more and more practical applications.

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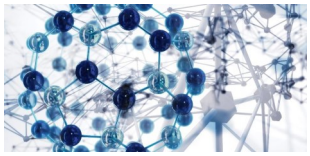


3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

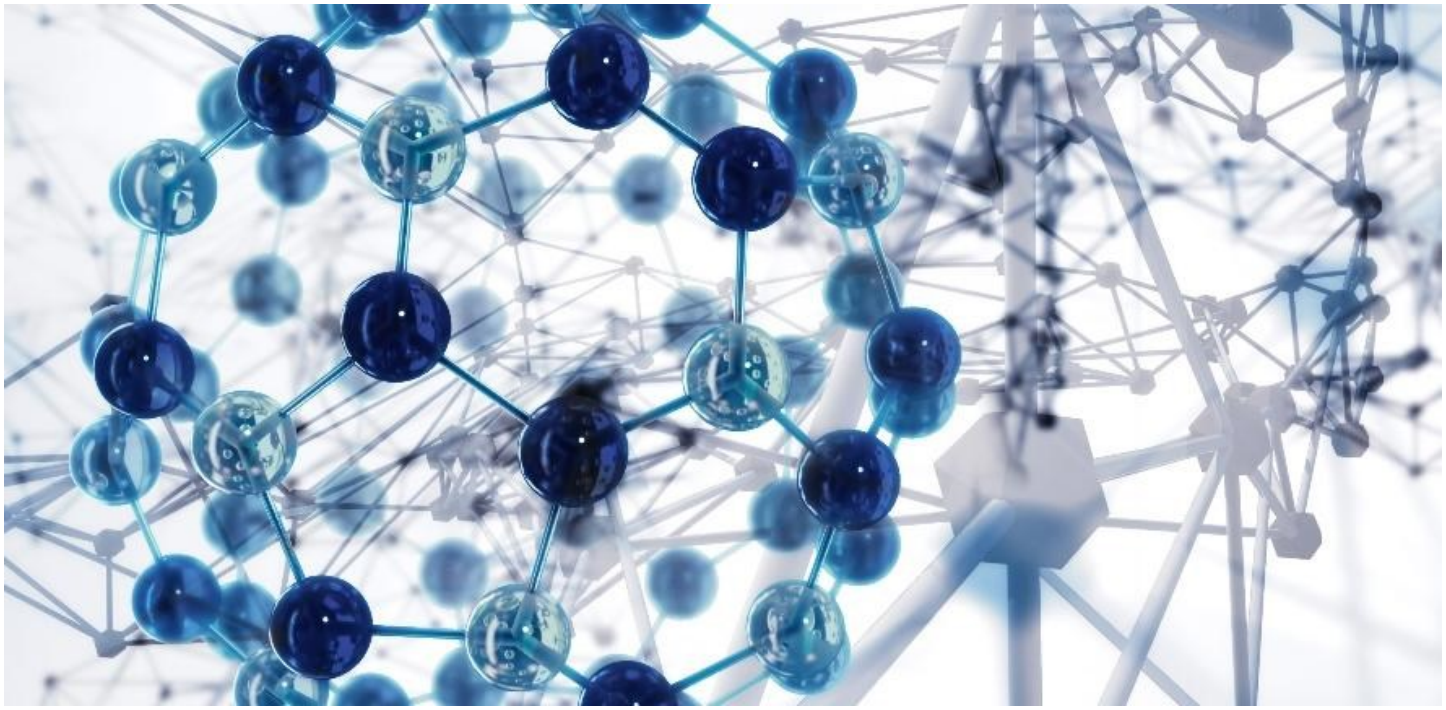
Electrochemical Multi-scale Science, Engineering and Technology

3.3 IRP3 — CAPRICORN

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

3.4 IRP4 — ICESO

Integrated Chemicals and Electrical Systems Operation



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

MUSCAT is led by PIs:

Prof Alexei LAPKIN (Cambridge)

Prof Yanhui YANG (NTU)

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Prof. Alexei Lapkin,

University of Cambridge

PI, IRP1

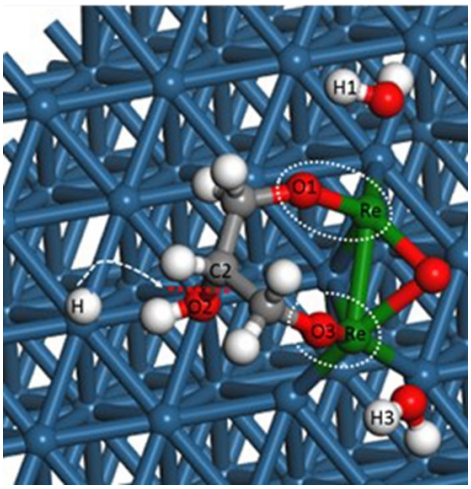
April 2017

3.1.1 IRP1 Research Overview

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

The work-packages currently in progress:

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



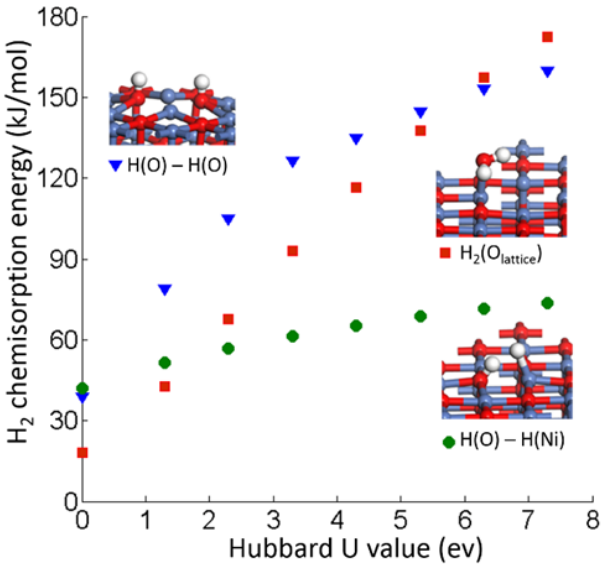
Over the reporting period between November 2016 and April 2017 IRP1 has initiated fundamental investigations into reactivity of catalysts to direct the design of better materials. This is reported in the studies by Dr Jithin J. Varghese on metal oxides and mixed oxides for chemical looping and for glycerol conversion to 1,3-propane diol, and Dr Yihu Dai on catalysts for CO_2 methanation. In material synthesis we expanded the work on complex mixed oxides systems by developing an innovative methodology for synthesis of precursor layered double hydroxides. This is reported in the work by PhD student Nick Jose and the Cambridge-based post-doc Dr Polina Yaseneva. In the carbon capture and fundamentals of adsorption, Dr Mark Purdue is completing installation and commissioning of the pilot plant, which will soon be used to generate new data on carbon capture from wet flue gas. In the multiscale modeling part of the project Dr Lianghqi Zhang have shown first results on the simulation of chemical looping reactor with chemical reaction, demonstrating a good match of predicted behaviour with the experimental data.

3.1.2 Update on work packages

WP 1.1: Chemical looping with advanced oxide carriers

Dr Jithin John VARGHESE (PO, NTU, IRP1) reported on his study of metal oxides and mixed metal oxides, extensively used in chemical looping processes, where they undergo repeated sequential cycles of reduction and oxidation. The reactivity of the metal oxides towards hydrocarbons like methane and the reducibility of the oxide surfaces are determined by the lattice oxygen binding strength on the surface. Large scale screening of reactivity/ reducibility of potential metal oxide/ mixed oxide systems can be done without tedious experimental investigations, using computer simulations of the hydrogen chemisorption on the surface. The hydrogen chemisorption energy values give an indirect estimate of the lattice oxygen binding strength. The H chemisorption energies on metal oxides can be calculated using the density functional theory (DFT) based modelling approach with the use of an additional corrective parameter referred to as the Hubbard U correction potential (DFT + U approach). Typically, this value which is different for different metal oxides is determined by fitting data on bulk properties of the material. Discrepancies in adsorption energies calculated using the Hubbard U values determined using bulk properties of the metal oxide are common. Thus, benchmarking the Hubbard U parameter for surface phenomena on metal oxides is essential for accurate and widespread use of computational screening tools.

With NiO as a prototype oxide, the effect of the Hubbard U parameter on hydrogen chemisorption energy on its various crystal facets is investigated using the DFT+ U approach. The H chemisorption energy is seen to differ by 30-120 kJ/ mol, depending on the adsorption configuration, with change in the Hubbard U value from 0 to 7.3 ev (see figure). Experiments are being planned to determine accurate adsorption energies and equilibrium hydrogen adsorption configurations to determine the apt Hubbard U value for modelling surface phenomena on NiO.



Variation of hydrogen chemisorption energy for three different configurations on NiO(100) surface as a function of Hubbard U parameter. Blue, red and white balls represent Ni, O and H atoms respectively.

Jingjing WANG's (PhD student, NUS, IRP1) research focused on Layered double hydroxides (LDHs) which show great potential in energy storage and conversion because of the flexibility in controls of their composition, structure and morphology. His objective is to prepare transition metal LDHs with novel structure or morphology and then convert them to other derives with more efficient performance in OER application and other catalytic applications. The methods used to prepare LDHs are co-precipitation and hydrothermal reactions. The functional material derivatives from LDH materials (or other supramolecular solid precursors) are transition metal oxides, sulphides and phosphides at the time being.

HUANG Jijiang (PhD student, NTU, IRP1) reported that Ni/Cu/Al LDHs (Layered Double Hydroxides) were prepared via hydrothermal syntheses and used as the precursors for binary Ni-Cu oxygen carriers. The LDH-derived solids were then investigated in chemical looping combustion (CLC) of methane with a laboratory fixed bed. This project was inspired by the carbon formation issue on the

oxygen carrier in CLC processes which will lower the overall carbon capture efficiency and may contribute to the deactivation of oxygen carriers. It was revealed that the carbon deposition can be limited with the binary Ni-Cu oxygen carriers compared with the ones based on single metal oxide. Furthermore, by taking the merits of the high reactivity of NiO for methane partial oxidation and the high oxygen mobility in CuO, enhanced reactivity was achieved in Ni-Cu oxygen carriers compared to the NiO-based oxygen carriers. The mixed metal oxides also presented superior stability in the redox cycles which was resulted from the reduced sintering effect. He plans to work on the catalysts development for oxidative dehydrogenation (ODH) of ethane/propane using the chemical looping concept.

Compared with steam cracking or catalytic dehydrogenation processes, ODH will not only enhance the alkane conversion by in-situ oxidation of hydrogen which removes the equilibrium constraints, but also convert the highly endothermic reaction (energy/carbon intensive) into a light exothermic reaction. Under a chemical looping scheme, the oxygen to remove the hydrogen will be provided by the lattice oxygen of the redox catalyst, inhibiting the non-selective reaction pathway. The explosion hazard will also be effectively reduced compared with the conventional gas phase ODH.

WP 1.2: CO_2 methanation and biomass conversion

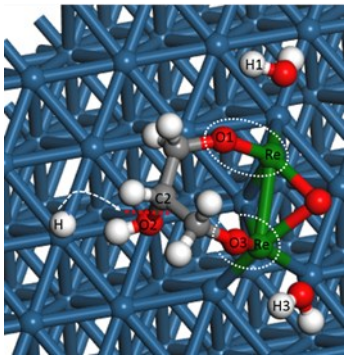
Bowen LI (PhD student, NUS, IRP1) has directed his research focus on designing stable and highly active integrated nanocatalysts (INCs) for dry reforming of methane. This dry reforming reaction takes two well-known greenhouse gases, methane and carbon dioxide, as feed while producing valuable syngas as product. A new morphologically controlled INC has been designed using Ni as the active metal and silica as support and it is now being tested for the above dry reforming reaction.

Dr Yihu DAI (SRF, NTU, IRP1) has systematically been investigating the role of metal-oxygen bridge Ru-O-Al bond in Ru/Al_2O_3 catalyst towards CO_2 methanation. Ru monolayers with all metal atoms directly interacting with the support are prevailing over 1% Ru/Al_2O_3, which exhibited a high selectivity to CO formation for the hydrogenation of CO_2 at ambient pressure. An increasing preference for methanation was observed on 2% and 3% Ru/Al_2O_3, over which a tendency for the formation of 3D Ru particles was observed. The dominant surface structure over Ru/Al_2O_3 catalysts with different loadings has been characterized by IRAS of CO adsorption. DFT calculations demonstrated that the energy barrier of RWGS is lower than the methanation on monolayers while CH_4 is preferentially produced on top sites of Ru_{35}/Al_2O_3. Moreover, a probable incorporation of the peripheral O of the metal particles into the final products of CO_2 hydrogenation was predicted by the theoretical calculations as an accompanied process by the RWGS at the metal-support interfaces, which was verified experimentally by isotope-labeled mass spectrometry experiments and EXAFS characterizations.

QIN Runze (PhD student,NUS, IRP1) has conducted several model reactions to test the activity of yttrium stabilized zirconium@$mSiO_2$ and the catalyst performance, activity and stability included, as super solid acid is superior. However, the acid site distribution and strength is to be investigated. Besides, for the copper silicate project, copper silicate nanotube hollow sphere@HKUST-1 (CuSiNT HS@HKUST-1) was successfully synthesized with enhanced stability and mechanical property compared to original metal-organic framework (MOF) material. Furthermore, CuSiNT HS@ZIF-8 and other MOFs can be synthesized by doping CuSiNT HS with other metals and in this way a universe catalyst system can be formed. The catalyst performance part work is still in progress.

Dr Jithin John VARGHESE (PO, NTU, IRP1), under supervision of Prof Samir Hemant MUSHRIF (Co-PI, NTu, IRP2, has been working on the catalytic conversion of glycerol, a low economic value by-product in the production of biodiesel, to value added chemicals like 1,2 and 1,3 Propane diols are desirable upgradation pathways. Production of the highly desired and valuable 1,3-propane diol (1,3 -PDO) from glycerol remains a challenge to the catalysis community due to limited yield and catalyst

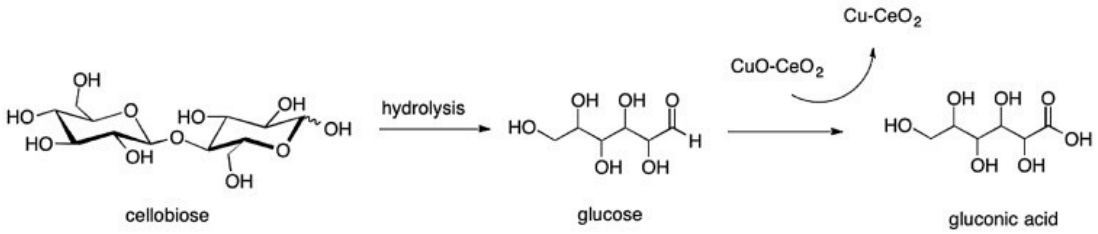
deactivation. Hence a comprehensive fundamental understanding of the catalytic reaction mechanism is vital to improve the selectivity and yield of 1,3-Propane diol from glycerol.



Representation of the 1,3 attachment of glycerol to hydroxylated Re_2O_3 on Ir (111) surface through the two primary hydroxyl Os (O1 and O3) subsequent to removal of H1 and H3. The 1,3 attachment allows preferential hydrogenolysis of the secondary OH (C2-O2 cleavage) which O1 and O3 are protected. The Re hydroxyls are eliminated as water molecules by H1 and H3. Blue, green, red, grey and white balls represent Ir, Re, O, C and H atoms respectively.

WOx modified Pt supported on alumina and ReOx modified Ir supported on SiO2 are among the most efficient catalysts reported till date in the aqueous phase high pressure hydrogenolysis reaction of glycerol to 1,3-PDO. The yield of 1,3-PDO although limited to 40%, is a lot higher on the ReOx/Ir/SiO2 catalyst compared to unmodified Ir/SiO2 catalyst where the selectivity is skewed towards 1,2-PDO with 8-10% conversion at best. Using density function theory (DFT) based computer simulations we suggest that the ReOx clusters dispersed on metallic Ir in the ReOx/Ir/SiO2 catalysts not only serves to anchor glycerol for subsequent reaction but also preferentially protects its primary OH group, preventing its removal during reaction (Fig.1). Activation barriers and energetics for the key steps in the conversion of glycerol to propane diols are being calculated for metallic Ir and ReOx modified Ir catalysts to explain the contrasting trends on these catalysts. The data from the DFT calculations will be used for Design of Experiments (DOE) modelling by members of Prof. Alexei Lapkin's group as well as to optimize the reaction parameters and catalytic system for better yield of 1,3 -PDO. The nature of metal-metal-oxide interface and interactions are being studied to guide in identifying other potential catalysts.

Dr Quang Thang TRINH (RF, NTU, IRP1), Prof YANG Yanhui (PI, NTU, IRP1) and Prof Samir H. MUSHRIF (Co-PI, NTU, IRP3) contributed into the study of the direct oxidation of cellobiose and glucose to gluconic acid on porous structured CuO-CeO_2 nanospheres. In this work, CuO-CeO_2 nanospheres were synthesized by a hydrothermal treatment and employed in the direct oxidation of cellobiose to gluconic acid. The presence of CeO_2 in the CuO-CeO_2 mixed-oxide composite results in a highly porous structure with enhanced surface area and also enhances the redox behaviour of the copper ions. The oxidation of cellobiose to gluconic acid on CuO-CeO_2 nanospheres proceeds by the hydrolysis of cellobiose via the Lewis acid sites of the catalyst, perpendicular end-on adsorption of glucose (cellobiose hydrolysis product) on surface lattice oxygen atoms of CuO-CeO_2 catalyst, abstraction of H-atoms from the formyl group, formation of gluconate and the hydrogenation of the gluconate to gluconic acid. ^{18}O-oxgen isotope labelled experiments coupled with XRD, HR-TEM, XPS, H_2-TPR and UV-Raman spectra analysis revealed that the lattice oxygen of the CuO framework, in the CuO-CeO_2 nanospheres composites, and not the lattice oxygen from CeO_2, was consumed during the oxidation reaction to form gluconic acid. ESI-MS and ^{13}C NMR analyses revealed that, indeed surface lattice oxygen was incorporated into glucose to form gluconic acid. The Cu^+ species finely dispersed on the surface of CeO_2, oxygen vacancies and lattice oxygen are advantageous for promoting the catalytic performance of the CuO-CeO_2 catalysts for the selective oxidation of cellobiose to gluconic acid. This work has been accepted for publication on Catalysis Today journal.



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

Dr Polina YASENEVA (RF, CAM, IRP1) has been working on circular economy ideology which advances development of novel ways of production of high value chemical molecules, from feedstocks that used to be regarded as waste. Waste of food or paper industries can be used as a potential source of terpenes which, in turn, can be converted in a range of intermediates, leading to functional polymers, to pharmaceuticals and other high-value products. However, it is often not obvious at a glance which potential process route is more sustainable and cost effective. Life cycle assessment (LCA) is a recommended methodology for the design of bio-based products and production processes for the emergent green and circular economy. This stems from the ability of LCA to explicitly evaluate the impacts from the change of feedstocks.

Dr Polina YASENEVA (RF, CAM, IRP1) developed a generic decision support framework for developing greener processes, which combines economic and environmental performance criteria using the example of production iso-carveol from two potential waste feedstocks (paper and food industries waste). Iso-carveol is an essential intermediate for producing perillyl alcohol, which has applications in flavour and fragrance industry, but more importantly, it has anticarcinogenic activity. In this study she considered only synthesis of iso-carveol from bio-waste derived limonene *via* epoxidation followed by ring opening. In the developed framework a state-of-the-art process modelling tool (gPROMS®) is used, allowing model development and statistical validation, and easy model maintenance; LCA is performed in a widely used commercial tool (Umberto®) in which instead of a gate-to-gate model the gPROMS model evaluation results are used. The two environments generate performance data that are then used for optimisation.

Comparison of environmental performance and cost effectiveness of terpenes derived from paper industry waste and from orange peels has shown that the former process is beneficial over the latter in both cases. Dr Polina YASENEVA (RF, CAM, IRP1) reported that this work is now being finalised as a publication which shall be submitted during March 2017.

YAN Yong (PhD student, NTU, IRP1) reported that two Y containing precursor were used to prepare Ni supported on Y_2O_3 catalysts, one obtained from precipitation that was identified as $Y_4O(OH)_9(NO_3)$ and the other one of Y_2O_3 calcined from the former. The resulted samples after the Ni loading via traditional impregnation method are attempted for CO_2 methanation. Catalytic test results suggested that the one prepared from $Y_4O(OH)_9(NO_3)$, denoted as Ni/Y_2O_3 series, with the optimal Ni loadings of 10%, demonstrated a superior catalytic performance for CO_2 hydrogenation into CH_4 at ambient pressure. Characterizations by CO_2-TPD and H_2-TPR revealed that using $Y_4O(OH)_9(NO_3)$ as the precursor favored a desired interaction between Ni and supports, resulting in the formation of abundant medium basic sites that highly efficient for the active adsorption of CO_2 . Moreover, the reaction mechanisms studied by *in situ* DRIDTS exhibited that the carbonates species formed by CO_2 adsorption was readily converted into formates regardless of the support precursor used. However, the further conversion of formates into CH_4 was clearly more favored over Ni/Y_2O_3, if compared to the reference catalyst that prepared from Y_2O_3 directly.

CAO Li Wei (RA, NTU, IRP1) focused on catalytic hydrogenolysis of glycerol to 1,3-propandiol. As glycerol is one of major by product of biodiesel production, transforming it into high value-added products is essential. In order to reach the goal, which is increasing the selectivity of 1,3-propandiol over 1,2-propandiol, a catalyst system was selected for collecting initial data to understanding and analysing the mechanism of the hedrogenolysis reaction. Computational calculation for the system was conducted based on density functional theory (DFT), and the experimental part will be run soon.

Dr Chao HE (RF, NTU, IRP1) has been carrying out experiments on dry reforming of methane and catalytic gasification of solid wastes with enhanced tar cracking using fluidized gasifier.

WP 1.3: New materials and MOFs

Project 1. Doped carbon-based material for CO_2 capture: Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1)

Carbon-based material is a type of promising sorbent for CO_2 uptake owing to low-cost, good durability and relatively mild regeneration condition. However, its efficiency is limited by the insufficient sorption sites and underdeveloped structure. Herein, we are preparing a series of porous doped carbon by pyrolysis of polymer precursor under inert gas for CO_2 uptake. Porous carbon with different morphologies (e.g., nanotubes, nanorods, nanospheres, and nano-networks) can be prepared by using polymers with different morphologies. Besides, by the combination of different monomers for the polymerization, mono-, bi-, and tri-doped carbon matrixes (e.g., with N, P, and S dopants) can be systematically obtained. Furthermore, the amount of dopants in the porous carbon can be facilely regulated via using different pyrolysis temperatures. Owing to their porous structures, large surface areas and increased active sites, these porous carbon materials display high sorption capacities at room temperature and 1 bar CO_2.

Project 2. Layered-double hydroxides (LDH)-based materials for CO_2 capture: Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1)

Layered-double hydroxides (LDHs) can serve as promising CO_2 sorbents for operation at intermediate-temperatures. In this project, we have prepared several kinds of LDH via an one-pot solvothermal route for CO_2 sorption. During synthesis, through changing the preparation conditions (e.g., solvent, temperature, and stirring mode), LDHs with different morphologies (i.e., flower-like spheres and thin nanosheets) can be obtained. Besides, by changing a certain amount of transition metal precursors, the corresponding transition-metal-doped MgAl-LDH can be facilely prepared. The resultant LDH materials have shown excellent CO_2 capture capacity at 200 °C and 1 bar CO_2.

YEO Jun Wen (PhD Student, NUS, IRP1) has directed his research effort towards exploring the above thesis. An overwhelming majority of literature pertaining to MOF synthesis makes use of metal salts in solutions as starting materials. On the other hand, metals in the solid state have been barely explored and their viability is as yet unknown in the scientific community.

A series of reactions were carried out, which can be broadly categorised into two groups:

- The first group of reactions involve the Galvanic displacement in MOFs by direct addition of Zinc solid metal to HKUST-1. In this series of experiments, the transmetallation in HKUST-1 MOF from Copper to Zinc is explored with galvanic displacement as the main driving force. Zinc solid is added to a dispersed solution of HKUST-1 and allowed to react at various temperatures.
- The second group of experiments In-situ synthesis of Cu@Zn-BTC with Zinc, Copper Chloride and Trimesic acid as starting reagents. In contrast to the above experiments where zinc metal was added to a ready-made HKUST-1 MOF, this series of experiments attempts to synthesize MOF from a solution containing metal powder, metal salt and organic linker, all added simultaneously.

He reported that interesting morphologies have been observed but more reactions are carried out to obtain more monodisperse and homogeneous product morphology.

Flow synthesis and characterization of hydrotalcites materials

Hydrotalcites (HTs) are naturally occurring layered double hydroxides (LDH) similar to brucite, where M^{2+} and M^{3+} cations form stacked sheets, and water molecules and anions (A^-) fill the inter-layers. Naturally occurring HTs consist of Mg^{2+} and Al^{3+}, while synthetic HTs can be prepared with varying concentrations of a number of transition metal cations with compatible ionic radii. HTs are increasingly used as adsorbents, catalytic supports and heterogeneous catalysts. One of the most attractive features of HTs as materials is the tunability of electronic and morphological properties, which can be used to optimize adsorption, catalytic activity, selectivity and lifetime.

Dr Polina YASENEVA (RF, CAM, IRP1) reported that in her study a series of hydrotalcite materials doped with different transition metals (Fe, Ni, Co, etc) was synthesized by a novel flow synthesis method which enabled to quickly make materials with reproducible properties. The effect of aging temperature on material's properties was studied. Structural properties of synthesized HTs were characterized by XRD, Raman and TEM, thermal properties – by TGA and morphological properties – by N_2 adsorption. It has been shown that doping of MgAl HT with other metals, even though with similar radii, greatly affect materials properties, especially surface area and porosity. This creates a potential for production of materials with tailor-made properties. This work is done in collaboration with George Washington University, USA. It is currently being finalised for publication, which should be submitted during March-April 2017.

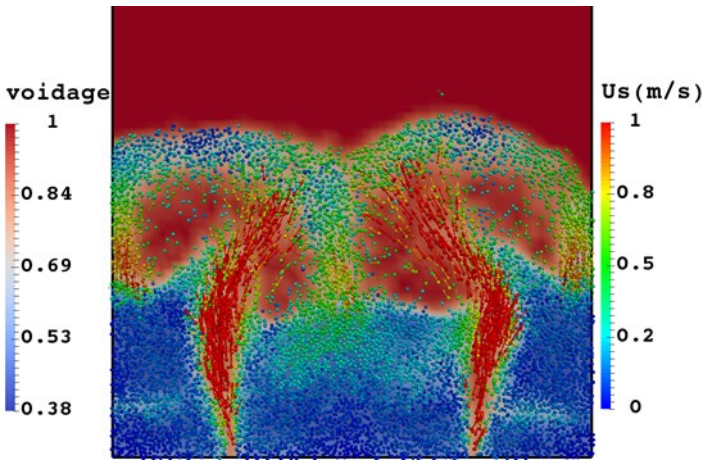
Nicholas Antonio JOSE (PhD student, CAM, IRP1) reported on his PhD project which focuses on the development of technologies to improve the design and synthesis of catalysts and adsorbents. Early October 2016, a high shear flow reactor for the continuous synthesis of layered double hydroxides (LDH) was built. The first version of the reactor can mix two streams on the order of a millisecond, as determined by an iodide reduction test reaction. Using this reactor, small crystalline LDH platelets as small as 10 nm have been produced, with minimal clogging. Current studies are investigating the dependence of particle size and crystallinity on the hydrodynamics of the reactor, using a combination of computational fluid dynamic modelling and experimental studies to glean further insights into the mechanism of LDH formation. Future studies involve partnering with others in CARES who utilize LDH-based materials to evaluate the performance enhancement these materials may have. Different material systems, such as metal-organic frameworks, will also be explored.

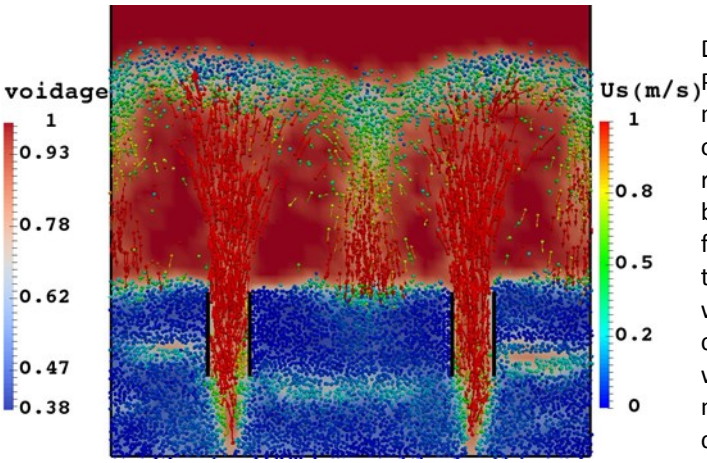
Prof Cate DUCATI (Co-PI, CAM, IRP1) reported that the research team has worked on adapting the design of continuous liquid flow TEM holders for in situ characterization of nanoparticles, in view of applications in catalysis and electrochemistry. With funding provided through Royce Instrument fund, we are in the process of purchasing a Protochips TEM holder (compatible with FEI microscopes), which will strongly enhance the capability for nanoscale characterization of working electrodes.

WP 1.4: Multi-scale modelling

Dr. Shiliang Yang (RF, IRP1, NTU) numerically studied the effect of draft plates and the corresponding length on the bed hydrodynamics and inter-chamber interactions in the two-chamber spout-fluid bed via CFD-DEM, as this kind of apparatus has been frequently adopted in the chemical looping combustion. Specifically, the gas and solid motion were resolved at the computational cell level and particle-scale level, respectively. The work demonstrated that the insertion of draft plates into the multi-chamber spout-fluid bed clearly alters the bed hydrodynamics and inter-chamber interaction of the system, which inevitably influences the system performance. In the practical operation, the design and optimization of the draft plates in the multi-chamber spout-fluid bed should first ensure stable spouting behavior, after which optimization can be carried out based on the specific requirements of the application.

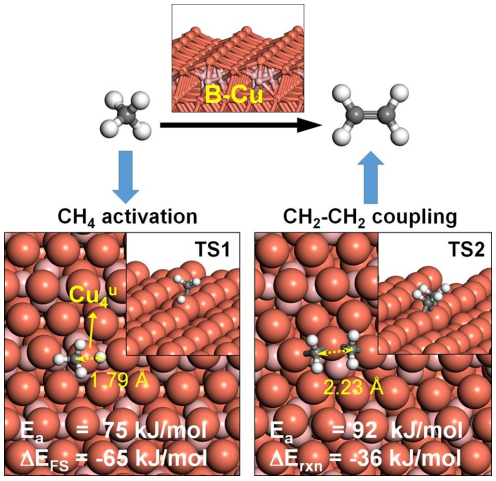
Dr. Shiliang Yang (RF, IRP1, NTU) studied and reported on: Effect of draft plate length in a spout-fluid bed investigated via CFD-DEM, Focus on impact on spouting stability and inter-chamber interaction, Interaction of bubbles with spout gives unfavorable dancing spout phenomenon, Draft plates enhance solid turbulent intensity in fountain and vertical dispersion in spout, Draft plate length has a significant influence on inter-chamber interaction.





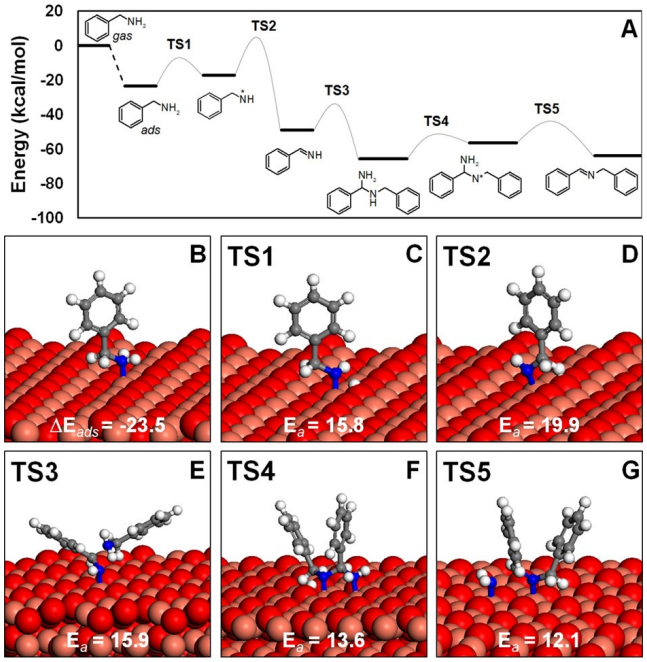
Dr. Liangqi ZHANG (RF, NTU, IRP1) and under the supervising of Prof. Jiawei CHEW (Co-PI, NTU, IRP1) has been working on the mathematical description of the fluid dynamics with the coupling of the chemical reactions. Firstly, Methanation reactor modelling is realized by applying a simplified Two-Phase fluidized-bed model based on the mass conservation in the reaction process, with the fluid variables given as empirical relations. It is pleasing to find that the resulting component concentration distributions accord well with the experimental predictions. However, for more reliable computations, the momentum and the energy conservations, as well as detailed particle and the surrounding fluid dynamics information, should be included for more realistic description. Secondly, complicated boundary condition implementations in CFD, with complicated mathematical descriptions (Neumann and Robin conditions) as well as geometrical complex boundary, are also under investigation, and the surface reaction, adsorption and conjugated internal interfacial conditions for heat and mass transfer in reaction systems are the possible applications. Thirdly, an overall understanding for the application of the continuum hydrodynamic framework to the micro-scale and nano-scale gaseous flows, as well as the mass and heat transfer phenomenon, is developed, the numerical description of the adsorption processes of CO2 in micro- and nano- channels is the further application.

Dr Quang Thang TRINH (RF, NTU, IRP1), Prof YANG Yanhui (PI, NTU, IRP1) and Prof Samir H. MUSHRIF (Co-PI, NTU, IRP3) conducted the design of efficient catalyst for the non-oxidative coupling of methane using computational simulation. In this study, the structure, activity and selectivity of a novel sub-surface monolayer boron doped Copper (B-Cu) catalyst were comprehensively investigated using density functional theory (DFT) calculations. Boron binds strongest at the subsurface octahedral site of Cu and the thermodynamic driving force for the diffusion of B from an on-surface to the sub-surface position in Cu is stronger than that for the experimentally synthesizable B-Ni (subsurface boron in Nickel) catalyst, providing a proof of concept for the experimental synthesis of this novel catalyst. Additionally, the first-principles computed free energy of the reaction to form B-Cu from boron precursor and Cu is also favorable. The binding energy of B in the subsurface layer increases with B coverage, and reaches the maximum at a monolayer coverage. The incorporation of a monolayer subsurface B into Cu make this B-Cu catalyst can activate methane C-H bonds efficiently, with an activation barrier for the first C-H dissociation of only 75 kJ/mol. Generated surface adsorbed CH_3^* species subsequently undergo dehydrogenation to form the stable CH_2^* species, which is a precursor for the C-C coupling reaction. The C-C coupling reaction, resulting in the for-



mation of surface adsorbed ethylene, is both thermodynamically and kinetically more favourable than the competitive dehydrogenation of CH_2^* to CH^* and subsequently to C^*, suggesting that methane could be converted to ethylene with high selectivity on the B-Cu catalyst. Hence, we predict that Cu doped with a monolayer subsurface boron can be a potential catalyst for the methane coupling reaction to form ethylene. The promotional effect of the sub-surface monolayer boron in enhancing the activity of Cu is due to the creation of corrugations on the Cu surface and the charge transfer from B to Cu, contributing synergistically. This work has been published on the Journal of Physical Chemistry C.

In addition, Dr Quang Thang TRINH (RF, NTU, IRP1), also performed Density Functional theory calculations to explain the shape-controlled oxidative coupling of aromatic amines on CuO nanocatalyst, which recently appeared to be the very good catalyst in both Biomass conversion and Methane activation. Different morphologies of CuO nanocatalyst were synthesized include the flake, dandelion-microsphere, and short-ribbon shapes and interestingly, these different CuO nanostructures exhibited different activity in the catalytic oxidative coupling reaction of aromatic amines to form imines, i.e., highly valuable building blocks for a variety of molecules of pharmaceutical significance. Our extensive DFT calculations were able to elucidate the detailed mechanism of the oxidative coupling reaction on the CuO surface for the first time and also helped us understand the different catalytic trend of different CuO morphologies in terms of how significantly the active facets are exposed. The research outcomes in this study provide a compelling molecular rationale for the structure-performance relationship of CuO nanostructures. The synergistic nature of our paper, based on experimental and computational studies, provides a solid foundation for future studies and applications of CuO-based heterogeneous catalysts.



Work Package 1.5: Fundamentals of adsorption and PSA

Dr Mark John PURDUE (RF, NUS, IRP1) carried out a review of available isotherm modelling approaches to characterize wet flue gas adsorption.. Mathematical modelling of wet flue gas adsorption on Zeolite 13X using data obtained from Grand Canonical Monte Carlo molecular simulations. This work involved the incorporation of lateral molecular interactions in the adsorbate phase on a heterogeneous surface and designed to be compatible with process simulations. Regression analysis of water vapour isotherms on Zeolite 13X was also considered in detail. Further molecular simulation data was obtained for trace levels of moisture and will be incorporated into the wet flue gas isotherm modelling work. This provides scope for when gas dehydration is performed in industry and accounts for the high sensitivity of Zeolite 13X to moisture. A vacuum swing adsorption experimental rig is currently being installed in the pilot room of the CARES laboratory. Dynamic column

breakthrough experiments using commercial Silica Gel and Zeolite 13X can begin once the rig is commissioned.

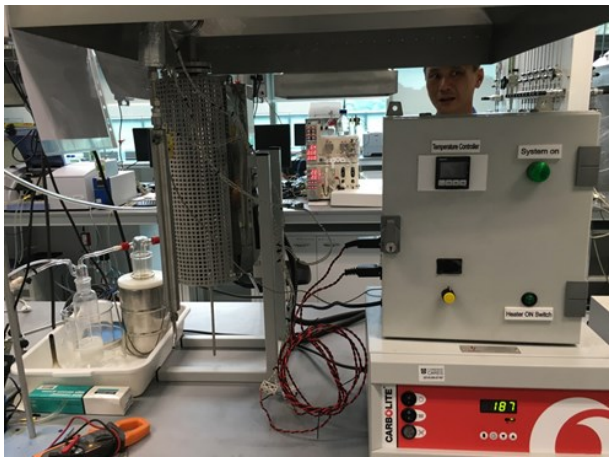
Prerna GOYAL (Phd Student, NUS, IRP1) conducted a preliminary literature review on carbon capture from flue gases using Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) processes The performance of a high potential metal organic framework adsorbent, UTSA-16, for adsorption of CO_2 in dry flue gas was further reviewed. This adsorbent was previously found to meet the US Department of Energy purity/recovery targets of 95/90%, respectively, while simultaneously obtaining a Levelized Cost of Electricity of $112/MWh in a 6 step VSA process using an evacuation pressure of 0.05 atm.

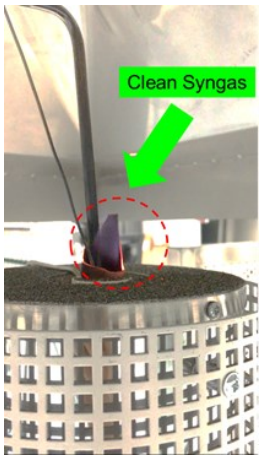
She reported that Grand Canonical Monte Carlo simulations of wet flue gas adsorption on UTSA-16 will be carried out using RASPA molecular simulation software to test the sensitivity of this adsorbent in the presence of moisture. Depending upon the results, these simulations can provide multicomponent equilibrium data for the development of a wet flue gas adsorption isotherm model.

In addition, Prerna GOYAL (Phd Student, NUS, IRP1) has developed an understanding of the new pilot plant rig in the CARES laboratory in order to become familiar with performing adsorption experiments. Dynamic Column Breakthrough experiments will initially be performed on commercial adsorbents for comparison with simulations using adsorption and desorption steps with dry flue gas. These experiments can subsequently be extended to the case of wet flue gas adsorption. For this purpose, Prerna GOYAL (Phd Student, NUS, IRP1) has initiated the development of process simulations of CO_2 capture from wet flue gas using MATLAB programming. She has also been working on implementing a process model using the finite volume discretization method with the weighted essential non oscillatory scheme to solve time-dependent ordinary differential equations that describe adsorption column material and energy balances.

Other Activities and Achievements

- Professor Hua Chun Zeng (PI, NUS, IRP1) has given lectures in the following two international conferences:
  - Feature Presentation, "Integrated Nanomaterials for Heterogeneous Catalysis", International Conference on Catalysis and Chemical Engineering (CCE-2017; Theme Title: Advances and Challenges in Applied Catalysis), Baltimore, USA, February 22-24, 2017.
  - Keynote Speaker, "Design and Synthesis of Integrated Nanocrystals", The 9th Singapore International Chemical Conference (SICC-9), Singapore, December 11-14, 2016.
- Professor Hua Chun Zeng (PI, NUS, IRP1) is securing an industrial grant with a locally registered foreign company (the company will pay a cash contribution at S$225,000, excluding contribution of manpower cost).
- Dr. Chao He (RF, NTU, IRP1) has followed up with Chevon International Pte Ltd to develop potential business partnership and further attract industrial fund for CARES.
- Dr. Chao He (RF, NTU, IRP1) has been awarded 2015 Applied Energy Award by Applied Energy under Elsevier Publisher.
- Dr. Chao He (RF, NTU, IRP1) has initiated the collaboration with CREATE-E2S2 and prepared intra-CREATE proposal on "**Integrated Gasification Chemical Looping Combustion (IGCLC) System for Bio-waste Management and Cost-effective CO_2 Capture**"
- Mark John PURDUE (RF, NUS, IRP1) presented at AIChE conference: https://www.aiche.org/conferences/aiche-annual-meeting/2016/proceeding/paper/649c-molecular-simulations-wet-flue-gas-adsorption-on-13x-zeolite





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.

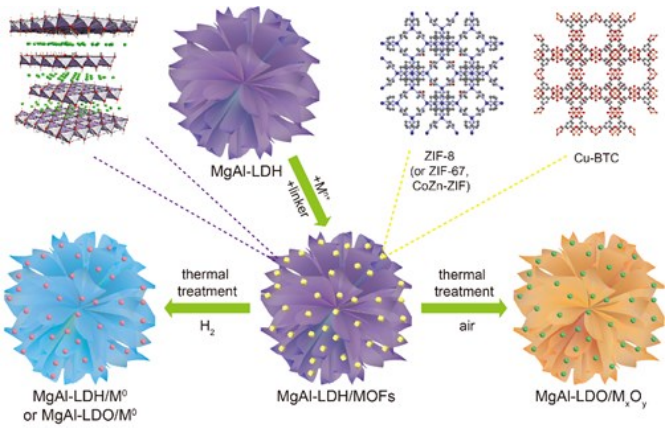
Immobilization of Metal-Organic Frameworks Nanocrystals for Advanced Design of Supported Nanocatalysts

P. Li and H.C. Zeng

DOI: 10.1021/acsami.6b11775

Abstract:

In recent years, metal-organic frameworks (MOFs) have been employed as heterogeneous catalysts or precursors for synthesis of catalytic materials. However, conventional MOFs and their derivatives usually exhibit limited mass transfer and modest catalytic activities owing to lengthy diffusion path and less exposed active sites. On the other hand, it has been generally conceived that nanoscale MOFs are beneficial to materials utilization and mass transport, but their instability poses a serious issue on practical application. To tackle above challenges, herein we develop a novel and facile approach to design and synthesis of nanocomposites through *in-situ* growth and directed immobilization of nanoscale MOFs onto layered double hydroxides (LDH). The resulting supported nano-MOFs inherit advantages of pristine MOF nanocrystals, and meanwhile gain enhanced stability and workability under reactive environments. A series of uniform nanometer-sized MOFs, including monometallic (ZIF-8, ZIF-67 and Cu-BTC) and bimetallic (CoZn-ZIF), can be readily synthesized onto hierarchically structured flowerlike MgAl-LDH supports with high dispersion and precision. Additionally, the resultant MgAl-LDH/MOFs can serve as a generic platform to prepare integrated nanocatalysts *via* controlled thermolysis. Knoevenagel condensation and reduction of 4-nitrophenol (4-NP) are used as model reactions for demonstrating the technological merits of these nanocatalysts. Therefore, this work elucidates that the synthetic immobilization of nanoscale MOFs onto conventional catalyst supports is a viable route to develop integrated nanocatalysts with high controllability over structural architecture and chemical composition.



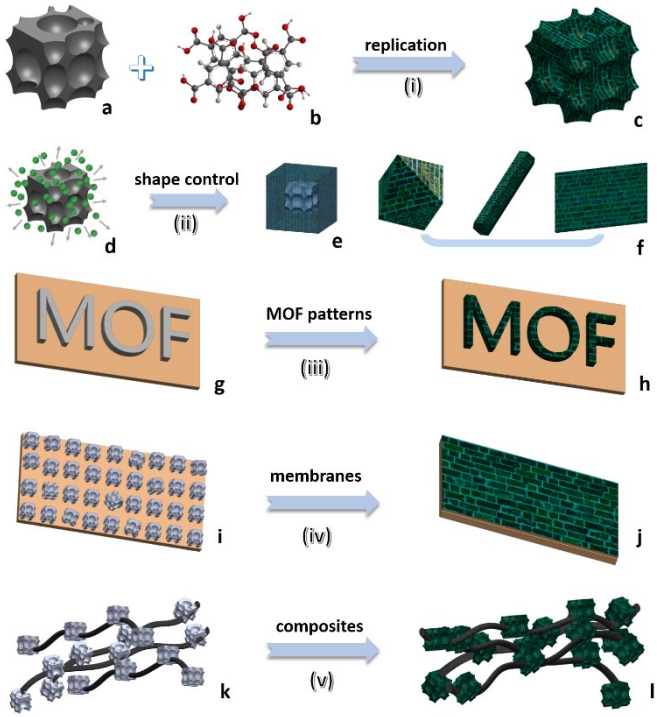
Synthesis procedure for hierarchical-structured MgAl-LDH/MOFs nanocomposites.

Alternative Synthetic Approaches for Metal–Organic Frameworks: Transformation from Solid Matters

G.W. Zhan and H.C. Zeng

Abstract:

Developing economic and sustainable synthetic strategies for metal–organic frameworks (MOFs) is imperative for promoting MOF materials into large scale industrial use. Very recently, an alternative strategy for MOF synthesis by using solvent-insoluble "solid matters" as cation reservoir and/or templates has been developed to accomplish this goal, in which the solid matters often refer to metals, metal oxides, hydroxides, carbonates, and so forth, but excluding the soluble metal salts which have been prevailingly used in MOF synthesis. Although most of pioneering activities in this field have just started in the past 5 years, remarkable achievements have been made covering the synthesis, functionalization, positioning, and applications. A great number of MOFs in powder form, thin-films, or membranes, have been prepared through such solid-to-MOF transformations. This field is rapidly developing and expanding, and the number of related scientific publications has strikingly increased over the last few years. The aim of this review is to summarise the latest developments, highlight the present state-of-the-art, and also provide an overview for future research directions.



Conceptual illustrations summarising various approaches used in conversion of solid matters of MOFs: (a) solid matters, (b) organic ligands, (c) replicated MOF, (d) solid matters with releasing metal ions (small green spheres), (e) core-shell structured solid@MOF, (f) shape-controlled MOFs, (g) solid matter patterns on substrate, (h) MOF assembly on substrate, (i) pre-allocation of solid matters on substrate, (j) MOF membrane or film on the substrate, (k) pristine solid matter composite, and (l) MOF-containing composite

Metal–Hydroxide and Gold–Nanocluster Interfaces: Enhancing Catalyst Activity and Stability for Oxygen Evolution Reaction

*Yao Zhou and Hua Chun Zeng**

DOI: 10.1021/acs.jpcc.6b11102

Abstract:

By engineering the interaction between the transition metal ions (M = Mn^{2+}, Co^{2+}, and Ni^{2+}) and the nanorod-shaped assemblages of Au nanoclusters (AuNCs), a series of tubular AuNCs@$M(OH)_2$ core–shell nanocomposites are produced in which numerous AuNCs are embedded beneath a thin layer of metal hydroxide with thickness below 4 nm and where the AuNCs within the same assemblage are partially connected with each other. Because of the synergistic effects from the abundant presence of the AuNCs–$M(OH)_2$ interfaces, the AuNCs@$M(OH)_2$ (M = Co and Ni) nanocomposites demonstrate evidently enhanced activity for oxygen evolution reaction (OER) in alkaline condition. Overpotentials of 0.350 and 0.375 V have been obtained at the current density of 10 mA cm^{-2} in 0.1 M KOH for the AuNCs@$Co(OH)_2$ and AuNCs@$Ni(OH)_2$, respectively. And at the overpotential of 0.42 V, the current density of AuNCs@$M(OH)_2$ (M = Co and Ni) nanocomposites is more than 10 times of those generated by their respective metal hydroxides. Compared with monophasic transition metal hydroxides, the AuNCs@ $M(OH)_2$ nanocomposites, especially the AuNCs@$Ni(OH)_2$, possess excellent OER catalytic stability.

Alternative kinetic theory based lattice Boltzmann model for incompressible axisymmetric flows

Zhang L, Yang S, Zeng Z, Yao L, Chew JW

doi.org/10.1016/j.camwa.2016.09.028

Abstract:

Based on the axisymmetric Boltzmann equation, an incompressible lattice Boltzmann model for axisymmetric flows is proposed within the framework of the kinetic theory based model developed by Guo et al. (2009). While retaining the advantages of the Guo et al. (2009) model in terms of the solid physics basis and simple source terms involving no gradient calculations, the present model further improves the numerical stability, and reduces compressibility errors and computational requirements. Armed with the assumption that the fluid density is a constant and thus the fluid pressure has no direct relation with the density, the incompressibility conditions are realized by applying the Hermite expansion. Then, the present model employs a novel way of calculating the fluid pressure which is derived from the modified second-order moment equation. Additionally, based on the regularized lattice BGK (RLBGK) model, an extra relaxation parameter pertaining to the ghost mode is introduced to enhance the numerical stability of the present model. The accuracy and applicability of the present model are verified by both the Chapman–Enskog theoretical analysis and numerical validations. It is demonstrated via well-acknowledged test cases that the present model is accurate and reliable for incompressible axisymmetric flows, and is able to effectively reduce the compressibility errors vis-à-vis the Guo et al. (2009).

The thermodynamics analysis and experimental validation for complicated systems in CO_2 hydrogenation process

Jia Chunmiao, Gao Jiajian, Dai Yihu, Zhang Jia, Yang, Yanhui

doi.org/10.1016/j.jechem.2016.10.003

Abstract:

Catalytic conversion of CO_2 into chemicals and fuels is an alternative to alleviate climate change and ocean acidification. The catalytic reduction of CO_2 by H_2 can lead to the formation of various products: carbon monoxide, carboxylic acids, aldehydes, alcohols and hydrocarbons. In this paper, a comprehensive thermodynamics analysis of CO_2 hydrogenation is conducted using the Gibbs free energy minimization method. The results show that CO_2 reduction to CO needs a high temperature and H_2/CO_2 ratio to achieve a high CO_2conversion. However, synthesis of methanol from CO_2 needs a relatively high pressure and low temperature to minimize the reverse water–gas shift reaction. Direct CO_2 hydrogenation to formic acid or formaldehyde is thermodynamically limited. On the contrary, production of CH_4 from CO_2 hydrogenation is the thermodynamically easiest reaction with nearly 100% CH_4 yield at moderate conditions. In addition, complex reactions with more than one product are also calculated in this work. Among the considered carboxylic acids (HCOOH, CH_3COOH and C_2H_5COOH), propionic acid dominates in the product stream (selectivity above 90%). The same trend can also be found in the hydrogenation of CO_2 to aldehydes and alcohols with the major product of propionaldehyde and butanol, respectively. In the process of CO_2 hydrogenation to alkenes, low temperature, high pressure, and high H_2 partial pressure favor the CO_2 conversion. C_4H_6 is the most thermodynamically favorable among all considered alkynes under different temperatures and pressures. The thermodynamic calculations are validated with experimental results, suggesting that the Gibbs free energy minimization method is effective for thermodynamically understanding the reaction network involved in the CO_2 hydrogenation process, which is helpful for the development of high-performance catalysts.

Integrated Experimental and Theoretical Study of Shape-Controlled Catalytic Oxidative Coupling of Aromatic Amines over CuO Nanostructures

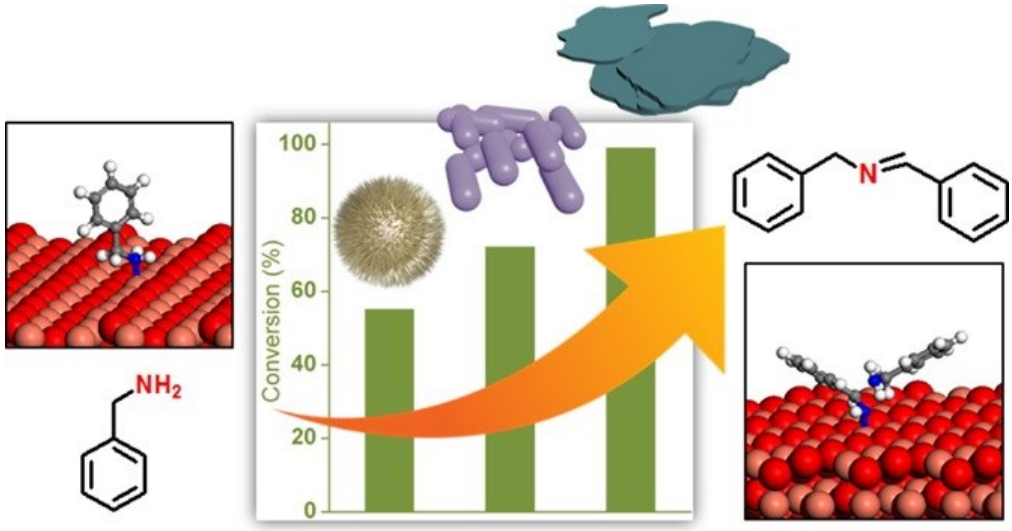
Ramana Singuru, Quang Thang Trinh, Biplab Banerjee, Bolla Govinda Rao, Linyi Bai, Asim Bhaumik, Benjaram Mahipal Reddy, Hajime Hirao,* John Mondal**

DOI: 10.1021/acsomega.6b00331

Abstract:

We have synthesized CuO nanostructures with flake, dandelion-microsphere, and short-ribbon shapes using solution-phase methods and have evaluated their structure–performance relationship in the heterogeneous catalysis of liquid-phase oxidative coupling reactions. The formation of nanostructures and the morphological evolution were confirmed by transmission electron microscopy, scanning electron microscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, energy-dispersive X-ray spectroscopy, elemental mapping analysis, and Fourier transform infrared spectroscopy. CuO nanostructures with different morphologies were tested for the catalytic oxidative coupling of aromatic amines to imines under solvent-free conditions. We found that the flake-shaped CuO nanostructures exhibited superior catalytic efficiency compared to that of the dandelion- and short-ribbon-shaped CuO nanostructures. We also performed extensive density functional theory (DFT) calculations to gain atomic-level insight into the intriguing reactivity

trends observed for the different CuO nanostructures. Our DFT calculations provided for the first time a detailed and comprehensive view of the oxidative coupling reaction of benzylamine over CuO, which yields *N*-benzylidene-1-phenylmethanamine as the major product. CuO(111) is identified as the reactive surface; the specific arrangement of coordinatively unsaturated Cu and O sites on the most stable CuO(111) surface allows N–H and C–H bond-activation reactions to proceed with low-energy barriers. The high catalytic activity of the flake-shaped CuO nanostructure can be attributed to the greatest exposure of the active CuO(111) facets. Our finding sheds light on the prospective utility of inexpensive CuO nanostructured catalysts with different morphologies in performing solvent-free oxidative coupling of aromatic amines to obtain biologically and pharmaceutically important imine derivatives with high selectivity.



Sub-Surface Boron-Doped Copper for Methane Activation and Coupling: First-Principles Investigation of the Structure, Activity, and Selectivity of the Catalyst

Quang Thang Trinh, Arghya Banerjee, Yanhui Yang, Samir H. Mushrif

DOI: 10.1021/acs.jpcc.6b09236

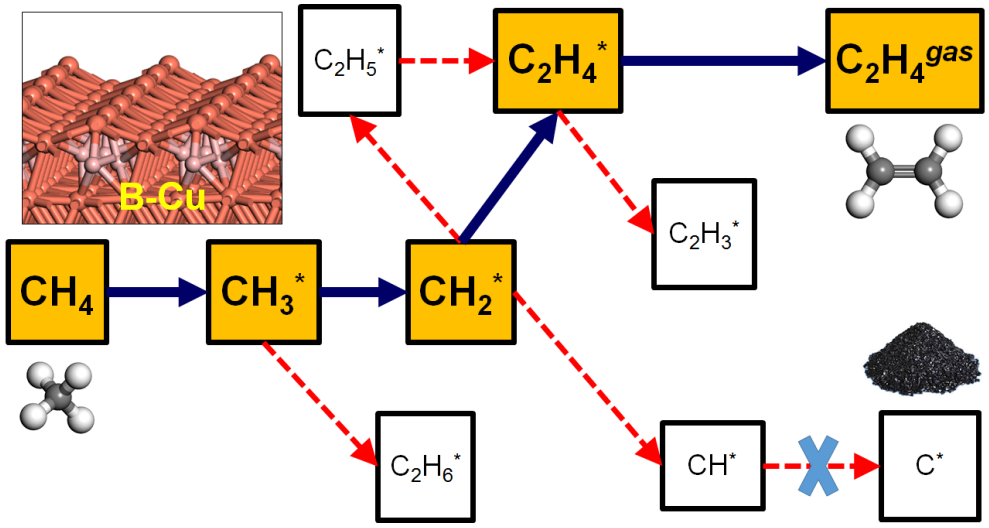
Highlights:

- Elucidate the most stable configuration of boron when doped in Cu, predict the sub-surface monolayer boron doped copper (B-Cu) as a novel catalyst.
- Provide a *proof of concept* for the experimental synthesis of the novel catalyst.
- Demonstrate the significant superior activity of the catalyst for methane activation and provide an explanation for it.
- Evaluate multiple competitive pathways for methane conversion and suggest the B-Cu catalyst to be an excellent potential candidate for obtaining high selectivity of ethylene.

Abstract:

Copper (Cu) is a commercial catalyst for the synthesis of methanol from syngas, low-temperature water gas shift reaction, oleo-chemical processing, and for the fabrication of graphene by chemical vapor deposition. However, high barriers for C-H bond activation and the ease of formation of carbon/graphene on its surface limits its application in the utilization and conversion of methane to bulk chemicals. In the present paper, using first principles calculations, we predict that Cu catalyst doped with a monolayer of subsurface Boron (B-Cu) can efficiently activate the C-H bond of Me-

thane and can selectively facilitate the C-C coupling reaction. Boron binds strongest at the subsurface octahedral site of Cu and the thermodynamic driving force for the diffusion of B from an on-surface to the sub-surface position in Cu is stronger than that for the experimentally synthesizable B-Ni (subsurface boron in Nickel) catalyst, providing a proof of concept for the experimental synthesis of this novel catalyst. Additionally, the first-principles computed free energy of the reaction to form B-Cu from boron precursor and Cu is also favorable. The presence of the monolayer subsurface B in Cu creates a corrugated step-like structure on the Cu surface and significantly brings down the methane C-H activation barrier from 174 kJ/mol on Cu(111) to only 75 kJ/mol on B-Cu. The subsequent dehydrogenation of the adsorbed CH_3^* to CH_2^* is also kinetically and thermodynamically feasible. Our calculations also suggest that, unlike most of the transition metals, complete decomposition of methane to carbon would not be favored on B-Cu. The dissociation of the surface CH_2^* moiety on B-Cu is limited due to the high activation barrier of 161 kJ/mol and lower relative stability of the resultant CH^* species, under reaction conditions. The coupling of CH_2^* fragments however is kinetically and thermodynamically favorable, with an activation barrier of only 92 kJ/mol; suggesting that B-Cu catalyst would have higher selectivity towards C_2 hydrocarbons. Furthermore, the formation of carbon from the adsorbed CH^* moiety has a very high activation barrier of 197 kJ/mol and the completely dehydrogenated C^* is relatively much less stable than CH^*, under reaction conditions; predicting that coking might not be an issue on the B-Cu catalyst. Evaluation of C-H activation on Cu (110) surface, which has a similar step-like surface structure as B-Cu, and Bader charge and density of states analyses of B-Cu reveal that the geometrical/corrugation effect and the charge transfer from B to Cu synergistically promote the C-H activation on B-Cu, making it as active as other expensive transition metals like Rh, Ru, Ir and Pt.



Porous structured CuO-CeO_2 nanospheres for the direct oxidation of cellobiose and glucose to gluconic acid

Prince Nana Amaniampong, Quang Thang Trinh, Kaixin Li, Samir H. Mushrif, Yu Hao, Yanhui Yang

DOI: 10.1016/j.cattod.2017.01.009

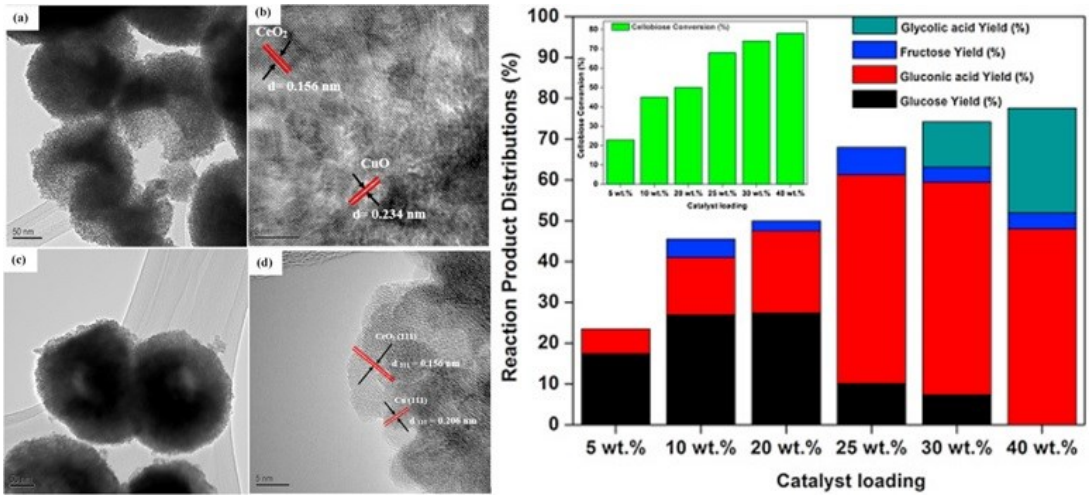
Highlights:

- Oxidation of glucose to gluconic is possible over CuO-CeO_2 catalysts.
- Lattice oxygen of CuO is responsible for the oxidation of glucose.

- Characterization results reveal that lattice oxygen of CeO_2 does not participate in the oxidation reaction.
- The synergy between CuO and CeO_2, is responsible for the loosely bound oxygen of CuO promoting C-H bond activation.

Abstract:

Porous-structured CuO-CeO_2 nanospheres were synthesized using a hydrothermal method and were tested as catalysts for the direct oxidation of cellobiose to gluconic acid. Catalytic reaction along with catalyst characterization results and ^{18}O-oxygen isotope labeled experiments revealed that the surface lattice oxygen of CuO in CuO-CeO_2 nanospheres was consumed during the oxidation of cellobiose. This provides a direct evidence of our previous work (Amaniampong et al., Angew. Chem. Int. Ed. 54 (2015) 8928–8933). Characterization results further suggested that the lattice oxygen in CeO_2 did not participate in the oxidation; nonetheless, the addition of CeO_2 to CuO enhanced the surface area of the catalyst composite which was crucial for the reaction. The spent catalyst upon re-oxidation regained its activity. In addition, isotope labeled deuterium oxide (D_2O) experiments suggested that hydrogen exchange between the solvent and the substrate (glucose) are not involved in the mechanistic formation of gluconic acid and confirmed the solvent had no direct influence in the formation of gluconic acid.



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

EMSET is divided into three work packages:

WP 2.1: Multi-Scale Electrochemical Modelling and Analysis

WP 2.2: Electrode Design and Development

WP 2.3: Electrochemical Reactor Engineering

The EMSET group is led by PIs:

Prof Adrian FISHER (Cam)

Prof Xin WANG (NTU)

Prof Jim Yang LEE (NUS)

Dr. Adrian Fisher,

University of Cambridge

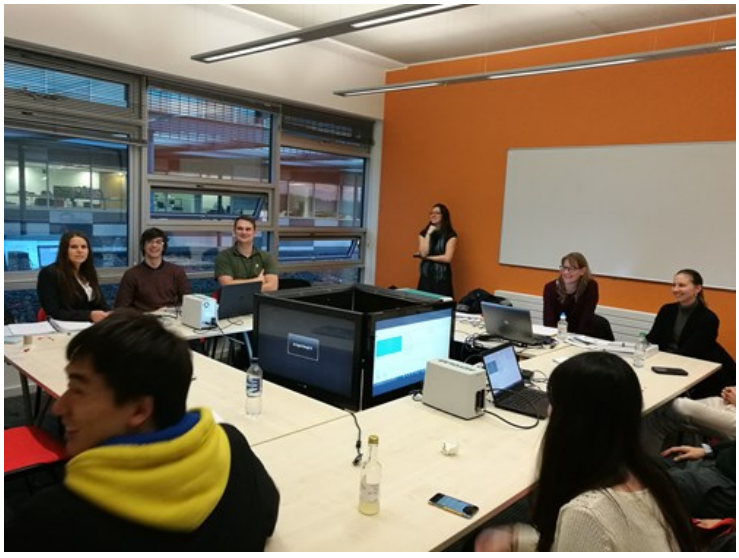
PI, IRP2

April 2017

3.2.1 IRP2 Research Overview

The IRP2 electrochemical programme is focused on the development and exploitation of novel technologies and processes which can lead to a net reduction in CO2 emissions in the production of either commodity or speciality chemicals. There are three core activities with the IRP (i) development of high resolution electrochemical methods and tools that can be exploited to gain quantitative understanding of the physical and chemical processes which limit efficient electrical conversion, (ii) the exploration of advanced catalysts, electrode architectures and the wiring of these complex structures to ensure optimal conversion rates and (iii) the development of integrated advanced reactor systems which allow novel, potentially disruptive processes for the synthesis of chemical products.
In the current reporting period significant advances in the core research areas have been achieved. In collaboration with Prof Erik BIRGERSSON, IRP2 PhD student Vishvak KANNAN has been working on advanced protocols for electrochemical control and analysis. His work has been focused on chronopotentiometry or galvanostatic cycling exploiting small and large amplitude periodic input wavefunctions. The highly non-linear characteristics of the electrochemical reactions and the rapid advances in complex electrode architectures is leading to the need for more resolving and high sensitivity methods to discern between the reaction pathways occurring. These activities have led to further industrial interest from local and international partners.

In parallel with numerical and theoretical studies, working in collaboration with Prof Xu ZHICHUAN, IRP2 RF Dr Chencheng DAI has recently discovered efficient strategies for the electrochemical production of lactic acid by oxidation of glycerol on AuPt electrode architectures in alkaline environments. In this work, he has reported a method to explore the production of lactic acid via direct electrochemical oxidation of glycerol, yielding a high selectivity, low energy pathway for production of the this valuable substrate. Advanced studies have been carried out to evaluate the surface catalysis characteristics of the reaction and explore the highest selectivity routes. It has been found that a 72.9% yield was achieved using AuPt nanoparticles with 13% surface Pt and a fixed external potential of of 0.45 V vs. reversible hydrogen electrode (RHE). The glycerol conversion rate was found to be 28.9% over a 12 hour period and these promising results suggest an efficient cheap and environmentally friendly method for lactic acid production.



The development of the IRP2 international outreach programme has also continued within the current reporting period. December 2016 saw the launch of the first advanced sensors MasterClass programme in Cambridge. This 2 day activity brought together local experts from industry and IRP2 staff to highlight advances made in the electrochemical monitoring aspects from WP1 and how these can be used for improved limit of detection and mechanistic resolution both in academic and industrial environments. The course comprised keynote lectures from IRP2 PI Adrian Fisher and 'hands on' training in the use of state of the art analysis techniques. The programme, sponsored by our long-term collaborator, Methrohm, was attended by 15 delegates, including, UK industry, University postdocs/Students and local consultancy firms. The first UK programme has to enhanced awareness of the IRP2 activities within the UK and led to further industrial links in the phase 1 programme and statements of support for the phase 2 proposal currently in preparation. Preparations are also underway for 3 further confirmed programmes in June, September and October in Singapore, China and the UK respectively. Provisional agreement has also been granted for a course in December in Australia.

3.2.2 Update on work packages

WP 2.1: Numerical multi-scale electrochemical modelling and analysis

Vishvak KANNAN (PhD student, NUS, IRP2) reported that chronopotentiometry or galvanostatic cycling and Electrochemical Impedance Spectroscopy (EIS) are popularly employed techniques to characterise different electrochemical processes. While galvanostatic cycling is popularly employed to evaluate the stability of electrochemical reactors and to study the charge/ discharge characteristics of batteries and fuel cells, EIS owing to its high precision is exploited to estimate the heterogeneous charge-transfer parameters and in the investigation of the double-layer structure. However, EIS is defined for only linear systems because of the existence of background currents in non-linear systems. These background currents give rise to harmonics for large amplitudes of input signal and affect the accuracy of measurement of impedance. Hence, it is important to investigate and characterise the harmonics for quantitative error estimations of impedance measurements, which in turn improves the reliability of the results. Vishvak KANNAN (PhD student, NUS, IRP2) defined a known electrochemical system- redox reaction of Ferrocyanide-Ferricyanide to evaluate the harmonics for galvanostatic conditions. Following successful implementation of phasors, he derived a closed form analytical solution for a system dominated by diffusion, with sinusoidal current input. The analytical solutions for the individual harmonics were also derived and the corresponding over-potential was elucidated using Butler-Vohlmer kinetics.

Peng SONG (RF, CAM, IRP2) worked with Yian WANG (PhD student, CAM, IRP2) on the AC voltammetry techniques on the rocking disc system for numerical studies. The rocking disc system is now fully functional in the CREATE Lab 2 since last summer. Other electrochemical mechanisms have been studied via AC voltammetry technique as well.

WP 2.2: Electrode Development and Testing

Dr Rui GUSMÃO (RF, NTU, IRP2), under the supervision of Prof Martin PUMERA (Co-PI, NTU, IRP2) carried out literature survey on Black Phosphorus (BP). The bulk form of BP was synthesized for the first time more than a century ago and very recently rediscovered, in 2014, joining the new wave of 2D layered nanomaterials. BP can be exfoliated to a single sheet structure with tunable direct band, semiconducting, high carrier mobility at room temperature and in-plane anisotropic layered structure. BP has been reported as a novel nanomaterial in batteries, transistors, sensors and photonics related fields. The applications of this material do CO_2 reduction are still to be explored. Currently, Dr. GUSMÃO is working on the liquid phase exfoliation of layered materials. Next, these materials will be explored for different electrocalalytic reactions and CO_2 reduction in saturated liquid solutions. The liquid and gas phases of the CO_2 reduction will be analysed to evaluate the outcome of the reactions.

Prof Richard WEBSTER (Co-PI, NTU, IRP2) research determined the impurities that are present in solvent systems that are commonly used in electrochemical measurements (including for dye-sensitized solar cells) and how the impurities effect the electrochemical results.

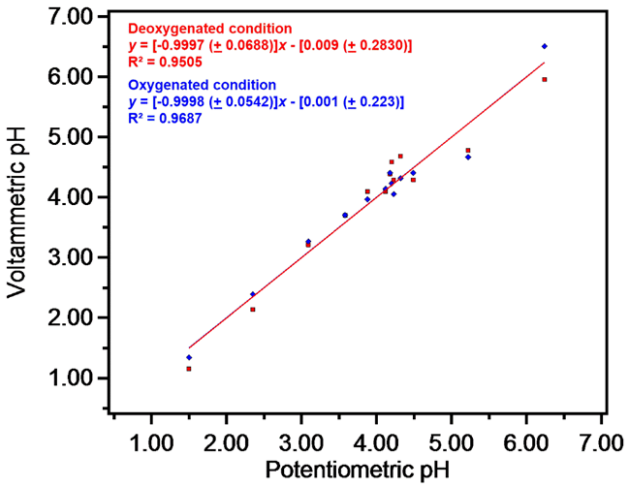
Dr Bahareh KHEZRI (RF, NTU, IRP2), under supervision of Prof Martin Pumera (Co-PI, NTU, IRP2), carried out a literature survey in Electrochemical CO_2 Reduction through heterogeneous catalysts and working in collaboration with Prof Zdenek SOFER from UCT, Prague (CARES C4T Visiting Scientist) to synthesize and work with 2D materials as new catalysts (mostly non-metallic or metal doped material (contain trace amount of metals)) for CO_2 conversion. In this stage the materials have been synthesized, characterized and Dr Bahareh KHEZRI (RF, NTU, IRP2) is currently studying electrochemical performance and will investigate the catalytic performance (activity, faradic efficiency and current density) in CO_2 saturated aqueous solution later on. The product of CO_2 conversion will be detected with GC, HPLC and NMR.

In addition, Dr Bahareh KHEZRI (RF, NTU, IRP2, under supervision of Prof Richard D Webster (Co-Pi, NTU, IRP2) , carried out a literature survey in Electrochemical CO_2 Reduction through homogenous catalysts . The aim of this project is the study of kinetic and thermodynamic of CO_2 conversion since in many studies the mechanism is unknown or it is only hypothesized. The product of CO_2 conversion will be detected with GC, HPLC and NMR.

Dr ZHANG Wenyu (RF, NTU, IRP2) reported on his studies on silicene-based materials for CO_2 reduction. Silicon is one of the most abundant elements in the earth. Silicon-based materials have been widely applied for contemporary industries all over the world, e.g. building materials, glasses, ferromagnetics and electronics. Silicene is a monolayer of silicon atoms with buckling honeycomb structures similarly as graphene. Due to the strong dangling bonds on the surface and edges of sp3 hybridized structure, silicene has been predicted to possess high affinity and high catalytic activity to water splitting and oxygen reduction reaction (ORR) . Besides, the properties of silicene can be easily adjusted by alloying, doping, functionalization and mechanical strains, which largely extends its implications. The intrinsic carrier mobility of silicene is predicted to be slightly lower than graphene but in the same order of magnitude. Last but not least, the abundance and low cost of silicon adds to the attractiveness of silicene-based materials for catalysis studies. Dr ZHANG Wenyu (RF, NTU, IRP2) carried out a literature review on related topics and reported that all instruments have been ordered and that most of them have been received. In addition, Dr ZHANG Wenyu (RF, NTU, IRP2) reported that silicon alloys have been prepared using ball milling and physical characterization on these materials has been finished, e.g. XRD, SEM and TEM. He foresees that the project will lead to a breakthrough in electrochemical catalysis and energy storage/conversion systems. This will significantly reduce the energy consumption and cost for CO_2 reduction, electric vehicles, energy storage systems and personal electronic devices, which will make the relevant commercial products more affordable.

Guo Xiong THAM (PhD Student, NTU, IRP2) has been working on achieving a disposable and vitamin-based electrochemical sensor whereby the working compound (riboflavin, and whose function is analogous to that of the working electrode) can provide a good Nernstian response across a wide range of pH values in unbuffered test solutions under deoxygenated and more importantly, oxygenated conditions.

A very small concentration (1.3 mM) yet sufficiently acidic buffer with KCl at a fixed pH was mixed with the varying pH of the acidified/basic KCl solutions (measured using a pH meter, and are also the unbuffered test solutions), and voltammetric results indicate a good Nernstian shift from the linear plot of the potential of riboflavin with respect to the vitamin E analogue (reference compound) against the pH of the unbuffered test solutions. A strong linear relationship in the form y = x was achieved by plotting the voltammetric pH against the potentiometric pH to assure the reliability of the pH measurements (refer to Section 8 for the plot).



Calibration plot of potentiometric pH against voltammetric pH with experimental data based on the square wave voltammograms of 4 mM VEa and 2 mM VB_2 in DMSO coated at a 3 mm diameter planar GC disk across varying pH of acidified/basic KCl test solution mixed with 1.3 mM PC buffer in equivalent volumes under deoxygenated (red plot) and oxygenated (blue plot) conditions at 22 (±2) °C.

Peng SONG (RF, CAM, IRP2) has been working on the area of electrochemical analysis for sensing of chemical products and this work has been published recently. A high temperature high pressure rig has been developed and the work is focused on the study of the sensor mechanism.

Naziah Binte MOHAMAD LATIFF (PhD student, NTU, IRP2) has been studying the toxicity aspects of various layered materials that have shown potential in energy applications such as the electrochemical conversion of water to hydrogen and other useful products. Previously, she looked at the vanadium dichalcogenides family (e.g. VS_2, VSe_2, VTe_2) and has been working on layered metal thiophosphate materials. These studies are necessary to be informed of the possible health hazards posed by such materials in view of their possible commercialization in the future.

Nur Farhanah Binte ROSLI (PhD student, NTU, IRP2) has completed her study on the cytotoxicity of thiobarbituric acid functionalized MoS_2 (MoS_2). This study serves as a platform to better understand the toxicity level of the newly proposed material, MoS_2-TBA, which has been synthesized for hydrogen evolution reaction (HER) application. HER is a clean method to produce hydrogen gas as an alternative fuel with zero carbon emission. This study is essential as MoS_2-TBA has greater possibility of commercial application in future as it has been reported to have excellent HER capabilities in a previous study. MoS_2-TBA can lead to health deterioration if they are released into the environment as a result of its utilisation in commercial applications if indeed it is proven toxic. Therefore, toxicity of MoS_2-TBA needs to be more understood before utilizing it in various applications in a larger scale. In summary, the results from the study concluded that MoS_2-TBA has higher toxicity than that of un-functionalized MoS_2.

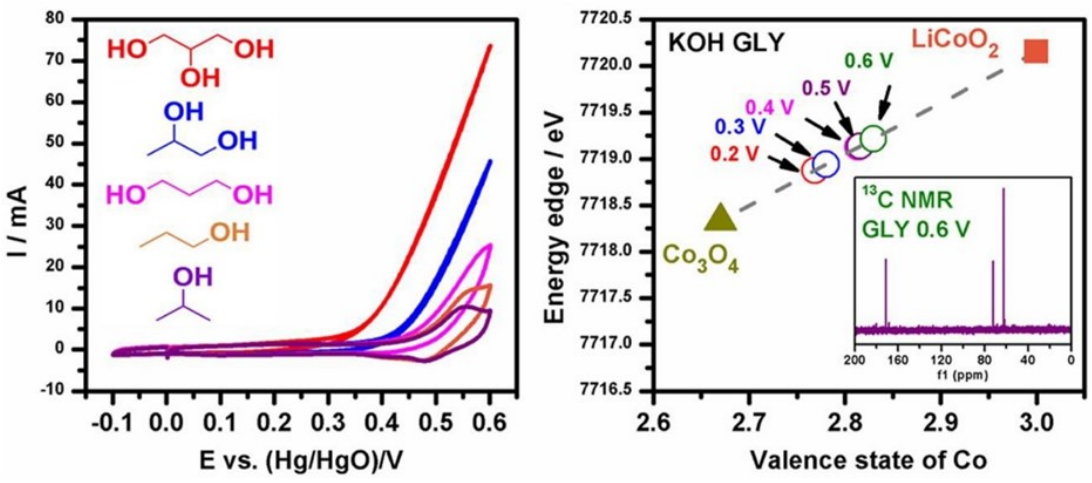
WP 2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

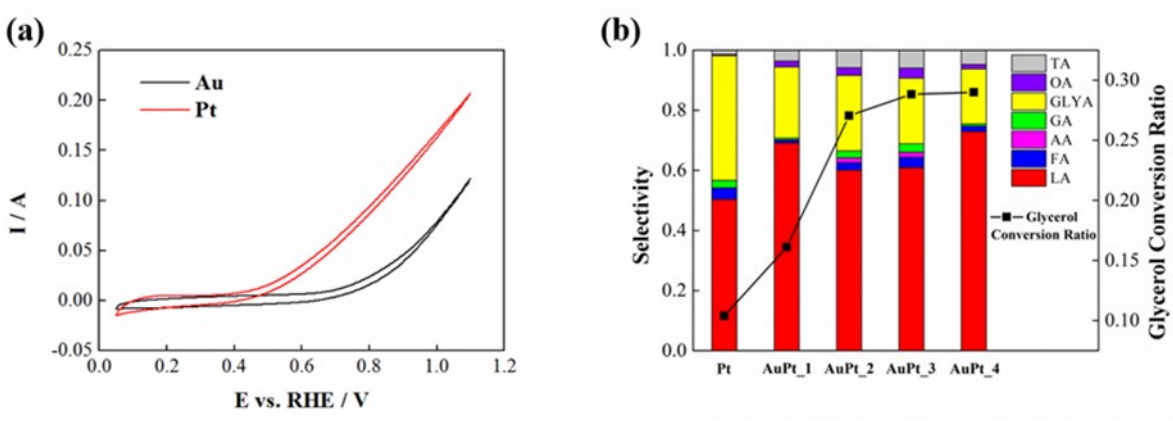
Dr Chencheng DAI (RF, NTU, IRP2) reported on his work on **Electrochemical production of lactic acid by oxidation of glycerol on AuPt in alkaline**. In this work, he developed the method to produce lactic acid through the electrochemical oxidation of glycerol directly with a high selectivity for the first time. This method utilized AuPt nanoparticles with tunable surface, which was achieved by heat treatment, to catalyze the electrochemical oxidation, and optimizes the performance of catalysts by tuning the Au/Pt surface ratio, and the applied potential. The surface of bimetallic nanoparticles has been studied using methods including voltammetry, TEM, STEM-EDS, XRD, TGA, ICP, etc. Both nuclear magnetic resonance (NMR) and high performance liquid chromatography (HPLC) were employed to analyze the products qualitatively and quantitatively. The highest selectivity was 72.9%, which was obtained using the AuPt nanoparticles with 13% surface Pt and an applied potential of 0.45 V vs. reversible hydrogen electrode (RHE), and the glycerol conversion rate was 28.9% after 12 hours. These results suggest an efficient, cheap and environmental-friendly method to produce lactic acid.

Lactic acid is a valuable chemical. It is a platform chemical for the production of biodegradable poly(lactic acid), polyester, as well as a feedstock for the synthesis of green solvents and various valuable commodity chemicals. It is also widely used directly in the pharmaceutical, food and detergent industries. Nowadays the production of lactic acid is mainly based on fermentation of carbon sources, resulting the disadvantages including severe conditions, unfriendliness to environment, and low efficiency, etc. Biodiesel is one of the promising solutions for the global energy crisis. Glycerol is an important by-product during the production of biodiesel. The global glycerol market size was 2.47 million tons in 2014 and expected to increase 6.5% from 2015 to 2022 annually. The market price of refinery glycerol (99.5%) is only approximately 500 USD/tons. There is an urgent demand for the valorization of glycerol considering the increasing demand for bio-

diesel. Therefore, the production of lactic acid from glycerol is supposed to facilitate the production of biodiesel at last, which can eventually promote the replacement of fossil fuel.

In addition, Dr Chencheng DAI (RF, NTU, IRP2) reported on his work on **Electrochemical oxidation of C3 saturated alcohols on Co_3O_4 in alkaline.** In this work, the electrochemical oxidation of C3 saturated alcohols (propanetriol (GLY), 1,2-propanediol (1,2-P), 1,3-propanediol (1,3-P), 1-propanol (1-P) and 2-propanol (2-P)) on Co_3O_4 in alkaline was studied. The Co_3O_4 electrode was prepared by the electrodeposition of $Co(OH)_2$ on graphite paper followed with a calcination step. The electro-oxidation of C3 saturated alcohols were investigated by a combination of cyclic voltammetry, multi-step chronoamperometry and electrochemical impedance spectroscopy techniques in KOH solution. The electro-oxidation studies at Co3O4 electrode followed an activity trend in the following order: GLY > 1,2-P > 1,3-P > 1-P > 2-P. The NMR analysis of the oxidized products showed that C-C bond cleavage occurred faster in alcohols with adjacent hydroxyl groups. X-ray absorption near-edge structure (XANES) spectroscopy study showed no significant difference in Co oxidation state in the absence and the presence of glycerol. It was also found that pH influenced electro-oxidation of alcohols bearing secondary hydroxy group (GLY, 1,2-P and 2-P) more dramatically than that of those primary alcohols (1,3-P and 1-P).

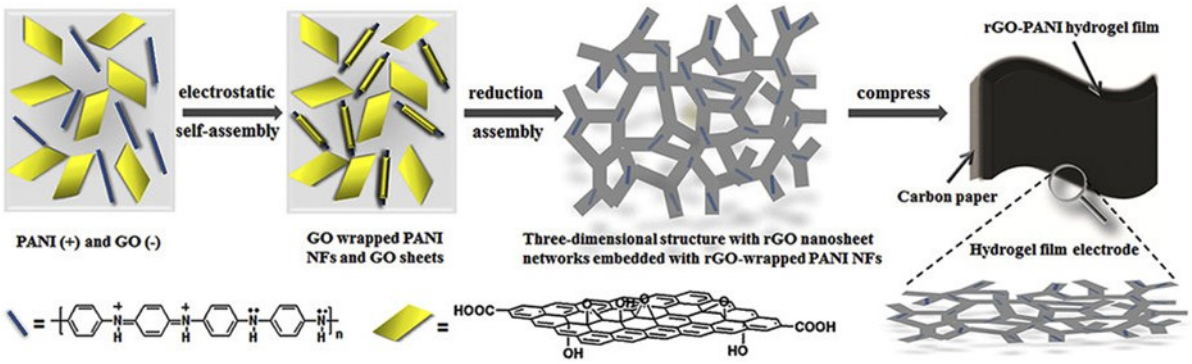




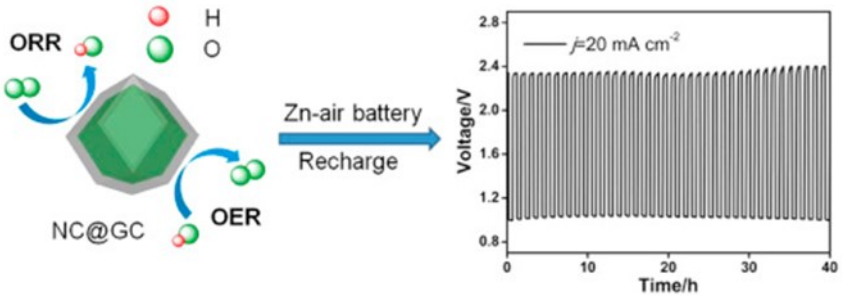
In addition to the study of glycerol oxidation mentioned above, the electrochemical oxidation of small molecular alcohols has attracted much attention in recent years due to their potentials as alternative fuels in fuel cells. A great effort has been made to investigate electrochemical oxidation of C1 alcohol (methanol) and C2 alcohols (ethanol and ethylene glycol) on noble metal and non-noble metal based materials. The electrochemical oxidation of C3 saturated alcohols is more challenging due to the complexity increase in molecular structure and types. However, C3 saturated alcohols are very attractive not only to fuel cells, but also the value-added C3 products, such as the lactic acid produced from glycerol as mentioned above.

Furthermore, Dr Chencheng DAI (RF, NTU, IRP2) has been working on **Three-dimensional skeleton networks of graphene wrapped polyaniline nanofibers.** In this work, a hierarchical three-dimensional structure where all of polyaniline (PANI) nanofibers (NFs) were tightly wrapped inside reduced graphene oxide (rGO) nanosheet skeletons for high performance flexible supercapacitors

(SCs) were reported. The as-fabricated film electrodes with this unique structure showed a highest gravimetric specific capacitance of 921 F/g and volumetric capacitance of 391 F/cm^3. The assembled solid-state SCs gave a high specific capacitance of 211 F/g (1 A/g), a high area capacitance of 0.9 F/cm^2, and a competitive volumetric capacitance of 25.6 F/cm^3. The SCs also exhibited outstanding rate capability (~75% retention at 20 A/g) as well as excellent cycling stability (100% retention at 10 A/g for 2000 cycles). Additionally, no structure failure and loss of performance were observed under the bending state. This structure design paves a new for engineering rGO/PANI or other similar hybrids for high performance flexible energy storage devices.



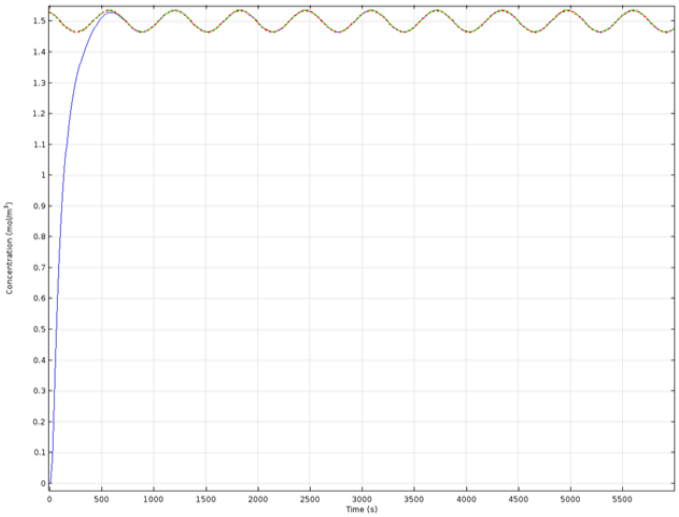
Dr Yizhong LU's (RF, NTU, IRP2) reported that Ultrathin Pt nanowires are obtained via a simple hydrothermal method. The pristine Pt nanowires with some defects exhibited enhanced activity and durability towards oxygen reduction reaction. He found that after simple thermal annealing at high temperature under Ar atomosphere, the contents of defects decreased significantly. Electrochemical studies showed that the smooth Pt nanowires exhibited a further improvement both in their activity and durablity. At 0.90 V vs. RHE, the smooth Pt nanowires showed an improvement factor of more than 1 order of magnititude in activity versus state-of-the-art Pt/C catalyst. More importantly, even after 10,000 cycles of accelerated durability test, the smooth Pt nanowires showed highest stability. He attributed the enhanced activity and durability of smooth Pt nanowires toward oxygen reduction reaction to their unique one-dimensional structure.

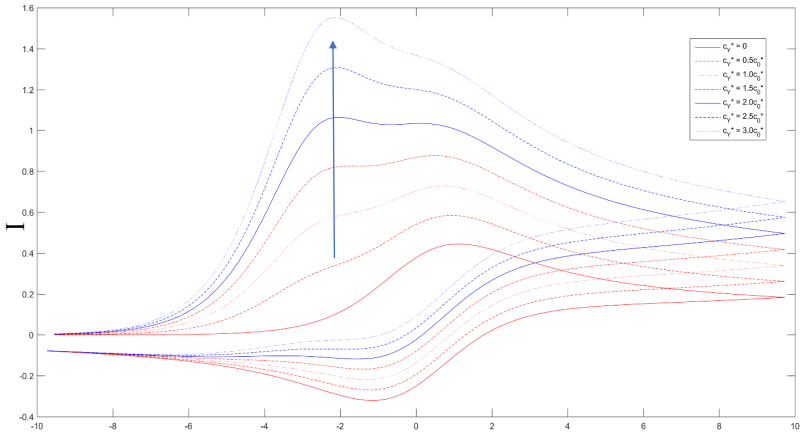


WANG Yian (PhD Student, NTU, IRP2) has been working on operator splitting is a numerical method of solving the differential equation by separating the original equation into two or more parts over a time step, conquering each subproblem with specialised algorithm, and combining the individuals to form a solution to the original equation. This approach is well known to resolve some highly complex models, like combustion, reactive flows, etc, which is very computationally demanding over the entire domain. Recently, a consistent-splitting scheme for a nonlinear chemical reaction followed by a transport step catches our interests. Splitting error is significantly reduced in a fully converged state. For calculation of a typical electrochemical reactions at planar electrode, the problem of mass transport coupled to electrokinetics is divided into a sequence of the steady-state subproblems. This framework also provides an efficient way to the modelling of rapid mass transport and homogeneous chemical reactions. The modelling of two one-dimensional scalar equations, a typical single-electron transfer process and an electrocatalytic EC' mechanism, is illustrated in the figure above and below.

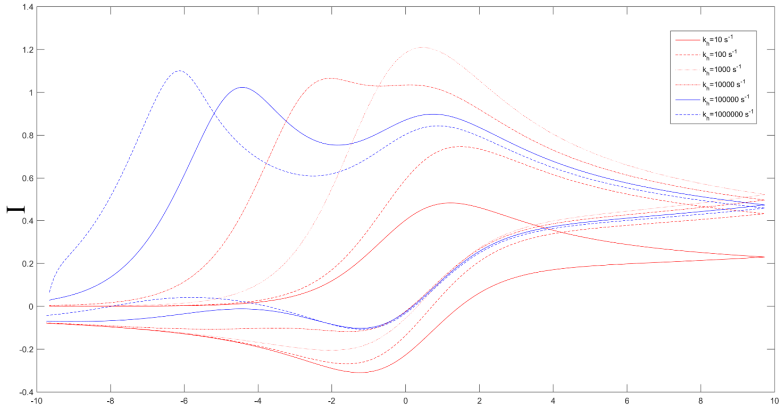
Dr Kamal ELOUARZAKI (RF, NTU, IRP2) reported on the aim and goals of his newly designed project. The novelty and overall objective of his project are to create bioreactors using tailored new hybrid nanometer scale biopolymer formulations, including biocatalysts, that provide eco-friendly, cost-

Dimensionless cyclic voltammogram with operator-splitting scheme: the plotted line is a combination of numerical solution (points) with rather high time interval $\Delta t = 0.01s$ *time step. There is a good agreement between the numerical solutions and analytical values in the literature. The relative error of the dimensionless peak current is less than* 2.2×10^{-2}





Dimensionless cyclic voltammogram of EC' mechanism for homogeneous reaction kinetics $k_h = 10^4\ s^{-1}$ *: increasing the initial concentration of substrate leads to the split wave. Fig.2(b), the effect of homogeneous reaction kinetics,* k_h *, to the value and position of split wave at* $c_Y^* = 2c_0^*$.



effective and biocompatible nanometer scale materials with increased surface area, miniaturization, increased packing, imprinting friendly, as well as, efficient electron shuttling. The specific goal is to produce micro-energy reactors powered by CO_2 and others fuel such as sugar energy. Thus, Dr Kamal ELOUARZAKI's (RF, NTU, IRP2) project uses as an energy precursor CO_2 and sugars in the driving force based on electron transfer reactions. He reported to be using a combinatorial number of biocompatible Smart nanomaterials in order to generate energy using living organisms, enzymes, and bioinspired compounds and solve efficiency issues by maximizing the electron transfer. The results of his research project will enable the design of a new generation of bioreactors, which will be a new and highly recommended research axis in CARES. Another outcome of the project will be developing hybrid reactors.

Shengliang ZHANG (PhD student, NUS, IRP2) has been focusing on the process of material preparation, spinning-coating, building a spectro-eclectrochemical cell for testing optical performance in order to optimize the condition of characterization. In addition, Shengliang ZHANG (PhD student, NUS, IRP2) reported on his research topic proposal on smart window. He intends to systhesize new composites (nancocrystal in glassy matrix) which can dynamically and selectively module the NIR and visible light based on the local surface plasomic resonance (LSPR) and intervalence change transfer mechanism separately. He has successfully changed the ligands of ITO capped with oleylamine into inorganic ligands (($H_2W_{12}O_{40}^{6-}$), which will decompose into WO_3 matrix. Shengliang ZHANG (PhD student, NUS, IRP2) will then characterize their optical performance.

Other Activities and Achievements

- Dr Kamal ELOUARZAKI (RF, NTU, IRP2) reported on the collaboration with Prof. Serge Cosnier's team at CNRS-University of Grenoble Alpes. A first important outcome was the submission of a Singapore-France joint grant between the French PI (Serge Cosnier, UJF), Singaporean PI (Lee Jong-Min, NTU), and Cambridge PI (Adrian Fisher, University of Cambridge), which was selected for the final evaluation.
- Dr Kamal ELOUARZAKI (RF, NTU, IRP2) reported on the submission of two grants including IRP2 researchers as lead PIs with local and international collaborators: 1)**INTRA-CREATE SEED COLLABORATION GRANT CALL (**Proposal Title: Rational bioelectrodes for an outstanding potentially implantable sugar biofuel cells (250,000SGD)**)** 2) **INTRA-CREATE COLLABORATIVE GRANT CALL (**Proposal Title: Ultrahigh nano-plasmonic field enhancement methodology and its applications in sensing, optoelectronics and energy harvesting (5,000,000SGD))
- Peng SONG (RF, CAM, IRP2) and Dr Adrian FISHER (PI, CAM, IRP2) ran a MasterClass Electrochemical Sensors course in Cambridge from 6^{th} – 7^{th} December 2016. This course is part of a series of MasterClasses, consisting of advanced lecturers, seminars, and hands-on experiments for industrialists and scientists wanting to expand their knowledge of analytical electrochemical methods for their research or industrial applications. This is a collaboration with Metrohm. The next Advanced Electrochemical Techniques MasterClass will take place in Singapore, CARES, CREATE Tower, 21-22 June 2017.

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.

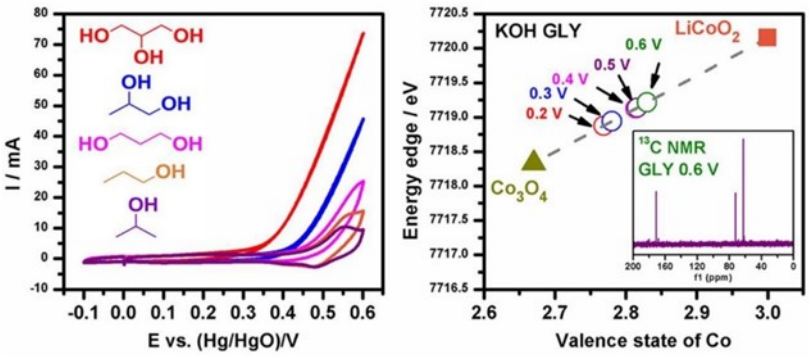
Electrochemical oxidation of C3 saturated alcohols on Co_3O_4 in alkaline

Sun, S.; Sun, L.; Xi, S.; Du, Y.; Prathap, M. U. A.; Wang, Z.; Zhang, Q.; Fisher, A. C.; Xu, Z. J.

DOI: 10.1016/j.electacta.2017.01.086

Highlights:

- A systematic study on the electrochemical oxidation of C3 saturated alcohols on Co3O4 in alkaline.
- Activity trend: propanetriol > 1,2-propanediol > 1,3-propanediol > 1-propanol > 2-propanol in 1.0 M KOH.
- The C-C bond cleavage occurred faster in alcohols having adjacent hydroxyl groups.
- The KOH concentration influenced electro-oxidation of those alcohols bearing secondary hydroxyl group more dramatically than that of those primary alcohols



Abstract: In this work, we present a systematic study on the electrochemical oxidation of C3 saturated alcohols (propanetriol, 1,2-propanediol, 1,3-propanediol, 1-propanol, and 2-propanol) on Co_3O_4 in alkaline. Co3O4 electrode was prepared by electrodeposition of Co(OH)2 on graphite paper followed with a calcination step. The electro-oxidation of C3 saturated alcohols were investigated by a combination of cyclic voltammetry, multi-step chronoamperometry, and electrochemical impedance spectroscopy techniques in KOH solution. The electro-oxidation studies at Co_3O_4 electrode followed an activity trend in the following order: propanetriol (GLY) > 1,2-propanediol (1,2-P) > 1,3-propanediol (1,3-P) > 1-propanol (1-P) > 2-propanol (2-P). The NMR analysis of the oxidized products showed that C-C bond cleavage occurred faster in alcohols having adjacent hydroxyl groups. X-ray absorption near-edge structure (XANES) spectroscopy study showed that there was no significant difference in Co oxidation state in the absence and the presence of glycerol. It was also found that the KOH concentration influenced electro-oxidation of those alcohols bearing secondary hydroxyl group (GLY, 1,2-P, and 2-P) more dramatically than that of those primary alcohols (1.3-P and 1-P).

A review on design strategies for carbon based matal oxides and sulphides nanocomposites for high performance Li and Na Ion battery anodes

Zhao, Y.; Wang, L. P.; Sougrati, M. T.; Feng, Z.; Leconte, Y.; Fisher, A. C.; Srinivasan, M.; Xu, Z. J.

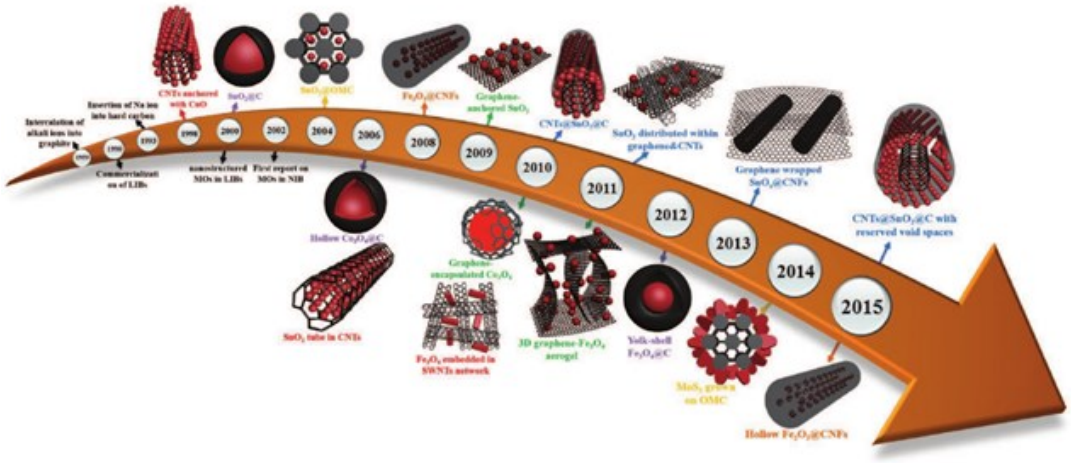
DOI: 10.1002/aenm.201601424

Highlights:

- This review article introduces the most recent and important progress of the design strategies for carbon based metal oxides and sulphides nanocomposites for high performance Li and Na ion battery anodes.

- Typical carbon matrices, metal oxides/sulphides and their nanocomposites are discussed in details.
- This review summarizes the modification methods of MOs/MSs with two carbon matrices.

Abstract: Carbon-oxide and carbon-sulfide nanocomposites have attracted tremendous interest as the anode materials for Li and Na ion batteries. Such composites are fascinating as they often show synergistic effect compared to their singular components. Carbon nanomaterials are often used as the matrix due to their high conductivity, tensile strength, and chemical stability under the battery condition. Metal oxides and sulfides are often used as active material fillers because of their large capacity. Numerous works have shown that by taking one step further into fabricating nanocomposites with rational structure design, much better performance can be achieved. The present review aims to present and discuss the development of carbon-based nanocomposite anodes in both Li ion batteries and Na ion batteries. The authors introduce the individual components in the composites,



i.e., carbon matrices (e.g., carbon nanotube, graphene) and metal oxides/sulfides; followed by evaluating how advanced nanostructures benefit from the synergistic effect when put together. Particular attention is placed on strategies employed in fabricating such composites, with examples such as yolk–shell structure, layered-by-layered structure, and composite comprising one or more carbon matrices. Lastly, the authors conclude by highlighting challenges that still persist and their perspective on how to further develop the technologies.

Three-dimensional skeleton networks of graphene wrapped polyaniline nanofibers: an excellent structure for high-performance flexible solid-state supercapacitors

Hu, N.; Zhang, L.; Yang, C.; Zhao, J.; Yang, Z.; Wei, H.; Liao, H.; Feng, Z.; Fisher, A. C.; Zhang, Y.; Xu, Z. J.

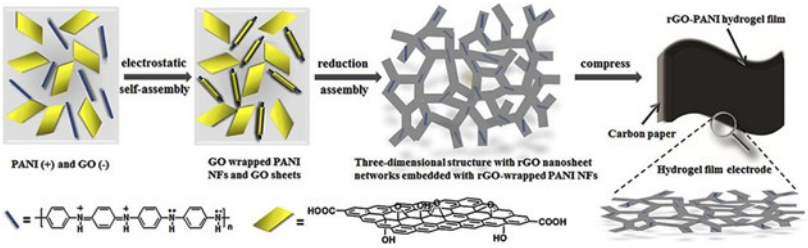
DOI: 10.1038/srep19777

Highlights:

- A novel hierarchial three-dimensional structure of graphene wrapped polyaniline nanofibers has been designed and fabricated for high performance flexible solid state supercapacitors.
- The as-fabricated film electrodes with this unique structure showed a highest gravimetric specific capacitance of 921 F/g and volumetric capacitance.
- The assembled solid-state SCs gave a high specific capacitance, a high area capacitance, and a competitive volumetric capacitance.
- The SCs also exhibited outstanding rate capability as well as excellent cycling stability.

- No structural failure and loss of performance were observed under the bending state.

Abstract: Thin, robust, lightweight, and flexible supercapacitors (SCs) have aroused growing attentions nowadays due to the rapid development of flexible electronics. Graphene-polyaniline (PANI) hybrids are attractive candidates for high performance SCs. In order to utilize them in real devices, it is necessary to improve the capacitance and the structure stability of PANI. Here we report a hierarchical three-dimensional structure, in which all of PANI nanofibers (NFs) are tightly wrapped inside reduced graphene oxide (rGO) nanosheet skeletons, for high-performance flexible SCs. The as-fabricated film electrodes with this unique structure showed a highest gravimetric specific capacitance of 921 F/g and volumetric capacitance of 391 F/cm^3. The assembled solid-state SCs gave a high specific capacitance of 211 F/g (1 A/g), a high area capacitance of 0.9 F/cm^2, and a competitive volumetric capacitance of 25.6 F/cm^3. The SCs also exhibited outstanding rate capability (~75% retention at 20 A/g) as well as excellent cycling stability (100% retention at 10 A/g for 2000 cycles). Additionally, no structural failure and loss of performance were observed under the bending state. This structure design paves a new avenue for engineering rGO/PANI or other similar hybrids for high performance flexible energy storage devices.



Black Phosphorus Rediscovered: From Bulk to Monolayer

Rui Gusmoa, Zdenek Sofer, Martin Pumera

DOI: 10.1002/anie.201610512

Abstract: Phosphorus is a non-metal with several allotropes, from the highly reactive white phosphorus to the thermodynamically stable black phosphorus (BP) with a puckered orthorhombic layered structure. The bulk form of BP was synthesized for the first time more than a century ago, in 1914, not receiving much attention until very recently rediscovered, in 2014, joining the new wave of 2D layered nanomaterials. BP can be exfoliated to a single sheet structure with tunable direct band, semiconducting, high carrier mobility at room temperature and in-plane anisotropic layered structure. Surface chemistry degradation can still be a holdback for the advancement of BP applications, thus compelling efforts to achieve effective BP passivation are ongoing, such as its integration in van der Waals heterostructures. Currently, BP has been tested as a novel nanomaterial in batteries, transistors, sensors and photonics related fields. In this review we take a look back at BP origin story, taking the path from bulk to nowadays few/single layer. Physical and chemical properties are summarized, highlighting the state-of-the-art in BP applications.

Core-shell carbon materials derived from metal-organic frameworks as an efficient oxygen bifunctional electrocatalyst

Zhijuan Wang, Yizhong Lu, Ya Yan, Thia Yi Ping Larissa, Xiao Zhang[c], Delvin Wuu, Hua Zhang, Yanhui Yang, Xin Wang

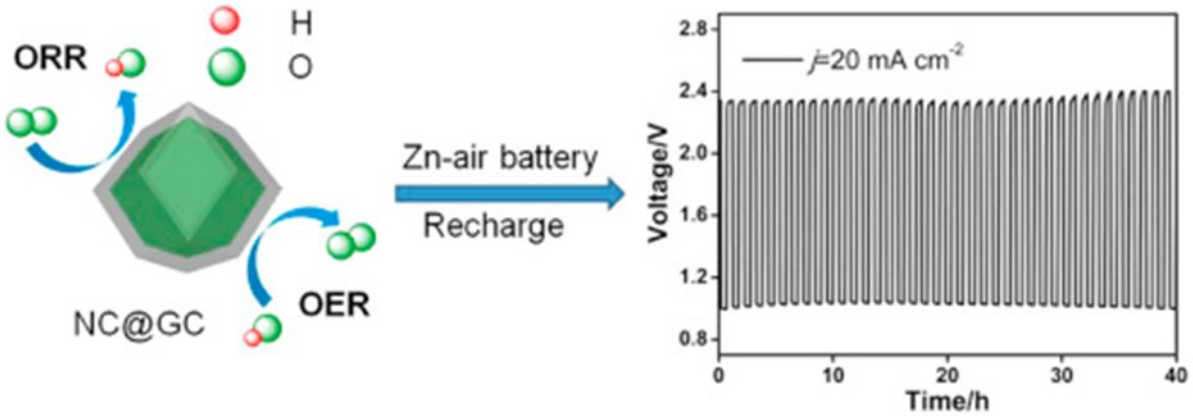
doi.org/10.1016/j.nanoen.2016.10.017

Highlights:

- ZIF-8@ZIF-67 core-shell metal-organic framework has been designed and prepared by a seed -mediated growth technique through a hydrothermal method.
- A novel structure consisting of nitrogen-doped carbon core and highly graphitic carbon shell is obtained by carbonization.

- Such carbon based catalyst showed high activity and stability towards oxygen reduction and oxygen evolution reactions.

Abstract: Noble-metal free and durable electrocatalysts with high catalytic activity toward oxygen reduction and evolution reactions are crucial to high-performance primary or rechargeable Zn-air batteries (ZnABs) and fuel cells. Herein, we report an efficient bifunctional electrocatalyst with core-shell structure obtained from ZIF-8@ZIF-67 through hydrothermal and carbonization treatment. The resulted material, i.e. highly graphitic carbon (GC, carbonized from ZIF-67) on nitrogen-doped carbon (NC, carbonized from ZIF-8) (NC@GC), combines the distinguished advantages of NC, including high surface area, presence of Co doping and high nitrogen content, and those of GC including high crystallinity, good conductivity and stability of GC. This unique core-shell structure with potential synergistic interaction leads to high activities towards oxygen reduction and oxygen evolution reactions. As a proof-of-concept, the as-prepared NC@GC catalyst exhibits excellent performance in the primary and rechargeable ZnABs. This study might inspire new thought on the development of carbon-based electrocatalytic materials derived from MOF materials.



Copper-Modified Gold Nanoparticles as Highly Selective Catalysts for Glycerol Electro-Oxidation in Alkaline Solution

Thia, L., Xie, M., Liu, Z., Ge, X., Lu, Y., Fong, W. E., et al

doi.org/10.1002/cctc.201600725

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Detecting the complex motion of self-propelled micromotors in microchannels by electrochemistry

Bahareh Khezri, James Guo Sheng Moo, Peng Song, Adrian C. Fisher, Martin Pumera

DOI: 10.1039/C6RA22059B

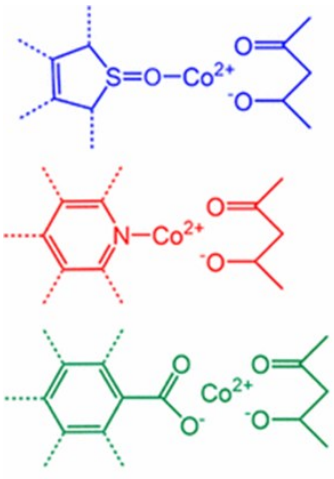
Autonomous self-propelled nano/micromotors are new frontiers in micro- and nanotechnology, with a plethora of possible applications in environmental remediation and biomedicine. However, key challenges remain, one of which is the monitoring of motion in these self-propelled nano- and

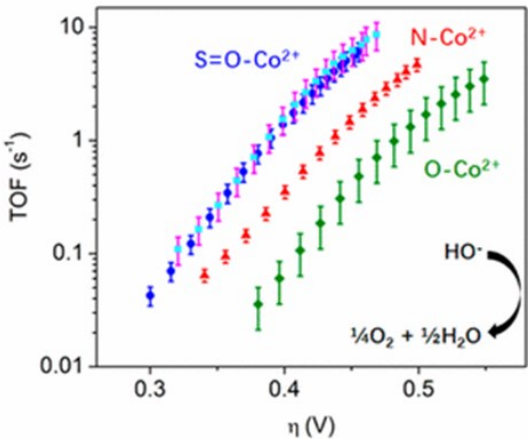
microdevices. Tracking of these miniaturized objects is typically done by optical microscopy. Such a manual methodology has several inherent challenges, ranging from demanding computational power for optical image analysis to following objects in opaque or non-transparent environments. Here we developed a monitoring system for an autonomous self-propelled micromotor in a microfluidic channel *via* the placement of electrodes in the pathways. The electrochemical detection methodology, based on the disturbances in the electrical double layer of an electrode surface in our devised instrumentation technique, allows for different modes of motion in micromotors in channel environments to be recognized. This ability to detect the motion of autonomous self-powered micromotors in opaque/non-transparent channels will find widespread applications in the future.

Heterogeneous electrocatalyst with molecular cobalt ions serving as the center of active sites

Jiong Wang, Xiaoming Ge, Zhaolin Liu, Larissa Thia, Ya Yan, Wei Xiao, and Xin Wang

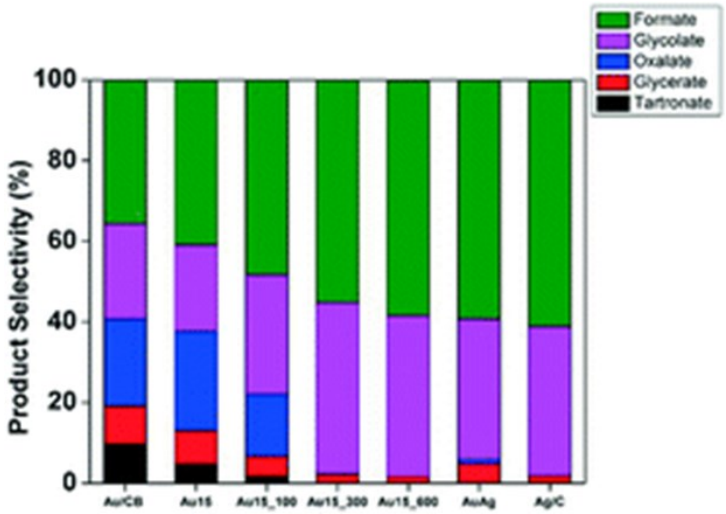
DOI: 10.1021/jacs.6b10307





Abstract:

Molecular Co^{2+} ions were grafted onto doped graphene in a coordination environment, resulting in the formation of molecularly well-defined, highly active electrocatalytic sites at a heterogeneous interface for the oxygen evolution reaction (OER). The S dopants of graphene are suggested to be one of the binding sites and to be responsible for improving the intrinsic activity of the Co sites. The turnover frequency of such Co sites is greater than that of many Co-based nanostructures and IrO_2 catalysts. Through a series of carefully designed experiments, the pathway for the evolution of the Co cation-based molecular catalyst for the OER was further demonstrated on such a single Co-ion site for the first time. The Co^{2+} ions were successively oxidized to Co^{3+} and Co^{4+} states prior to the OER. The sequential oxidation was coupled with the transfer of different numbers of protons/hydroxides and generated an active Co^{4+}□O fragment. A side-on hydroperoxo ligand of the Co^{4+} site is proposed as a key intermediate for the formation of dioxygen.



Ag containing porous Au structures as highly selective catalysts for glycolate and formate

Larissa Thia Mingshi Xie, Donghwan Kim and Xin Wang

DOI: 10.1039/C6CY02580C

Abstract:

Formic acid and its salts are important chemical intermediates. Industrial production of formic acid involves liquid phase carbonylation of methanol to methyl formate followed by hydrolysis to formic acid. Alternatively, formic acid can be generated during glycerol electro-oxidation when glycerol undergoes C–C bond cleavage. Silver based catalysts such as carbon supported silver–gold alloys significantly improve selectivity to formic acid

during glycerol electro-oxidation. However, these catalysts tend to suffer from poor electrochemical activity. Herein, we examined the ability of Ag containing, porous Au structures to tune the glycerol oxidation pathway towards formate and glycolate whilst maintaining high electro-catalytic activity. Our catalyst consisted of an Au rich porous framework that possessed residual amounts of Ag within its pores. When tested for glycerol electro-oxidation, the Ag containing porous Au catalyst exhibited both high selectivity towards formate and high electrochemical activity.

Copper-Modified Gold Nanoparticles as Highly Selective Catalysts for Glycerol Electro-Oxidation in Alkaline Solution

Thia, Larissa, Xie, Mingshi, Liu, Zhaolin, Ge, Xiaoming, Lu, Yizhong, Fong, Wenmei Eileen, Wang, Xin

doi.org/10.1002/cctc.201600725

Abstract: The C3 selectivity of carbon-supported Au nanoparticles for glycerol electro-oxidation was significantly enhanced by the interaction of Au with electro-deposited Cu species. Notably, the C3 selectivity of supported Au nanoparticles doubled after 90 min of Cu electro-deposition at +0.015 V. This result was obtained if glycerol electro-oxidation was performed at +0.1 V for 2 h. The most selective catalysts contained an Au+ species that was generated by an interaction between Au and electro-deposited Cu2O. The presence of Au+ increased the selectivity to glycerate and tartronate and suppressed C–C bond cleavage to glycolate and formate simultaneously.

Carbon Abatement in the Petroleum Refining Industry: A Control and Optimisation Research Network, or, CAPRICORN, aims at answering the question of how to minimise CO2 emissions while optimally running a modern industrial park including complex refinery operations to produce downstream fuel blends. The research uniquely combines and advances the state-of-the-art in low carbon research encompassing fields of surrogate fuel modelling, fuel blending using nonlinear correlations, fuel-engine mapping for emissions regulation compliance, inorganic and organic nanoparticle flame synthesis. Uncertainty propagation, Bayesian parameter estimation, dynamic optimisation of refinery operations and associated energy loads, and model predictive control are methods used to develop sustainable low-carbon refinery operations.

CAPRICORN is split into five interacting work packages:

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

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

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

WP 3.4: Modelling and optimisation of unit operations

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

The CAPRICORN group is led by PIs:

Prof Markus KRAFT (Cam)

Prof Raymond Wai Man LAU (NTU)

Prof Iftekhar KARIMI (NUS)

Prof. Markus Kraft,

University of Cambridge

PI, IRP3

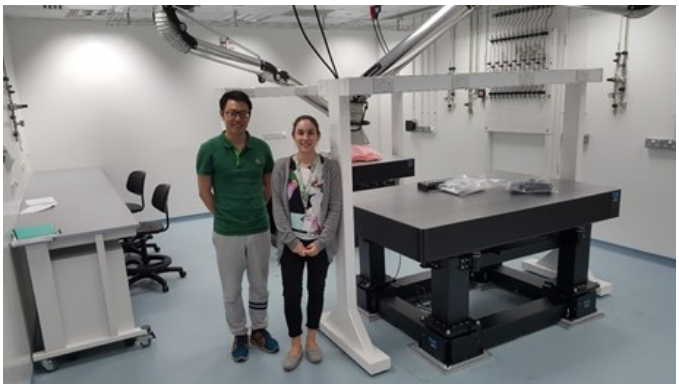
April 2017

3.3.1 IRP3 Research Overview

The last six months have seen great progress in our flagship research outcome, the J-Park Simulator (JPS). The JPS has the ambition to virtualise Jurong Island in its entirety, *i.e.* representing every entity on Jurong by an avatar which not only records data but also knowledge about its own behaviour in the form of computational models, thus enabling simulations and optimisation studies for example. We have now accomplished the key step of representing the data and models underlying the JPS by means of an ontology – an extensible data structure widely used as part of Semantic Web technologies which focuses on entities and the relationships between them. This paves the way towards or at least facilitates machine-to-machine (M2M) communication applications and thus takes us a step closer to realising Industry 4.0. Furthermore, the ontological data representation will help us to continue to evolve the JPS into an expert system capable of responding to intelligent queries from stakeholders and policy makers. In both of these areas, we have already achieved first successes in this reporting period.

Progress in the laboratory, both in Singapore and in Cambridge, has been equally successful, in a number of areas. We have synthesised a class of fuel additives with potential for pollutant suppression, particularly soot, in internal combustion engines. Sooting flame experiments are also under way, with the added capability to release liquid fuel additives into the flame in a controlled fashion. Analysing the resulting soot particles by means of high-resolution transmission electron microscopy (HRTEM) and other techniques will then provide insights into the effects of the additives on soot composition and morphology. In addition, great efforts have been invested into the flame synthesis of inorganic nanomaterials for water-splitting applications. Materials considered include titania in various forms, iron and cobalt oxides, and composites thereof, some of which have shown promise in terms of catalytic performance.

Alongside these ongoing activities, we continue to expand our experimental facilities: New optical tables have been delivered (see Fig. 3.1), which will form the basis of significantly enhanced laser-diagnostic capabilities, and thus an analysis tool which will help us understand nanoparticle synthesis processes in more detail. In Cambridge, having finally moved to our new premises, we have commissioned a new flame rig, designed specifically for flame-synthesis of organic and inorganic nanoparticles in a variety of configurations, in particular with composites in mind for catalytic applications.

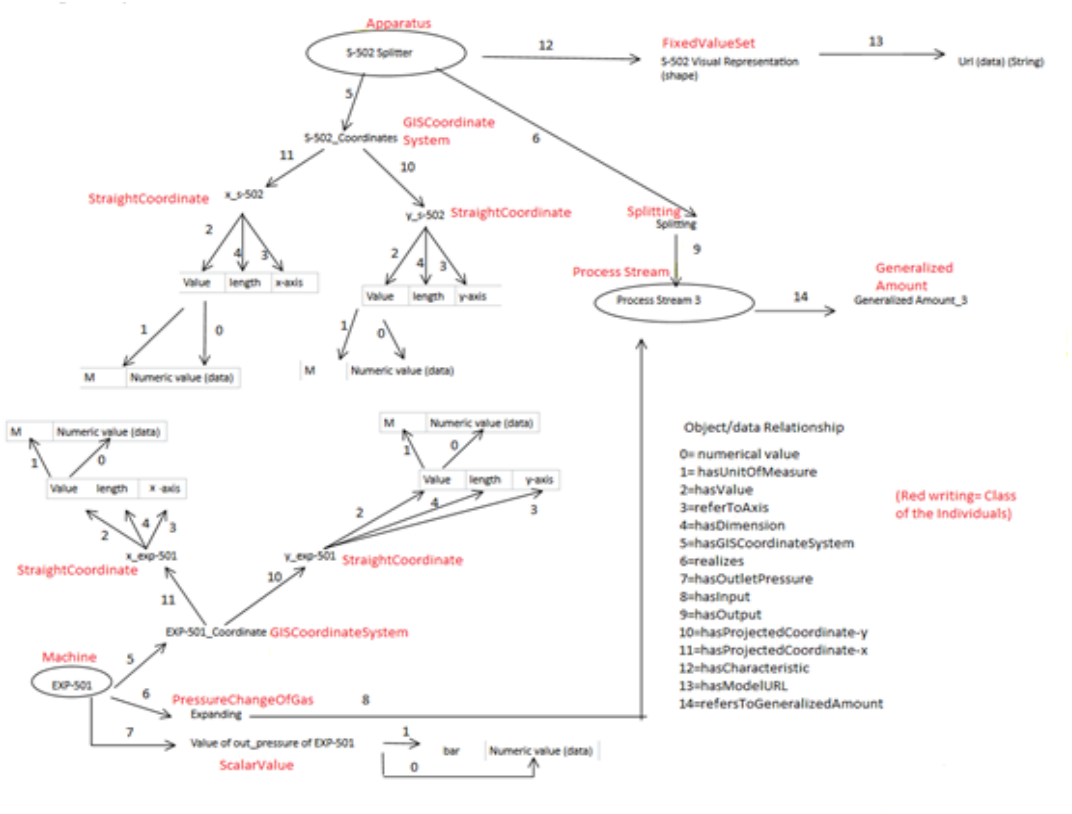


NUS research fellows Drs ZONG Yichen and Maria BOTERO with the newly delivered laser tables.

3.3.2 Update on work packages

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

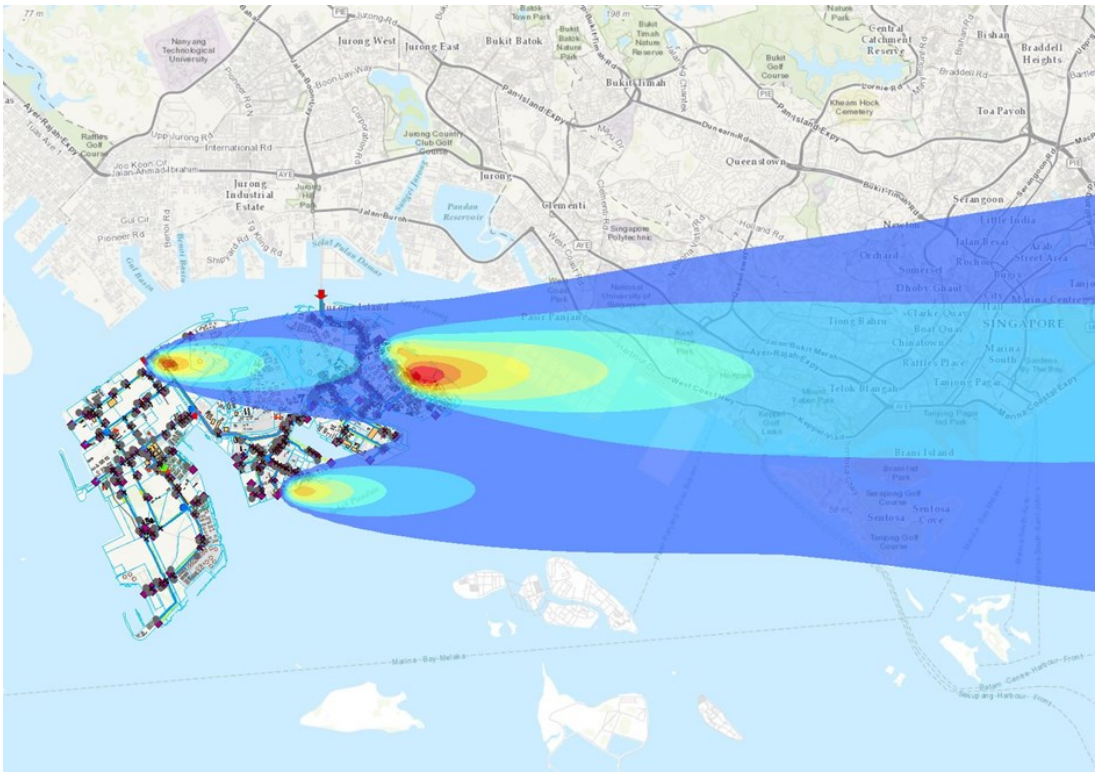
During the reporting period, the 'core developer team' of the eco-industrial park expert system J-Park Simulator (JPS) designed, developed, and implemented a number of major advances in the way knowledge is represented within the JPS. The team, which includes ZHOU Xiaochi, ZHANG Shaocong, Kevin ADITYA, Meiqi LIM, Martin KLEINELANGHORST (SRF, NTU, IRP3)) and Dr ZHOU Li (RF, NUS, IRP3), have upgraded the JPS so that all underlying data and models are stored in an ontology. Previously, all data was held in feature layers stored in ArcGIS, hosted on an external server, which meant no flexibility allowing for extensions to novel features. The migration of the JPS to Web Ontology Language (OWL) represents a key development and an important milestone of the JPS project towards a Semantic Web based platform that enables machine-to-machine (M2M) communication. ArcGIS is now only used as a front-end to visualise selected subsets of the data held in the ontology. In order to take this step, it was necessary to first of all develop a suitable ontology for the database of every layer in the JPS. The class structure of the ontology was created first, then the individuals were assigned to the correct class with the relations between them using the object relationship or data relationship for linking the individuals and data. Then, remaining inconsistencies were identified using logical reasoning. A methodology was developed to add new features, objects and data to the JPS using the open-source Protégé software platform in an automated procedure. Building upon this new infrastructure, the JPS team, coordinated by Dr ZHOU Li (RF, NUS, IRP2), has been developing sets of ontology files for the technical components on Jurong industrial park, contributing to the knowledge base for the J-Park Simulator. An example is shown in Fig. 3.2. A paper titled "Towards an ontological infrastructure for chemical process simulation and optimisation in the context of eco-industrial parks" has been submitted to Applied Energy. For instance, a model for the overall profit optimisation of a biodiesel plant has been built based on a surrogate model developed



Example ontological representation of chemical plant data.

by Janusz SIKORSKI (PhD student, UCAM, IRP3). Five process simulation models were developed using ASPEN HYSYS based on a literature review and other publicly available information. The developed models represent some of the plants operating on Jurong Island in order to extend the basis for energy and material networks within the J-Park Simulator. This involved developing ontologies for these five process simulation models using OntoCAPE and Protégé. As an example of a cross-domain application, the JPS ontology was extended to include the electricity grid, in collaboration with SUN Lu (PhD student, NUS, IRP4).

A new service is being developed that allows automated import of data from the Web that are used as input for the calculation and near real-time visualisation of air pollution on Jurong Island and its impact on the rest of Singapore (see figure). A paper is being finalised which presents an ontology of the Atmospheric Dispersion Management System (ADMS) and demonstrates how the ontology can enhance the services of the JPS. In particular, it is shown how the ADMS-extended JPS can be used to visualise and quantify the impact of heat or pollutants released from the power plants of an eco-



Concentration of CO_2 released by the power plants on Jurong Island and covering the southern districts of Singapore including the Central Business District (CBD), as simulated by ADMS.

industrial park on nearby residential areas and the central business district (CBD) in real time.

Khamila Nurul KHAQQI (PhD student, NTU, IRP3) currently works on designing a blockchain application for carbon emission trading. With the rise of Industry 4.0 and system automation, blockchain will be one of the driving technologies that make it possible for machines to communicate with each other in a secure manner with limited human intervention. An emission trading scheme or cap-and-trade scheme is a policy that has the objective to gradually reduce industrial carbon footprint by decreasing the amount of permits to produce industrial carbon emissions. It is also expected that the increase in the permit price due to the diminished supply will in turn stimulate the investment in clean technology. So far, while the policy has been able to encourage reduction in industrial emission production, it has not made significant progress in stimulating the research and adoption of clean technology. Therefore, new measures are deemed necessary to promote this investment. Our current research into blockchain applications for emission trading is addressing this problem. By providing incentives that are distributed automatically in a blockchain network, participants are encouraged to emphasise clean technology investment rather than any other measures of reducing

industrial emissions. The incentives used in this application are trading advantages that are automatically distributed based on the participant's reputation. Participants that adopt clean technology for their business process will have a better reputation and consequently have an advantage in the trading process. This, along with the status that comes from the reputation system itself, is then expected to be the driving motivation that will increase participant enthusiasm in clean technology research and adoption. In the application, a reputation system is added to the traditional cap-and-trade scheme that is executed on a blockchain network. It is used to distribute trading benefits in order to shape participant behaviour into putting greater weight on the effects of their actions on the environment and climate change. The reputation system is evaluating participant behaviour in regards to their compliance with the scheme and their business practice in order to reduce their emissions. An algorithm has been created for implementation into a blockchain environment which regulates the trading process for carbon credits, taking into account participants' reputation.

Janusz SIKORSKI (PhD Student, UCAM, IRP3) aims to contribute towards understanding of complex industrial networks and development of methodology required to investigate them effectively with particular focus on Jurong Island. Most recent research activities focused on machine-to-machine (M2M) communications and applications of blockchain technology in an industrial setting, in particular the chemical industry as it interacts with the electricity market. The primary outcome was an article on this subject submitted to Applied Energy. It demonstrates that it is possible to successfully employ the blockchain technology to facilitate M2M interactions and establish an M2M electricity market in the context of the chemical industry via the Internet of Things. This work contributes a proof-of-concept implementation of the described scenario and its technical details. Furthermore, all participants are supplied with realistic data produced by process flow-sheet models of industrial equipment. Current activities include simulating a chemical plant which takes advantage of the global commodities market in an automated fashion.

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

Dr Maria BOTERO (RF, NUS, IRP3) has been commissioning experimental rigs built to conduct flame studies, and has been working on two fronts: Firstly, the synthesis and characterisation of an oxygenated additive with potential pollutant suppression in the combustion of liquid fuels, and secondly, detailed understanding of soot formation in flames.

On the first front, together with TAN Yong Ren (NUS, IRP3) and Dr SHENG Yuan (RF, NTU, IRP3), pollutant suppression, particularly soot, from fuel combustion using fuel additives has been investigated. Oxygenated additives have been identified as a promising class of compound for the pollutant suppression, especially in soot reduction. An extensive literature review has been performed on existing research work regarding effect of oxygenated additives in fuel combustion in order to identify suitable candidates for further investigation. The polyoxymethylene dimethyl ether (PODE) family has been identified to have the potential to be a good pollutant reduction additive, illustrated from results published in literature. This promising additive has been successfully synthesised, employing existing synthetic methods, yielding a mixture of PODE 1-8. Among the PODE mixture, the PODEs that are of particular interest are PODE 2-5, due to their known suitability in physical properties to be blended in fuels and used in engines. Separation of the PODE mixture has been performed to obtain the individual PODE 2-5 so as to investigate on their independent contribution to the pollutant suppression property in fuel combustion. With in-depth understanding of the effect of each of the PODE 2-5 in fuel combustion, this will allow us to formulate a fuel mixture with the best performance in terms of pollutant reduction. Our aim is to investigate the influence of each PODE fraction in the pollutant formation of its mixture with commercial and surrogate fuels.

On the second front, Dr Maria BOTERO (RF, NUS, IRP3) is studying the nanostructure evolution of soot in a well-defined co-flow diffusion flame of ethylene on a Yale burner. The experimental conditions have been carefully selected to allow the direct comparison with flame simulations performed

by Dr Edward YAPP (PO, NTU, IRP3). The flame temperature profile is fully mapped with thermocouples and samples along different positions in the flame are taken for further analysis. The evolution of soot morphology and nanostructure in the flame will be quantified using HRTEM analysis of soot samples and this will give the research team some information of the estimated size of the molecules present in the soot particles in different flame regions. This will also allow the research team to observe the growth of the primary particles and aggregates and their oxidation. Currently the research team are also building a system that allows the evaporation of liquid fuels into these ethylene flames. This evaporation system will enable the study of additives such as PODE into the ethylene flames, and a more fundamental study of the soot formation from liquid fuels.

The team has also started measurements of particle size distributions and source apportionment of PM2.5 from marine vessels and chemical industry emissions. This investigation will lead to important information on the impact of marine engine emissions and chemical technology on the air quality in Singapore. This data will be used by the J-Park Simulator to study the dispersion of such emissions through the island. The research team is currently developing a methodology to perform these measurements in the environment which poses several challenges as the conditions in Singapore are very harsh for the instruments.

Jacob MARTIN (PhD student, UCAM, IRP3) has been focusing on two aspects of soot formation. The first one is the extent to which soot can oxidise from within. A paper has been published on this subject in the journal Carbon. There is also experimental evidence for the uniform burning of nascent soot particles. This suggests that the early soot fragments are particularly vulnerable to oxidation, and highlights the formation of a hard shell around the outside the soot particle as it progresses through the flame. He reported that he has begun to explore the partitioning of mixed polycyclic aromatic hydrocarbon (PAH) clusters using molecular dynamics simulations. Alongside this, the team has developed a Monte Carlo method to sample lowest energy configurations to supplement the molecular dynamic simulations. The goal is to determine whether the partitioning observed in soot particles with a hard exterior and soft inside is due to size-dependent PAH partitioning or due to carbonisation. Carbonisation is to be anticipated to be the origin of the hard crust and have experimental evidence of cross-linking occurring from nanoindentation studies. The second aspect is the role of curvature in the formation of soot. Curved fringes have been observed in electron microscopy studies and curved aromatic molecules have been extracted from within soot. Early simulations using classical force-fields (where the electrostatics of the molecule were described by single point charges at each atom), however, produced incorrect dipole moments and incorrect dimer structures in molecular dynamics simulations. Thus, an in-depth study of the electrostatics was conducted. Using electronic structure calculations on a collection of curved aromatic molecules the origin, magnitude and impact of this dipole moment on dimerisation could be determined. This work also provides a method for describing these complex electrostatics making use of atom-centred distributed multipoles fitted to the quantum mechanical calculated electronic density. The permanent dipole moment on curved aromatics might play a role in soot formation as it allows for strong interactions between the molecules and chemions present in the flame. Many studies have found a correlation between ionic species and soot formation, however to date no possible interaction could be imagined to explain this correlation. To test this hypothesis, experimental work has begun alongside Dr Jochen DREYER (RF, UCAM, IRP3) in Cambridge.

In addition, a coflow diffusion flame has been developed which allows metals to be injected into the flame, as well as charged plasma containing non-reactive ions. The experiments together with simulations using distributed multipoles will seek to elucidate the role that ions and curved molecules play in the nucleation of PAH into nascent soot.

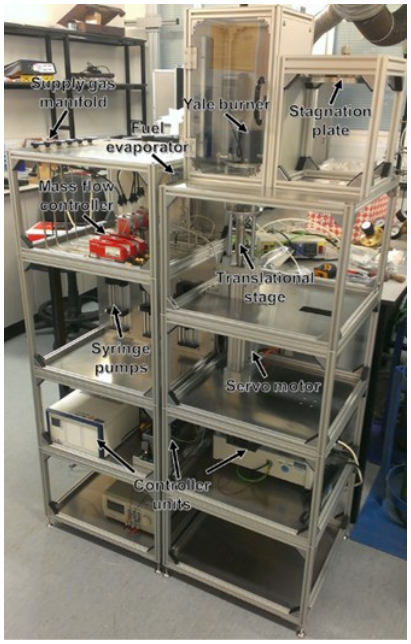
WU Shaohua's (PhD student, NUS) research goal is to develop a mathematical model that is simple, fast and accurate to describe the dynamics of soot particle formation in flames. Previously, he has developed such a model, called Moment Projection Method, and has now published two papers on this model in Journal of Computational Physics. This soot model has also been implemented into a

software which can be used to efficiently simulate the combustion processes in burners, reactors, and internal combustion engines.

WP3:3 Nanoparticle/film flame synthesis – kinetics and application

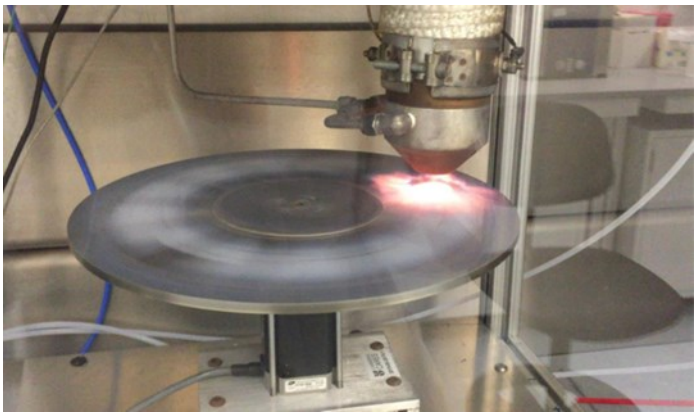
Dr WANG Weijing (RF, NTU, IRP3) has been working on the synthesis and study of photocatalytic abilities of titania nanoparticles. On the synthesis side we have been switching to $TiCl_4$ as the new precursor because of its solubility with other metal oxide precursors. Upon using $TiCl_4$ it was discovered that the range for producing blue reduced titania can be extended to higher equivalence ratios. Given that blue reduced titania is photocatalytically more reactive than pure titania, especially at visible wave-lengths, being able to produce fine-crystalline reduced titania is promising. With this in mind, the kinetics behind the formation of blue reduced titania have also been investigated. By observing the formation and oxidation of blue reduced titania in the experiments, kinetic simulation efforts of the synthesis process have been initiated. By including the reaction mechanism of $TiCl_4$ in the simulation we are hoping to be able to identify the reaction paths of $TiCl_4$ and thus fully understand the kinetics of the process of Ti^{3+} formation and its oxidation. On the photocatalysis side we have been testing both pure titania and blue reduced titania in solar water-splitting experiments for hydrogen production. For pure titania, our hydrogen production rate over the full spectrum proved to be better than commercial P25 TiO_2 and also most literature data. By finely tuning both synthesis conditions and also photocatalysis parameters we are aiming for even higher hydrogen production rates. Blue reduced titania is particularly useful as it has so far achieved a production rate of about 200 µmol/h/g in the visible light region, with literature ranges from 10-1000 µmol/h/g. Work is in progress to improve upon that further by tuning the precursor loading rate in order to achieve smaller particles with even higher specific surface areas. Also, some post-processing of the particles will be applied to control the amount of defects in the particles so that it can be optimised for solar water-splitting in the visible light region.

SHENG Yuan (PhD student, NUS, IRP3) has developed flame synthesis methods for iron, cobalt, and mixed iron-cobalt oxide nanoparticles using a divergence-stabilised burner, in pursuit of high-performance, low cost transition metal oxide catalysts for electrochemical water-splitting. Delivery of metal precursors to the burner at stable rates has been a major challenge and extensively experimented on. Two methods of precursor delivery, namely evaporation of precursor solutions and sublimation of solid precursors, have been tested and optimised. For this purpose, necessary modifications to the burner were made which include the assembly of a precursor cartridge and a temperature controlling system. So far, uniform Fe_2O_3, Co_3O_4, and Fe-doped Co_3O_4 nanoparticles with sizes below 5 nm have been synthesised successfully as confirmed by HRTEM and XRD analyses. The characterisation results also suggest possibilities of tuning chemical composition and crystallographic phase of the product (*e.g.* Co_3O_4 versus CoO) by changing the equivalence ratio of the flame. Furthermore, active electrodes for water oxidation have been prepared by *in situ* deposition of flame-synthesised Fe_2O_3, Co_3O_4, or Fe-doped Co_3O_4 particles on indium-tin oxide (ITO)-coated glass or graphite sheet substrates. Also, co-deposition of carbon and metal oxide was achieved by sooty flames doped with the corresponding metal precursor. All of the electrodes thus obtained showed activity in oxygen evolution reaction (OER) in alkaline electrolyte, with graphite-based electrodes being significantly superior. In particular, the flame-synthesised Co_3O_4 on graphite electrodes exhibited comparable initial activity with wet-chemically synthesised Co_3O_4 nanoparticles. Further improve-



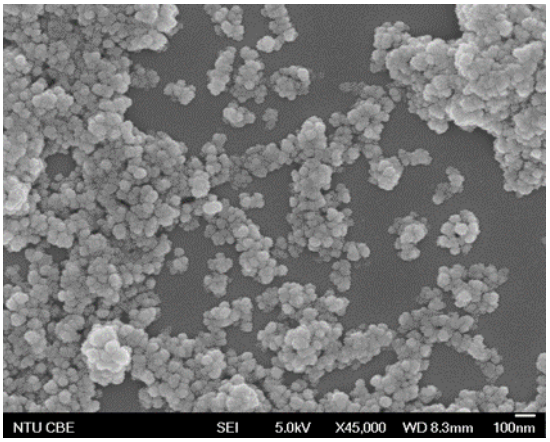
Newly constructed flame rig to support soot formation and inorganic nanoparticle synthesis research in WPs 2 and 3 (Dr Jochen DREYER, UCAM).

ment has been achieved by Fe-doping to bring down the over-potential to about 330 mV at an OER current density of 10 mA/cm^2. The next step is to improve the stability of the flame-synthesised catalyst films to suit requirements in practical applications.



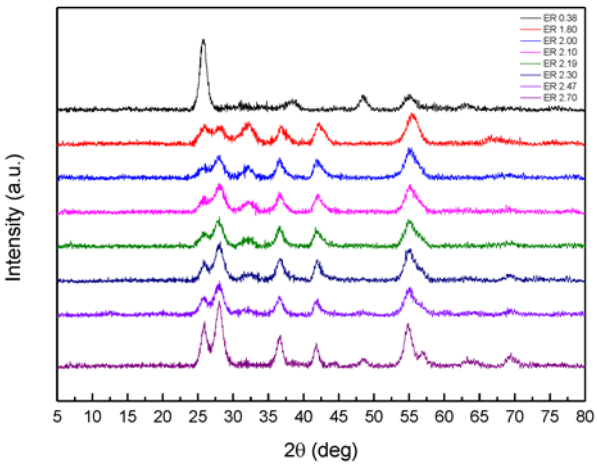
Flame synthesis set-up to deposit TiO_2 on a coverslip placed on a rotating disk (WU Shuyang, PhD student, NTU).

Dr Jochen DREYER (RF, UCAM, IRP3) has designed and built a new flame rig to support the experimental work in WP2 and WP3 (see Fig. 3.4). The fuel is delivered to the burners with the aid of syringe pumps, enabling the usage of liquid fuels and their mixtures. Soot formation as function of fuel structure and flame conditions can be studied with an open co-flow diffusion or premixed flame as well as a stagnated premixed flame. Mixing metal containing precursors with the fuel allows the synthesis of metal oxide nanoparticles. They can either be collected from the gas stream and used as powder or directly deposited onto the water-cooled stagnation plate. Parameters such as gas and fuel flow rates, evaporation temperature, vertical flame position, *etc.* are controlled through a custom-made LabVIEW graphical user interface. A number of novel experimental procedures were developed to take samples from within the flame and to directly measure particle size distributions and number densities or to deposit the particles onto a substrate. The deposited samples are analysed by techniques such as UV/Vis, AFM, TEM, DRIFTS, or Raman spectroscopy to investigate the fundamentals of nanoparticle nucleation and growth in flames.



FESEM image of TiO_2 samples (WU Shuyang, PhD student, NTU).

WU Shuyang (PhD student, NTU) has been working on two projects, firstly, the photocatalytic water splitting for hydrogen generation using flame-synthesized titania, and secondly, the electrochemical oxygen reduction reaction (ORR) for hydrogen peroxide generation. The first project aims to utilise sunlight and water as abundant natural resources which can be used to produce renewable energy in the form of hydrogen through photocatalytic water-splitting. Despite great progress, the research in this field is still at an early stage. The efficiencies of photocatalytic water-splitting for the production of hydrogen are still relatively low and remain to be improved. The flame-synthesised titania (see figures) has many advantages over traditional titania made by wet chemistry. The specific surface area is measured to be around 150 m^2/g, which exceeds most results in the literature. Since the TiO_2 nanoparticles are synthesized in the reductive environment, the phase remains mostly as rutile phase (see figure). The small particle size, the large specific surface area, the simple procedure and mass production can improve the hydrogen generation rate significantly



XRD spectra revealing the crystal phase of TiO_2 samples. Only the leanest case, with an equivalence ratio (ER) of 0.38, is seen to produce mostly anatase, whereas the rich cases produce mostly the rutile phase (WU Shuyang, PhD student, NTU).

compared to other catalysts. Besides, the excellent durability and environment-friendly properties can make the TiO_2 nanoparticles a promising substitute for toxic heavy metal catalysts such as CdS, CdO, and MoP. The catalytic performance of the TiO_2 exceeds most results showed previously. The highest hydrogen generation rate we have achieved so far is larger than most results reported in the literature under similar experimental conditions.

The main purpose of the second project is to seek a green and effective method to synthesize hydrogen peroxide, namely the electrochemical oxygen reduction reaction (ORR). Hydrogen peroxide is one of the 100 most important chemicals in the world. The most elegant and efficient reaction pathway would be the direct conversion of elemental hydrogen and oxygen. However, such a process creates the danger of explosion. Electrochemical flow reactors, such as the polymer electrolyte membrane fuel cell (PEMFC), represent an attractive alternative by separating oxygen reduction and hydrogen oxidation under cogeneration of energy. 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. The mesoporous nitrogen-doped carbon electrocatalyst promises to be a highly active, cheap, and selective metal-free catalyst for the electrochemical synthesis of hydrogen peroxide. Using this catalyst as a substitute for the traditional noble metal Pt catalyst could lower the cost of this reaction substantially.

Manoel MANUPUTTY (PhD student, UCAM, IRP3), assisted by Dr Maria BOTERO (RF, NUS, IRP3), carried out a study of TiO_2 nano-film synthesis in flames. Some custom sampling techniques have been developed in order to analyse the particle size, morphology and phase. The aim is to understand the influence of the synthesis conditions, such as flame equivalence ratio, the distance from the flame to the deposition surface and the loading of the TiO_2 precursor, on the characteristics of the nano-film. Ultimately this will enable simulating the process and tuning it to obtain the desired film properties.

On the modelling side, Astrid BOJE (PhD student, UCAM, IRP3) has been focussing on modelling titania synthesis in an industrial context. A model for the reactor and cooler units used for industrial titania synthesis has been developed, 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. This work has been conducted in close collaboration with the industrial sponsor (Huntsman), and has been published in Chemical Engineering Science.

Casper LINDBERG (PhD student, UCAM, IRP3) has developed a detailed particle breakage model which relates morphological descriptors to the milling behaviour of flame-synthesised titanium dioxide. The milling model allows relating reaction conditions during particle synthesis to the milling properties of the particles. This research has been published in Chemical Engineering Science. Furthermore, he is developing a detailed population balance model for titanium dioxide and improving how particles are represented and evolve under surface growth and sintering processes. This includes in particular the crystal phase of the particles. Such a model can be used to study the relationship between the reactor conditions under which nanoparticles form and their performance in the post-synthesis milling process.

WP 3.4: Modelling and optimisation of unit operations

Aravind DEVANAND (PhD student, NUS, IRP3) has been investigating a carbon-free scenario in the J-Park Simulator by designing a nuclear hybrid power system capable of providing power to all plants on Jurong Island. This power system model comprises of modular nuclear plants, solar panels, and suitable power storage systems like batteries. An ontology for the proposed model of the power system has been developed using the Web Ontology Language (OWL). The mathematical formulation for designing the best suited power system then leads to two optimisation problems. The objective of the first problem is to determine the optimum capacities of each power generation unit in the system. The second problem focusses on the operational flexibility and reliability of the power

system. These problems were formulated and a mathematical model for each power generation unit was developed. The next step is establishing communication between the database created in Protégé and the optimisation problem formulated in GAMS. This could provide the optimal carbon-free power system for Jurong Island. Another aspect of the problem involves taking geographical data from the J-Park Simulator and using it to carry out feasibility studies for finding the suitable locations for the modular nuclear plants.VO Chi Hung (PhD Student, NUS) has recently joined IRP3 to focus on the methanogen M. maripaludis S2. This organism can capture CO_2 and produce a useful chemical product – methane. A literature review has been completed on the metabolic pathways within M. maripaludis S2, metabolic engineering techniques and in silico modelling. An experiment has been designed for the analysis of the gaseous and aqueous products secreted by M. maripaludis S2. The next steps for the immediate future are set-up, commissioning, and conducting the experiments. Knowledge gained from investigating the metabolic reactions of this organism will allow genetic modification to enhance its CO_2 capture. The long-term goal is to demonstrate the feasibility of a bioreactor which can convert CO_2 into useful fuel or other organic products.

Pulkit CHHABRA (PhD student, NTU, IRP3) has been working on developing a generalised kinetic model for a biodiesel production process. The model is based on a reaction scheme consisting of each glyceride and ester formed by the different fatty acids present in oil. The model consists of 71 species and 257 reactions. A Bayesian approach is used to estimate the model parameters, which comprise pre-exponential factors and activation energies of certain reactions. He is also working on the automatic updating of model parameters in the J-Park Simulator. The idea is to collect data from any, real or simulated, process running on Jurong Island, storing it in an ontology, using the data to estimate the parameters in a model, and returning the parameters to the ontology. The process is then repeated automatically whenever new data is received in order to keep the parameters up to date.

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

Sushant GARUD (PhD student, NUS, IRP3) has been working on achieving a better understanding of complex systems and their functionality through smart and computationally inexpensive design and analysis of computer simulations. This involves modelling and simulating complex chemical processes using custom-made process simulators, studying various sampling techniques for designing computer experiments, developing adaptive intelligent sampling techniques for surrogate approximation, analysing computer simulations with the help of parameterisation, and studying the parameterisation on different levels in complex systems. During an extended visit to Cambridge, he finished implementing a generalised smart sampling algorithm (SSA). Moreover, two papers on smart sampling algorithms for surrogate model development have been published, and a review paper “Design of Computer Experiments: A Review” has been submitted. Currently, he is investigating higher-dimensional surrogates.

Other Activities and Achievements

- Dr ZHOU Li (RF, NUS, IRP3) gave a talk on “System development for eco-industrial parks using ontological innovation” at the 8th International Conference on Applied Energy in Beijing.
- Several C4T researchers visited ICES-A*Star on Jurong Island.
- Dr Sebastian MOSBACH (SRF, UCAM, IRP3) presented the J-Park Simulator at the Second International Conference on Internet of Things, Data and Cloud Computing (ICC 2017) at Churchill College, University of Cambridge, on 22 March 2017.

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.

Smart Adaptive Sampling for Surrogate Modelling

Garud Sushant, Karimi Iftekhar, Kraft Markus

DOI: 10.1016/B978-0-444-63428-3.50110-7

Abstract:

In this paper, we present a novel technique to systematically select data points in an adaptive and optimized manner for model building, which assures that the points are placed in the regions that exhibit complex behaviour and/or poorly sampled. Our proposed algorithm is designed to enhance the overall accuracy of the surrogate model and reduce computational burden. It involves solving a series of point placement optimization problems which is formulated as a nonlinear programming problem (NLP). It allows us to generate enough data points in the most plausible regions. Performance of our algorithm is compared with the conventional techniques viz. uniform sampling, random sampling and quasi-random sampling based on Sobol sequence. For these analyses, key performance indicators (KPIs) and loss ratios are defined based on the model quality attributes. The algorithm has been implemented and assessed for a literature test problem. The results are promising, as our algorithm outperforms the conventional methods in terms of the predefined KPIs and loss ratio. Overall performance (based on the total loss ratio) in the case of our algorithm is improved up to 18% compared to uniform sampling and Sobol sampling while it performs far better compared to random sampling.

Numerical and Experimental Study on Internal Nozzle Flow and Macroscopic Spray Characteristics of a Kind of Wide Distillation Fuel (WDF) - Kerosene

Yu Wenbin, Yang Wenming, Mohan Balaji, Tay Kunlin, Zhao Feiyang, Zhang Yunpeng, Chou Siawkiang, Kraft Markus, Alexander Malcolm Andrew, Young Alfred, Lou Kwokhow

DOI: 10.4271/2016-01-0839

In this study, the internal nozzle flow and macroscopic spray characteristics of a kind of wide distillation fuel (WDF) - kerosene were investigated both with numerical and experimental approaches. Simulation results indicate that compared with diesel fuel, kerosene cavitates more due to higher turbulent kinetic energy as a result of lower viscosity. The results from experiment indicate that under lower charge density, the spray penetration for kerosene is obviously shorter than that for diesel, especially for the lower injection pressure. This is because lower fuel viscosity results in a reduction in the size of the spray droplets, leading to lower momentum. However the spray angle of kerosene is larger compared with diesel due to stronger turbulence in the nozzle flow caused by increased cavitation for kerosene, which also accords well with the simulation results.

A kinetic mechanism for the thermal decomposition of titanium tetraisopropoxide

Buerger Phillipp, Nurkowski Daniel, Akroyd Jethro, Kraft Markus

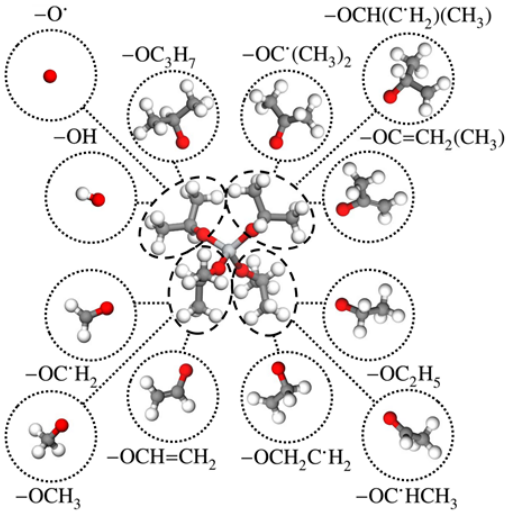
Highlights:

- A thermodynamically consistent mechanism describing the thermal decomposition of Ti (OC3H7)4 (TTIP) is proposed.
- Mechanism has been derived by drawing analogy from isopropanol decomposition.
- Three main decomposition pathways have been identified. -

- Calculated reaction rates are similar to their isopropanol analogue.
- Mechanism was assessed against experimental ignition delay measurements.

Abstract:

This work presents the first systematically derived and thermodynamically consistent mechanism to describe the thermal decomposition of titanium tetraisopropoxide (TTIP). The mechanism is based on an analogy between the decomposition of the isopropoxide branches and the decomposition of isopropanol. Flux and sensitivity analyses were used to identify the main reaction pathways in the proposed mechanism as the step-wise release of C3H6 via four-member ring transition states, the successive abstraction of CH3 radicals via C-C bond cleavage followed by hydrogen abstraction to form C=C double bonds, and hydrogen abstraction from the isopropoxide methyl groups followed by the release of C3H6. The final decomposition product was titanium hydroxide, Ti(OH)4. Rate constants were calculated using conventional and variational transition state theories for reactions in the first two pathways. The calculated rates are similar to the rates calculated for the corresponding isopropanol reactions, providing support for the analogy with isopropanol. The mechanism was used to simulate the ignition delay of isopropanol and TTIP. Excellent agreement was observed with experimental data for isopropanol. However, the mechanism over predicted the ignition delay for TTIP. The discrepancy was shown to be unlikely to be caused by the modest difference between the true reaction rates for the TTIP system and those assumed based on the analogy with isopropanol. It was found that the sensitivity of the TTIP decomposition to the presence of water must be caused by additional chemical pathways than the ones given by isopropanol analogy.



Unique P-Co-N Surface Bonding States Constructed on g-C3N4 Nanosheets for Drastically Enhanced Photocatalytic Activity of H2 Evolution

Li Chunmei, Du Yonghua, Wang Danping, Yin Shengming, Tu Wenguang, Chen Zhong, Kraft Markus, Chen Gang, Xu Rong

DOI: 10.1002/adfm.201604328

Abstract:

Developing high-efficiency and low-cost photocatalysts by avoiding expensive noble metals, yet remarkably improving H2 evolution performance, is a great challenge. Noble-metal-free catalysts containing Co(Fe)-N-C moieties have been widely reported in recent years for electrochemical oxygen reduction reaction and have also gained noticeable interest for organic transformation. However, to date, no prior studies are available in the literature about the activity of N-coordinated metal centers for photocatalytic H2 evolution. Herein, a new photocatalyst containing g-C3N4 decorated with CoP nanodots constructed from low-cost precursors is reported. It is for the first time revealed that the unique P(δ-)-Co(δ+)-N(δ-) surface bonding states lead to much superior H2 evolution activity (96.2 µmol/h) compared to noble metal (Pt)-decorated g-C3N4 photocatalyst (32.3 µmol/h). The quantum efficiency of 12.4% at 420 nm is also much higher than the record values (≈2%) of other transition metal cocatalysts-loaded g-C3N4. It is believed that this work marks an important step toward developing high-performance and low-cost photocatalytic materials for H2 evolution.

Parameterisation of a biodiesel plant process flow sheet model

Sikorski Janusz, Brownbridge George, Garud Sushant, Mosbach Sebastian, Karimi Iftekhar, Kraft Markus

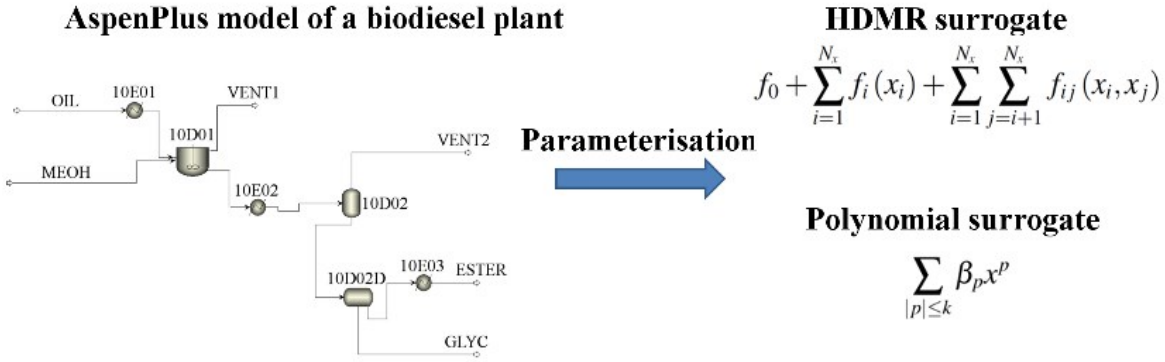
DOI: 10.1016/j.compchemeng.2016.06.019

Highlights:

- A process flow sheet of a biodiesel plant is described with two types of surrogate models: polynomial and high-dimensional model representation (HDMR). -
- Third order polynomial and HDMR surrogates achieve best and similar degree of accuracy. -
- Polynomials of order higher than 3 suffer from overfitting, especially in high-dimensional scenarios. -
- Global sensitivity analysis indicates that interaction terms have negligible effect on heat duties of the biodiesel plant.

Abstract:

This paper presents results of parameterisation of typical input–output relations within process flow sheet of a biodiesel plant and assesses parameterisation accuracy. A variety of scenarios were considered: 1, 2, 6 and 11 input variables (such as feed flow rate or a heater's operating temperature) were changed simultaneously, 3 domain sizes of the input variables were considered and 2 different surrogates (polynomial and high dimensional model representation (HDMR) fitting) were used. All considered outputs were heat duties of equipment within the plant. All surrogate models achieved at least a reasonable fit regardless of the domain size and number of dimensions. Global sensitivity analysis with respect to 11 inputs indicated that only 4 or fewer inputs had significant influence on any one output. Interaction terms showed only minor effects in all of the cases.



A novel methodology for the design of waste heat recovery network in eco-industrial park using techno-economic analysis and multi-objective optimization

Zhang Chuan, Zhou Li, Chhabra Pulkit, Garud,Sushant, Aditya Kevin, Romagnoli Alessandro, Comodi Gabriele, Dal Magro Fabio, Meneghetti Antonella, Kraft Markus

DOI: 0.1016/j.apenergy.2016.10.016

Highlights:

- A methodology for Eco Industrial Park waste heat recovery is proposed.
- Single objective and multi-objective optimization are used.

- Multi objective optimization can provide trade-off of different objective functions.
- Waste heat discontinuity greatly influences waste heat recovery network optimization.

Abstract:

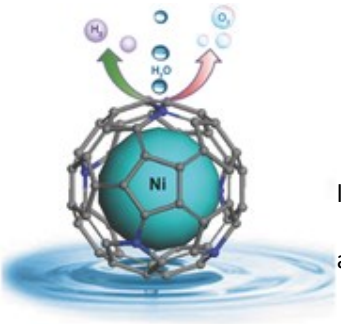
Based on share of energy, materials, resources and information, Eco Industrial Park (EIP) has become a popular form of industry cluster. Waste Heat Recovery (WHR) in EIP can significantly increase the total energy efficiency of the whole park, meanwhile reducing its greenhouse gas emission. The current paper proposes a methodology to assess the opportunities of WHR in EIP at park level. Four different steps are included in this methodology. The first step is identification of waste heat source plants and sink plants in EIP; the second step is the establishment of the waste heat transportation system; the third step is a Single-Objective Optimization Problem (SOOP); the fourth step is Multi-Objective Optimization Problem (MOOP). An EIP on Jurong Island Singapore comprising of five plants and two communities is used as a case study to demonstrate the capability of this methodology. Two different operation modes for the EIP are considered: with continuous waste heat and with discontinuous waste heat over time. The first scenario shows that SOOP and MOOP will deliver different WHR networks; the second scenario shows that waste heat discontinuity has great influence on the optimization of the WHR network.

Nickel Nanoparticles Encapsulated in Few-Layer Nitrogen-Doped Graphene Derived from Metal–Organic Frameworks as Efficient Bifunctional Electrocatalysts for Overall Water Splitting

Xu You, Tu Wenguang, Zhang Bowei, Yin Shengmin, Huang Yizhong, Kraft Markus, Xu Rong

DOI: 10.1002/adma.201605957

Abstract:



Nickel nanoparticles encapsulated in few-layer nitrogen-doped graphene (Ni@NC) have been synthesized by using a Ni-based metal–organic framework as the precursor for high-temperature annealing treatment. The resulting Ni@NC materials exhibit high-efficient and ultrastable electrocatalytic activity toward hydrogen evolution reaction and oxygen evolution reaction as well as overall water splitting in alkaline environment.

A Big Data Framework to Validate Thermodynamic Data for Chemical Species

Buerger Phillip, Akroyd Jethro, Martin Jacob, Kraft Markus

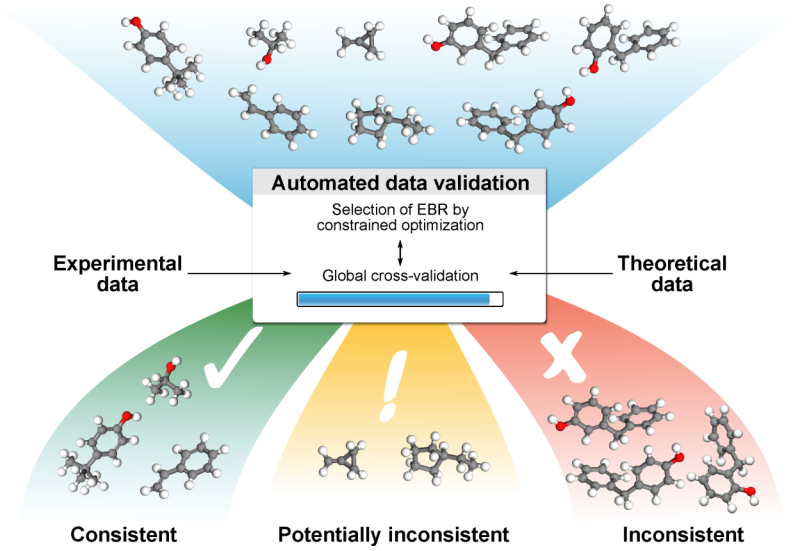
DOI: 10.1016/j.combustflame.2016.11.006

Highlights:

- Automated global cross-validation of large data sets of thermodynamic data.
- Evaluated reliability of the standard enthalpies of formation for 920 hydrocarbon-based species.
- Informed estimate of the standard enthalpy of formation is calculated using error-cancelling-balanced reactions.
- Automated identification and exclusion of unreliable data.
- Rapid convergence of the calculations towards chemical accuracy.
- Recommend future experiments and calculations for unreliable species.

Abstract:

The advent of large sets of chemical and thermodynamic data has enabled the rapid investigation of increasingly complex systems. The challenge, however, is how to validate such large databases. We propose an automated framework to solve this problem by identifying which data are reliable and recommending what future experiments or calculations are required. The framework is applied to validate data for the standard enthalpy of formation for 920 hydrocarbon species retrieved from the NIST Chemistry WebBook. The concept of error-cancelling balanced reactions is used to calculate a distribution of possible values for the standard enthalpy of formation of each species. The method automates the identification and exclusion of unreliable data. We find that this enables the rapid convergence of the calculations towards chemical accuracy. The method can exploit knowledge of the structural similarities between species and the reliability of the data to identify which species introduce the most error and recommend what future experiments and calculations should be considered.



Development of a multi-compartment population balance model for high-shear wet granulation with Discrete Element Method

Lee Kok Foong, Dosta Maksym, McGuire, Andrew, Mosbach Sebastian, Wagner Wolfgang, Heinrich Stefan, Kraft Markus

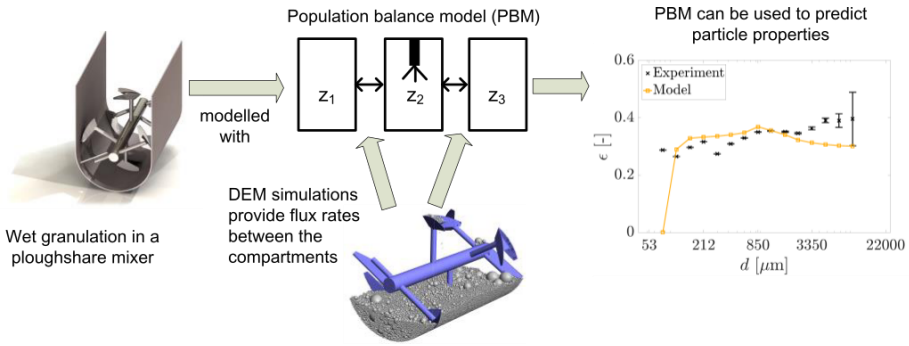
DOI: 10.1016/j.compchemeng.2017.01.022

Highghlights:

- A granulation process is modelled using a population balance model (PBM) and DEM.
- Particles in the population balance model are five-dimensional.
- The population balance model has 3 compartments to consider spatial inhomogeneity.
- The PBM is used to model particle size and porosity distributions.
- The performance of the PBM is improved by utilising information from DEM.

Abstract:

This paper presents a multi-compartment population balance model for wet granulation coupled with DEM (Discrete Element Method) simulations. Methodologies are developed to extract relevant data from the DEM simulations to inform the population balance model. First, compartmental residence times are calculated for the population balance model from DEM. Then, a suitable collision kernel is chosen for the population balance model based on particle-particle collision frequencies extracted from DEM. It is found that the population balance model is able to predict the trends



exhibited by the experimental size and porosity distributions by utilising the information provided by the DEM simulations.

Extension of moment projection method to the fragmentation process

Wu Shaohua, Yapp Edward, Akroyd Jethro, Mosbach Sebastian, Xu Rong, Yang Wenming, Kraft Markus

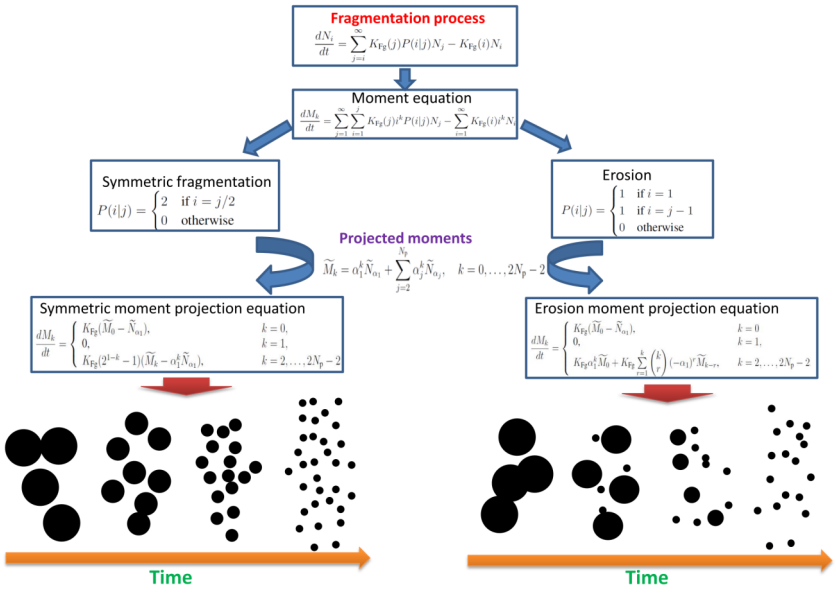
DOI: 10.1016/j.jcp.2017.01.045

Highlights:

- The moment projection method (MPM) is extended to include the fragmentation process
- MPM is tested for symmetric fragmentation and erosion fragment distribution functions and shows high accuracy
- MPM is also able to accurately simulate the combined processes of inception, growth, shrinkage, coagulation and fragmentation

Abstract:

The method of moments is a simple but efficient method of solving the population balance equation which describes particle dynamics. Recently, the moment projection method (MPM) was proposed and validated for particle inception, coagulation, growth and, more importantly, shrinkage; here the method is extended to include the fragmentation process. The performance of MPM is tested for 13 different test cases for different fragmentation kernels, fragment distribution functions and initial conditions. Comparisons are made with the quadrature method of moments, hybrid method of moments and a high-precision stochastic solution calculated using the established direct simulation algorithm and advantages of MPM are drawn.



A moment projection method for population balance dynamics with a shrinkage term

Wu Shaohua, Yapp Edward, Akroyd Jethro, Mosbach Sebastian, Yang Wenming, Kraft Markus

DOI: 10.1016/j.jcp.2016.10.030

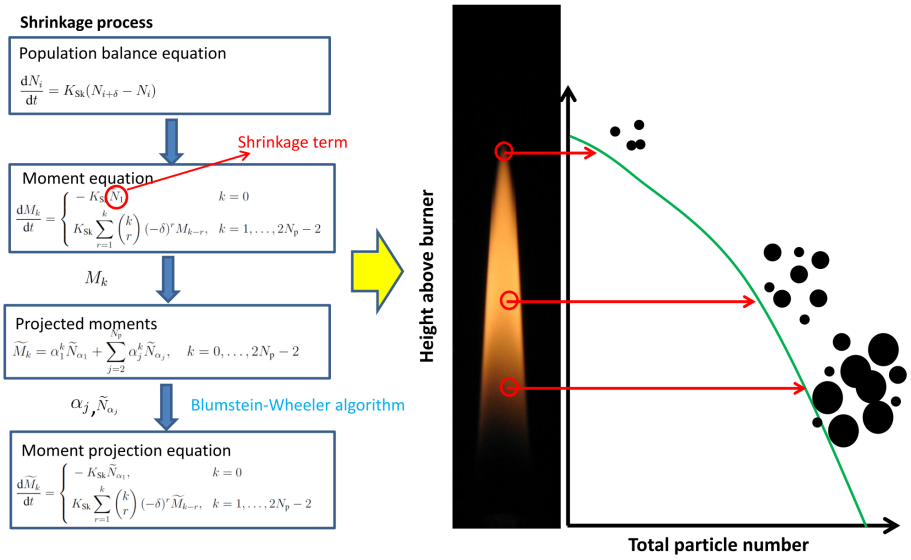
Highlights:

- A moment projection method for solving particle population balance equations is developed.
- A Blumstein-Wheeler algorithm is adopted in this method to track the number of the smallest particles.

- This method is tested for modelling particle shrinkage process and showed high accuracy.
- The method developed has the advantages of ease of implementation and numerical robustness.

Abstract:

A new method of moments for solving the population balance equation is developed and presented. The moment projection method (MPM) is numerically simple and easy to implement and attempts to address the challenge of particle shrinkage due to processes such as oxidation, evaporation or dilution. It directly solves the moment transport equation for the moments and tracks the number of the smallest particles using the algorithm by Blumstein and Wheeler [Phys. Rev. B, 8:1764-1776, 1973]. The performance of the new method is measured against the method of moments (MOM) and the hybrid method of moments (HMOM). The results suggest that MPM performs much better than MOM and HMOM where shrinkage is dominant. The new method predicts mean quantities which are almost as accurate as a high-precision stochastic method calculated using the established direct simulation algorithm (DSA).



Modelling TiO2 formation in a stagnation flame using method of moments with interpolative closure

Manuputty Manoel Y., Akroyd Jethro, Mosbach Sebastian, Kraft Markus

DOI: 10.1016/j.combustflame.2017.01.005

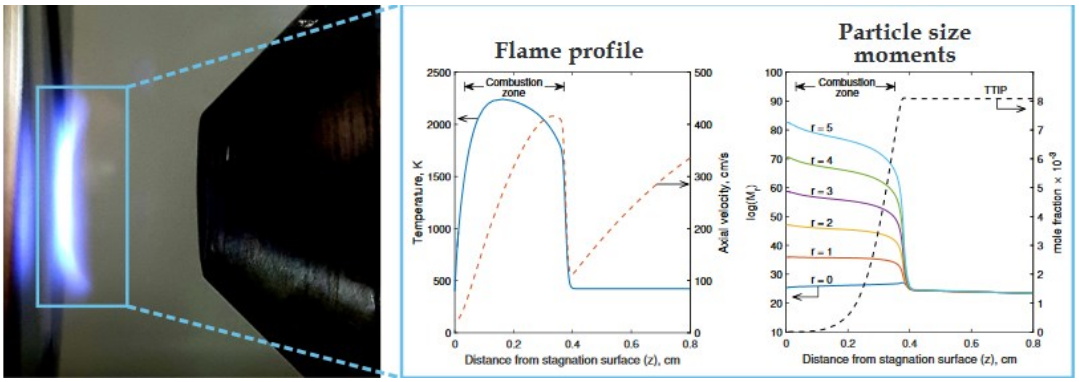
Highlights:

- Particle population balance model of TiO2 synthesis from titanium tetraisopropoxide (TTIP) is solved using method of moments with interpolative closure (MoMIC).
- A simple reaction model for TTIP decomposition is sufficient to simulate the particle sizes in a flame stabilized on rotating surface (FSRS) experiment.
- Particle size is found to be sensitive to the sampling location near the stagnation surface, especially for high TTIP loading and stagnation temperature.
- Surface growth plays an important role in the initial growth stage of particles.

Abstract:

The stagnation flame synthesis of titanium dioxide nanoparticles from titanium tetraisopropoxide (TTIP) is modelled based on a simple one-step decomposition mechanism and one-dimensional stagnation flow. The particle model, which accounts for nucleation, surface growth, and coagulation, is fully-coupled to the flow and the gas phase chemistry and solved using the method of moments with interpolative closure (MoMIC). The model assumes no formation of aggregates considering the high temperature of the flame. In order to account for the free-jet region in the flow, the computational distance, H = 1.27 cm, is chosen based on the observed flame location in the experiment (for nozzle-stagnation distance, L = 3.4 cm). The model shows a good agreement with experimentally

measured mobility particle size for stationary stagnation surface with varying TTIP loading, although the particle geometric standard deviation, GSD, is underpredicted for high TTIP loading. The particle size is predicted to be sensitive to the sampling loca- tion near the stagnation surface in the modelled flame. The sensitivity to the sampling location is found to increase with increasing precursor loading and stagnation temperature. Lastly, the effect of surface growth is evaluated by comparing the result with an alternative reaction model. It is found that surface growth plays an important role in the initial stage of particle growth which, if neglected, results in severe underprediction of particle size and overprediction of particle GSD.



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

The research programme is divided into six work packages:

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

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

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

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

WP 4.5: Model building, integration and maintenance

WP 4.6: Demonstration of proposed algorithms on pilot scale

The ICESO group is led by PIs:

Prof Gehan AMARATUNGA (Cam);

Prof Jan MACIEJOWSKI (Cam);

Prof Keck Voon LING (NTU);

Prof Sanjib Kumar PANDA (NUS)

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

University of Cambridge

PIs, IRP4

April 2017

3.4.1 IRP4 Research Overview

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

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

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

3.4.2 Update on work packages

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

Ashok KRISHNAN (PhD student, NTU, IRP4) has been working on multi-energy scheduling of generators. This is a non-trivial problem owing to the significant coupling between various components in the system and is very much related to efficiency enhancement and cost optimization in power plant operation. A large percentage of Singapore's licensed energy is generated from combined cycle technology. Optimal scheduling of these plants will help in saving both energy and cost. Industries are large consumers of electrical energy. In addition, many industries also require steam for their processes. Some industries also require cooling. Operating the power plants in combined heat and power (CHP) mode or combined cooling, heat and power (CCHP) mode helps in improving efficiencies. In addition to this, emerging technology such as battery energy storage systems (BESSs), thermal energy storage (TES) and renewable energy sources (RESs) need to be accounted in the energy mix. Smart grid concepts like demand response through load curtailment and rescheduling have also gained prominence recently. Ashok KRISHNAN (PhD student, NTU, IRP4) has been working on building an integrated modelling framework in which all these diverse elements are easily accommodated. His model includes detailed formulation of the behaviour of CHP plants, BESSs, TES and loads. The model accounts for various possible operating configurations of the CHP plant. An optimization problem for optimal scheduling of all these elements is formulated for dispatching heat and electric loads in the network. This problem is solved in the model predictive control (MPC) framework. The mixed logical dynamical (MLD) approach is used for constructing models for individual elements. Currently, he has completed modelling individual elements in the system and is studying different scheduling problem formulations for dispatching electric power and thermal loads.

The electrical and chemical systems in petrochemical plants are usually analysed separately. This makes it more difficult to explore synergies between these domains to optimize plant operations. A combined analysis would allow chemical engineers and electrical engineers to better understand the coupled interactions between chemical processes and electrical systems. Dr. FOO Yi Shyh Eddy (Co-Investigator, IRP4, NTU) has been focusing on finding a relationship between the electrical and chemical models of petrochemical plants to enable combined analysis of both domains. The biodiesel plant was chosen as an exemplar plant for developing this relationship. The chemical process model of a 600 tonnes/day capacity biodiesel plant was developed in AspenPlus using flow sheets from Lurgi GmbH. This model was developed on a computer located in the CREATE Tower. In addition, an electrical single-line diagram (SLD) of the same plant was developed using Hypersim platform on the OPAL-RT simulator hosted in NTU. A Python script was developed to link these two models through a common parameter, namely the power consumption in kW. Temperature, pressure and flow rate were inputs to the AspenPlus model. The outputs from this model were kW demand values of individual plant loads which were used directly in the Hypersim model for further analysis. Steady-state analysis was performed on the electrical model developed in Hypersim. The transient analysis of the Hypersim model following electrical faults was also performed. The biodiesel plant is quite stable in its operation and rarely requires changes in its operating setpoint. Work is currently ongoing to extend this approach to analyse plants exhibiting more dynamic behaviour including plants with batch processes. The long term objective is to study the impact of changes or faults in the electrical network on chemical processes and vice versa. This work is a collaborative effort involving researchers in IRP 4 and IRP 3 led by Dr. FOO Yi Shyh Eddy (Co-Investigator, IRP4, NTU).

Prof Jan MACIEJOWSKI (PI, Cambridge, IRP4) and Prof Keck Voon LING (PI, NTU, IRP4) have been supervising work by Dr Bhagyesh PATIL (RF, NTU, IRP4) on the development of global optimisation algorithms based on Bernstein polynomials, and the application of these algorithms to non-convex problems in power systems. In particular we have applied these algorithms to the optimal power flow problem in a multi-area power distribution system. Prof Jan MACIEJOSWKI (PI, Cambridge,

IRP4) has also supervised work by Thuy Van DANG (PhD student, NTU, IRP4) on exploiting the banded structure, which often occurs in model predictive control problems, to accelerate the solution of these problems. Arrangements are being made to allow Thuy Van DANG (PhD student, NTU, IRP4) to implement some of his algorithms in power-control devices manufactured by A. Eberle GmbH in Germany – a suitable Memorandum of Understanding is being negotiated to allow this.

DANG V Thuy (PhD Student, NTU, IRP4) has proposed computationally efficient techniques and algorithms for optimization-based control algorithms, particularly those that can be formulated as quadratic programs, such as Model Predictive Control or Moving Horizon Estimation. Of particular interest is exploitation of the structures that exist in the problem formulation, leading to a reduction or speed up in the computation for real-time application in the power grid. DANG V Thuy (PhD Student, NTU, IRP4) has also been working on the journal version of his conference paper which is about the anytime control algorithm. He has also submitted a paper to the IFAC World Congress 2017 which has been accepted. In this paper, we proposed a new ADMM-based QP algorithm which exploits a banded null basis for solving the linear MPC problem.

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

PATIL Bhagyesh Vijay (RF, NTU, IRP4) has been working on the development of a new hybrid global optimization network for nonlinear optimal power flow problems as well as on the development of a decentralized nonlinear MPC scheme for an excitation of multimachine power systems.

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

Prof Jan MACIEJOSWKI (PI, Cambridge, IRP4) and Prof Keck Voon LING (PI, NTU, IRP4)have been supervising work by Dr Anthony TRAN (SRF, NTU, IRP4) on the application of the Quadratic Dissipativity Constraint in the solution of the Automatic Generation Control problem for a 4-area power distribution system. Prof Jan MACIEJOSWKI (PI, Cambridge, IRP4) also worked with Dr Anthony TRAN (SRF, NTU, IRP4) on securing the theoretical foundations of the use of the Quadratic (and General) Dissipativity Constraint in model predictive control problems.

Srinivasa Rao KAMALA (PhD student, NUS, IRP4) reported that the Variable Speed Drives (VSDs) used in the petroleum processing industry cause distortions to the voltage/ current waveforms in the network and affect the operation of the power system. Renewable energy based distributed generation (DG) systems such as solar photo-voltaic (PV) devices are being connected to the distribution network and these could contribute ancillary services such as harmonic compensation as well as active/reactive power support. In addition, Srinivasa Rao KAMALA (PhD student, NUS, IRP4) has carried out a Matlab/Simulink based simulation of the distribution system with solar PV supplying nonlinear loads to mitigate harmonics and to supply active/reactive power to the loads. He noted, however, that the distributed generation (DG) systems connected to the PCC through power electronic converters made the system potentially susceptible to oscillations and created a small signal stability problem in the distribution system. Srinivasa Rao KAMALA (PhD student, NUS, IRP4) reported that an impedance based stability analysis is being carried out to investigate the small signal stability of the distributed system with solar photovoltaic (PV) systems supplying non-linear load (pump load) in the MATLAB/Simulink environment.

Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported on the experiments using the PLECS real time simulation box that are being carried out presently to validate the feasibility of inverter operation using Selective Harmonic Optimization (SHO). This involves construction of an H-bridge, integration with the driver circuit, and testing the hardware initially using Hysteresis Band Current Control. Before hardware testing, the algorithm is executed in the PLECS real time simulation box, with a model built using the PLECS library, and tested offline. Figures 1 and 2 show sample behaviour of voltage

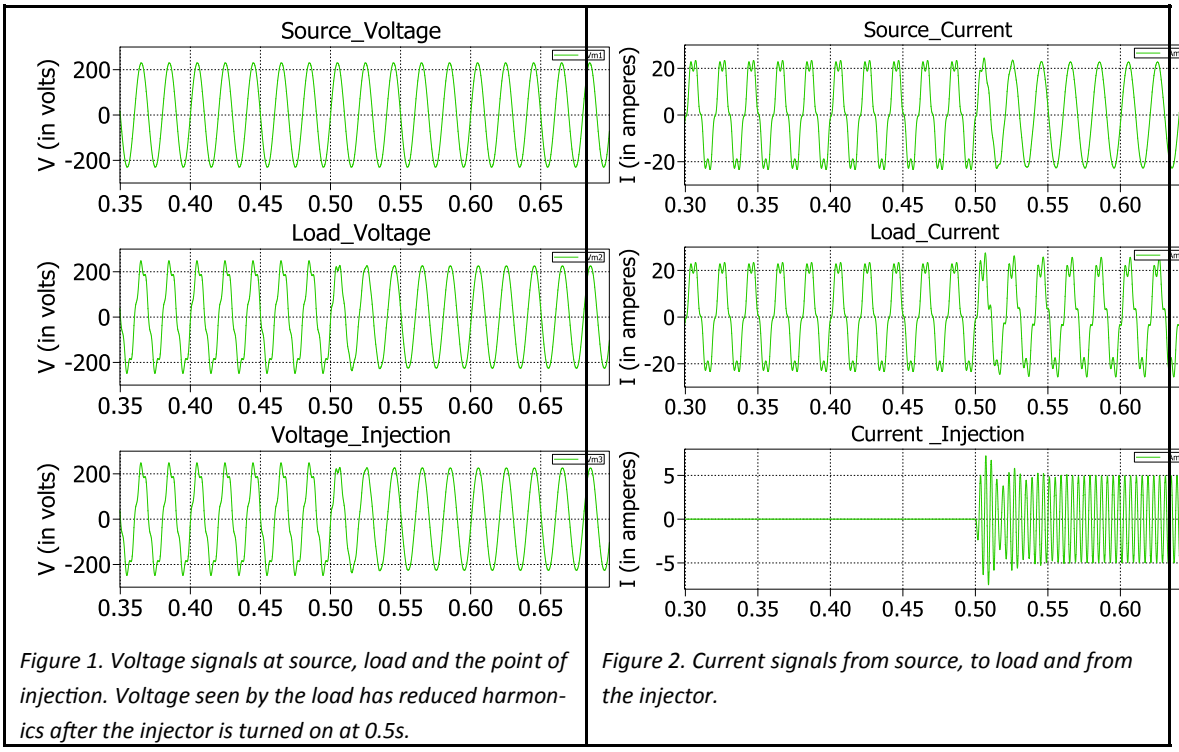
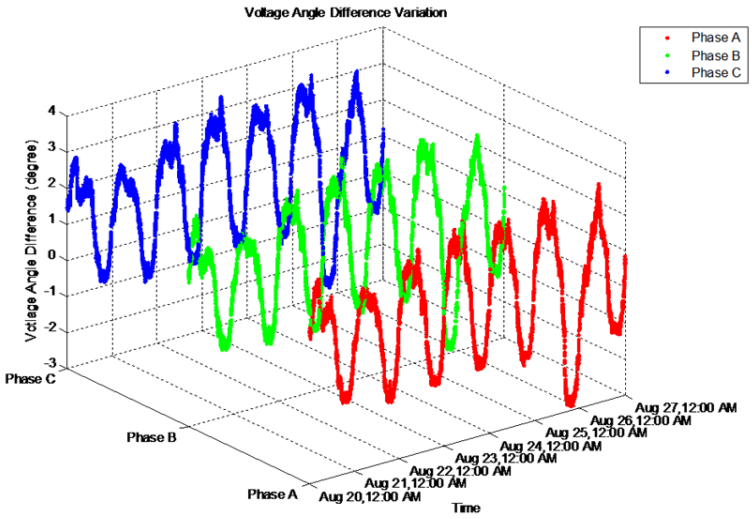


Figure 1. Voltage signals at source, load and the point of injection. Voltage seen by the load has reduced harmonics after the injector is turned on at 0.5s.

Figure 2. Current signals from source, to load and from the injector.

and current signals. From Fig. 1, it is clear that after injecting the harmonics signal at the point of common coupling at 0.5 secs, the source voltage and load voltage profiles became uniform.

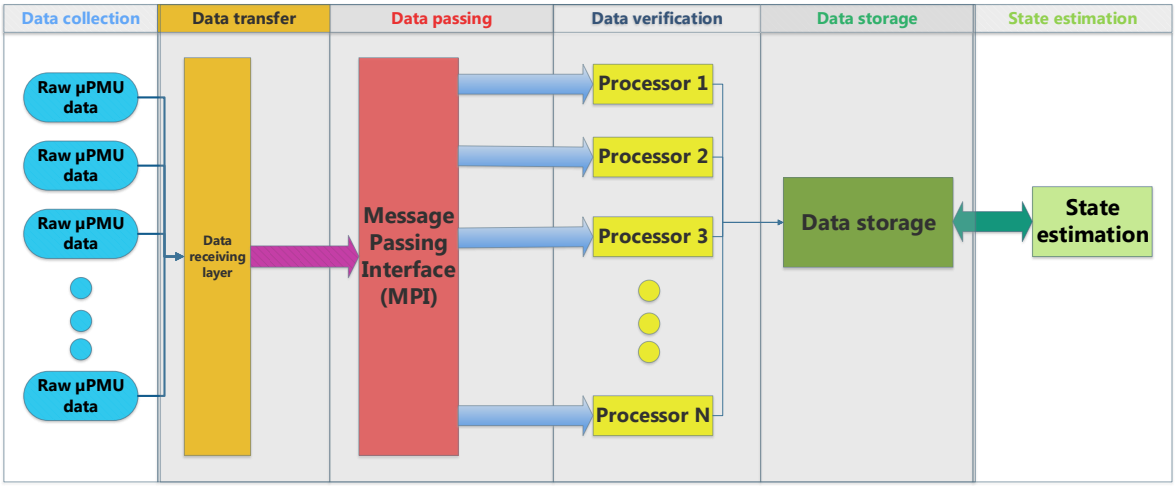
CHEN Xuebing (PhD Student, IRP4, NTU) and Dr Yuhao SUN (SRF, NTU, IRP4), under the supervision of Associate Prof RUSLI (Co-PI, IRP4, NTU) and Prof Gehan AMARATUNGA (PI, CAM, IRP4) , reported on state monitoring of future power distribution grid using micro-Phaser Measurement Unit (μPMU) and state estimation. CHEN Xuebing (PhD Student, IRP4, NTU) explained that the use of PMUs at each bus can lead to a simplified linear state because furnishing a selected subset of buses with PMUs can make the entire system observable. An efficient optimal placement strategy for PMUs is proposed to identify all solutions that minimize the number of PMUs and maximize measurement redundancy. The proposed method uses integer linear programming to fix the minimum number of PMUs first. The multiple placements having the same number of PMUs are then generated by slightly changing the coefficient of objective function of integer programming. Network buses can be classified according to multiple solutions. After that, uncertain buses are grouped and sub-networks are formed. With the optimization of each sub-network, all solutions that maximize redundancy can be



Voltage angle difference variation in a 7-day period (3D view)

identified. The proposed method has been tested on a system that contains more than one hundred buses. It has been checked that the proposed method is able to find all the solutions that satisfy the constraints within a reasonable time.

The fast processing of the vast amount of data generated by PMUs requires extensive computing resources and data storage, which implies the need for high performance computing (HPC) techniques. CHEN Xuebing (PhD Student, IRP4, NTU) reported that HPC techniques are used to solve computationally intensive problems, and has been improved in the form of cluster computing, multi -core computing, grid computing, cloud computing and graphic processing units. CHEN Xuebing (PhD Student, IRP4, NTU) reported that, together with researchers in IRP1, they are developing a multicore computer based parallel signal processing method to handle fast data streaming from the large number of µPMU instruments as shown in the figure below



Schematic diagram of the parallel computation adopted for the data verification process.

Dr Anthony TRAN (SRF, NTU, IRP4) reported that work has commenced on a detailed study of Automatic Generation Control (AGC) in a multi-area power transmission and distribution system. The previously-developed Quadratic Dissipativity Constraint is being used in a Model Predictive Control framework, investigating centralised, distributed and decentralised architectures. A 4-area model of a power system is being used for this study.

Dr Anthony TRAN (SRF, NTU, IRP4) reported that work has continued on investigating the control of large-scale interconnected systems using a partially decentralized control architecture. Particular focus has been placed on designing a partially decentralized controller which is resilient in the face of intermittent data losses in communication channels. This work is relevant to multi-area power transmission and distribution systems, in which there are communication links between 'control areas' – some of them spanning long distances, with sporadic data losses occurring quite frequently. Related to this is the problem of state estimation in power systems in the presence of intermittent data losses. A novel approach to solving this problem using a 'distributed moving horizon state estimation' method was developed, which made use of a novel 'incremental dissipativity constraint'.

In addition, some assistance was given with the supervision of an NTU final-year project, involving improved software engineering of a Simulink power system model, and its translation to the OPAL-RT real-time simulation environment.

Lu SUN (PhD student, NUS, IRP4) worked on the paper "Optimum Placement of Phasor Measurement Units in Power Systems". The paper has been submitted to IEEE Trans. Power System in December. The paper is about using statistical tools to approximately calculate the state estimation error variance. This is then used to evaluate / determine the optimal placement of smart meters on the electrical network.

Lu SUN (PhD student, NUS, IRP4) reported that he also worked with CHEN Tengpeng (PhD Student, NTU, IRP4) on the paper "Robust State Estimation Analysis in Power Systems". The paper has been

submitted to "International Journal of Electrical Power and Energy Systems" in January. The paper is about deriving an analytical equation that can be used to calculate the state estimate variance for a DC power system. The paper was initially completed in early 2016 and this is a modification-plus-resubmission. In addition, he worked with CHEN Tengpeng (PhD Student, NTU, IRP4) on the paper "Robust Power System State Estimation Using t-Distribution Noise Model". The paper has been submitted to IEEE Trans. Smart Grid. In the paper, an estimator is proposed where the measurement noise is assumed to have t-distribution and the system is assumed to be in steady state.

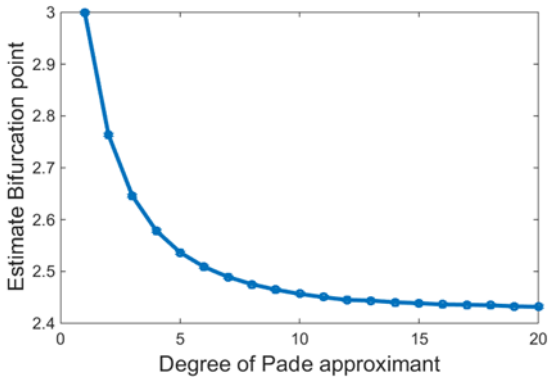
Partha Pratim BISWAS (PhD student, NTU, IRP4) reported on the topic of his PhD thesis: "Power System Optimization using Evolutionary Algorithm". The primary objective is to improve efficiency, increase output, reduce operational cost of electrical power system. The research is primarily focused on trying a couple of variants of Differential Evolution algorithms and constraint handling method to selected optimization problems. During his research, Partha Pratim BISWAS (PhD student, NTU, IRP4) has come across basic Differential Evolution (DE) algorithm and its variants in the form of JADE and L-SHADE. Partha Pratim BISWAS (PhD student, NTU, IRP4) reported that he learned about the constraint handling methods, superiority of feasible solutions (SF) and self-adaptive penalty (SP) for constrained optimization problems. Recently, he has been applying L-SHADE and Ensemble of constraint handling techniques in windfarm layout optimization and optimal power flow in standard bus test systems. The output results are better than previous studies performed by other researchers using different evolutionary algorithms or equivalent methods.

In future, Partha Pratim BISWAS (PhD student, NTU, IRP4) will study and apply multi-objective optimization in more complex power system optimization problems, possibly incorporating stochastic wind and solar energies.

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

Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported that holomorphic analysis of power flow has been extended to study voltage stability analysis. Voltage stability problems occur when the system components are heavily stressed and are being operated beyond their limits. Saddle-node bifurcation point is one of the indicators employed to identify the voltage stability margin. Predicting the bifurcation point has become more critical due to rapid growing electric power demand and intermittent renewable distributed generators that are connected to the grid. Conventional methods like Newton-Raphson, Gauss-Seidel could fail to converge near the maximum loading point, causing numerical errors in calculating the voltages.

In addition, Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported that a few test cases (4 bus system, 12 bus system, and 209 bus system) have been considered to find the bifurcation point of power systems, with estimations using holomorphic variable embedded power-flow equations. The figure shows the estimated bifurcation point as a function of the degree of the Pade approximant for the four bus system. The voltage collapse point can be evaluated by using this bifurcation point. The variation of the bus voltages with an increase in the loading parameter (s) is shown in Fig. 4. It means that for a given power-flow state of the system, the stability would be maintained only untill the point where loading increases 2 to 2.4 times the current loading.

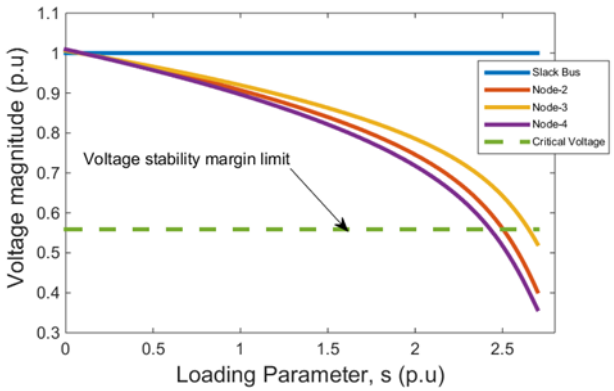


Estimated bifurcation point for different degrees of Pade approximant

Xueheng QUI (PhD student, NTU, IRP4) reported on his project "Load Demand Forecasting and Fault Prediction in Power Systems". Its primary objective is to reduce the probability of faults occurring with the

help of accurate fault prediction methods. Currently, his research field is focused on deep learning methods and ensemble algorithms. In his study, various kinds of time series forecasting algorithms have been reviewed, including Artificial Neural Network (ANN), Support Vector Regression (SVR), Random Forest (RF), Kernel Ridge Regression (KRR), Deep Belief Network (DBN) and ensemble methods. An Empirical Mode Decomposition based deep learning approach has been proposed for load demand forecasting, which has been published in the journal Applied Soft Computing.

Bus voltages for different power system loading



In addition, Xueheng QUI (PhD student, NTU, IRP4) also investigated into a randomized version of neural network, which is called Random Vector Functional Link Network (RVFL), and proposed an effective and efficient learning model for short term electricity load demand forecasting by combining Discrete wavelet transform (DWT), EMD and RVFL with incremental learning. This work has been submitted to IEEE Transactions on Smart Grids. He reported that 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

Work on WP5 is currently largely subsumed under IRP3 modelling activity (WP3.5).

WP 4.6: Demonstration of proposed algorithms on pilot scale

In lieu of pilot-scale implementations, this WP is being pursued using the OPAL-RT simulator and the hardware micro-grids.

Other Activities and Achievements

- Prof Keck Voon LING (PI, NTU, IRP4) visited Technische Universitaet Muenchen (TUM), Institute for Real-Time Computer Systems (RCS), and presented a seminar at TUM entitled: "Event-triggered Sequence-based Anytime Control as an Event-triggered Markov Jump System" (14 Dec 2016)
- Prof Keck Voon LING (PI, NTU, IRP4), together with CREATE partners SMART and TUM, and with NTU and NUS, submitted an Intra-CREATE proposal entitled "Synergistic Design of Vertical Technologies for Smart and Secure Transportation Systems: A Cyber-Physical System of Systems Approach" (31 Jan 2017).
- Prof Keck Voon LING (PI, NTU, IRP4) has been elected a Churchill College Visiting By-Fellow for Michaelmas Term 2016.
- Prof Jan MACIEJOWSKI (PI, CAM, IRP4) was invited to deliver the William Mong Distinguished Lecture at the University of Hong Kong in November 2016.
- Dr Joymala MOIRANGTHEM (RF, NUS, IRP4) reported that *"GIS Integrated Automation of a Near Real-Time Power-Flow Service for Electrical Grids"* has won the **BEST PAPER AWARD** at the 4th IEEE International Conference on Sustainable Energy Technologies (IEEE-ICSET 2016), conducted at 14-16 November 2016, Hanoi, Vietnam. The prize comprises the certificate and 100 USD cash.
- Dr Anthony TRAN (SRF, NTU, IRP4) initiated some research collaboration, in his own time, with the University of Technology Sydney (Australia), experimenting with 'dependable control systems with the Internet of Things and a private machine cloud'. This has involved the construction of a 'breadboard' set-up using low-cost hardware.
- Dr Anthony TRAN (SRF, NTU, IRP4) has been appointed an honorary 'Adjunct Senior Research Fellow' at Curtin University in Australia (2016-2018)
- Lead by Dr Yuhao SUN (SRF, NTU, IRP4), IRP4 has made a proposal with BEARS under the Intra CREATE Seed Funding Grant Call. The project involves several research fellows and PhD students. It aims at real time measurement collection, state estimation, parallel computation and big data analysis of real power networks in Singapore.
- IRP4 hosted a very successful visit by Prof. Karl Johan ÅSTRÖM of Lund University, Sweden, from 20 to 31 March 2017, under the CREATE Visiting Scientists Programme. Prof. Åström delivered two very well-attended lectures, and had one-to-one meetings with most of the IRP4 PIs, post-docs and students, as well as with Prof. KRAFT (CARES Director), Prof. FISHER (PI, CAM, IRP2) and Mr KLEINELANGHORST (RF, NTU, IRP3).

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.

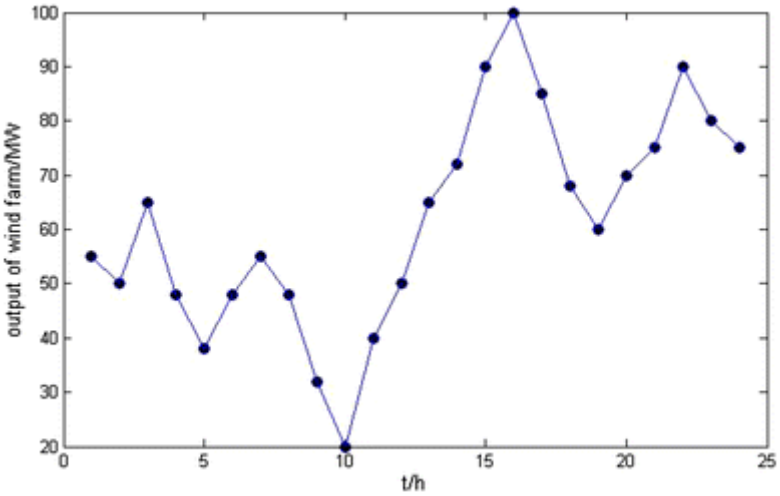
Solving dynamic economic emission dispatch problem considering wind power by multi-objective differential evolution with ensemble of selection method

B. Y. Qu, J. J. Liang, Y. S. Zhu, P. N. Suganthan

DOI: 10:1007/s11047-016-9598-6

Abstract:

Clean energy resources such as wind power are playing an important role in power generation recently. In this paper, a modified version of multi-objective differential evolution (MODE) is used to tackle the extended dynamic economic emission dispatch (DEED) problem by incorporating wind power plant into the system. DEED is a nonlinear and highly constrained multi-objective optimization problem and the predicted load is varying with time. Fuel costs and pollution emission are the two objectives to be optimized and the valve point effect, spinning reserve, real power loss as well as the ramping rate are considered. To solve the model effectively, an ensemble of selection method is used in the MODE algorithm. The real-time output adjustment and penalty factor methods are used to deal with the complex constraints. The proposed method is firstly examined on several multi-objective benchmark problems and the DEED problem without considering the wind power to test its effectiveness of solving multi-objective optimization problems. Secondly, the model considering wind power is solved and the results show that the proposed algorithm is effective in handling such problems.



Forecast output of wind farm

Economic emission dispatch problems with stochastic wind power using summation based multi-objective evolutionary algorithm

B.Y. Qu, ,J.J. Liang, Y.S. Zhu, Z.Y. Wang, P.N. Suganthan

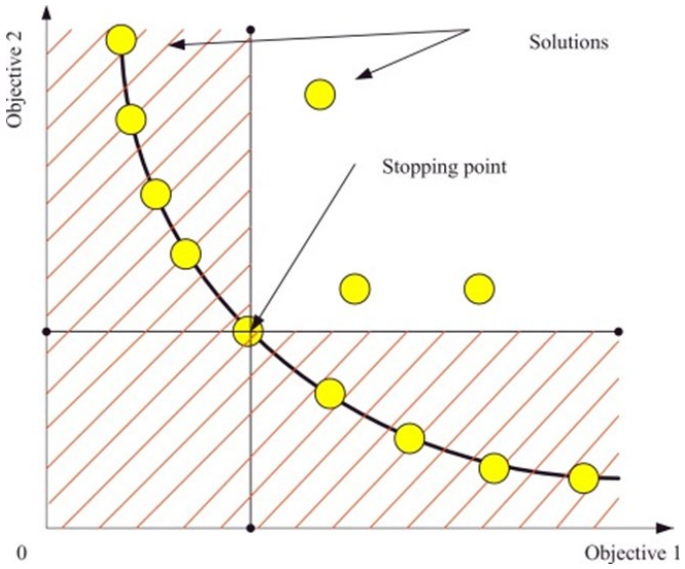
doi.org/10.1016/j.ins.2016.01.081

Abstract:

In recent years, renewable energy sources such as wind energy have been used as one of the most effective ways to reduce pollution emissions. In this paper, a summationbased multi-objective differential evolution (SMODE) algorithm is used to optimize the economic emission dispatch problem with stochastic wind power. The Weibull probability distribution function is used to model the stochastic nature of the wind power and the uncertainty is treated as the system constraints with stochastic variables. The algorithm is integrated with the superiority of feasible solution constraint handling technique. To validate the effectiveness of the proposed method, the standard IEEE 30-bus 6-generator test system with wind power (with/without considering losses) is studied with fuel cost

Illustration of the stopping point

and emission as two conflicting objectives to be optimized at the same time. Besides, a larger 40-generator system with wind farms is also solved by the proposed method. The results generated by SMODE are compared with those obtained using NSGAII as well as a number of techniques reported in literature. The results reveal that SMODE generates superior and consistent solutions.



Examining the Bernstein global optimization approach to optimal power flow problem

Bhagyesh V. Patil, , L. P. M. I. Sampath, Ashok Krishnan, K. V. Ling, and H. B. Gooi,

doi.org/10.1063/1.4965386

Abstract:

This work addresses a nonconvex optimal power flow problem (OPF). We introduce a 'new approach' in the context of OPF problem based on the Bernstein polynomials. The applicability of the approach is studied on a real-world 3-bus power system. The numerical results obtained with this new approach for a 3-bus system reveal a satisfactory improvement in terms of optimality. The results are found to be competitive with generic global optimizations solvers BARON and COUENNE.

A Hierarchical EMS for Aggregated BESSs in Energy and Performance-Based Regulation Markets

T. Zhang, S-X. Chen, H.B. Gooi and J.M. Maciejowski

doi:10.1109/TPWRS.2016.2598186.

Abstract:

Battery energy storage systems (BESSs) are being increasingly installed in power systems, especially with the growing penetration rate of renewable energy sources. However, it is difficult for BESSs to be profitable due to their high capital costs. In order to boost the economic value of BESSs, this paper proposes a hierarchical energy management system (HiEMS) to aggregate multiple BESSs, and to achieve multi-market business operations. The pro-

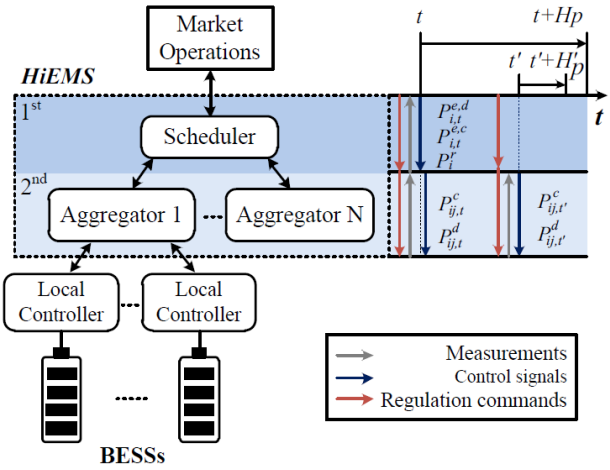


Fig. 2. Proposed HiEMS integration and its working time scheme.

posed HiEMS optimizes the multi-market bids considering a realistic BESS performance model, and coordinates the BESSs and manages their state of charge (SOC) values, according to their price penalties based on dynamically generated annualized cost. By taking part in the energy market and regulation market at the same time, the cost-performance index (CPI) of the BESS aggregation is greatly improved. The impact of photovoltaic generation (PV) on system performance and CPI is also studied.

A.1 Publications

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

A1.1 Joint IRP Publications

IRP1 and IRP3

- Amaniampong, Prince N., Quang Thang Trinh, Kaixin Li, Samir H. Mushrif, Yu Hao, and Yanhui Yang. 2017. 'Porous Structured CuO-CeO2 Nanospheres for the Direct Oxidation of Cellobiose and Glucose to Gluconic Acid'. *Catalysis Today*, January. doi:10.1016/j.cattod.2017.01.009.
- Amaniampong, Prince N., Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, and Samir H. Mushrif. 2015. 'Biomass Oxidation: Formyl C□H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves'. *Angewandte Chemie International Edition* 54 (31): 8928–33. doi:10.1002/anie.201503916.
- Amaniampong, Prince Nana, Amin Yoosefi Booshehri, Xinli Jia, Yihu Dai, Bo Wang, Samir H. Mushrif, and Armando Borgna. 2015. 'High-Temperature Reduction Improves the Activity of Rutile TiO2 Nanowires-Supported Gold-Copper Bimetallic Nanoparticles for Cellobiose to Gluconic Acid Conversion'. *Applied Catalysis A: General* 505 (September): 16–27. doi:10.1016/j.apcata.2015.07.027.
- Azadi, Pooya, George Brownbridge, Immanuel Kemp, Sebastian Mosbach, John S. Dennis, and Markus Kraft. 2015. 'Microkinetic Modeling of the Fischer-Tropsch Synthesis over Cobalt Catalysts'. *ChemCatChem* 7 (1): 137–43. doi:10.1002/cctc.201402662.

IRP1 and IRP2

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

IRP1 and IRP4

- Yang, Shiliang, Andy Cahyadi, Yuhao Sun, Jingwei Wang, and Jia Wei Chew. n.d. 'CFD–DEM Investigation into the Scaling up of Spout-Fluid Beds via Two Interconnected Chambers'. *AIChE Journal*. doi:DOI:10.1002/aic.15188.
- Yang, Shiliang, Yuhao Sun, Jingwei Wang, Andy Cahyadi, and Jia Wei Chew. n.d. 'Influence of Operating Parameters and Flow Regime on Solid Dispersion Behavior in a Gas–solid Spout-Fluid Bed'. *Chemical Engineering Science* 142: 112–25. doi:http://dx.doi.org/10.1016/j.ces.2015.11.038.
- Yang, Shiliang, Yuhao Sun, Liangqi Zhang, Ya Zhao, and Jia Wei Chew. 2016. 'Numerical Investigation on the Effect of Draft Plates on Spouting Stability and Gas-Solid Characteristics in a Spout-Fluid Bed'. *Chemical Engineering Science*, March. doi:10.1016/j.ces.2016.03.010.

IRP3 and IRP4

- Chen, Tengpeng, Dexiang Zhou, Tri Tran, Catharine Kastner, K-V. Ling, K-J. Tseng, and Jan M.

Maciejowski. 2015. 'Distributed Moving Horizon Estimation for Power Systems'. In , 1–5. IEEE. doi:10.1109/PESGM.2015.7286281.

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A.2 CARES C4T Visiting Scientists Programme

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

Dr. Oliver Inderwildi, ESSEC Business School

November 2016

Dr. Oliver Inderwildi, ESSEC Business School, Energy, Commodities & Environment, November 2016

Abstract: Rapid technological advancements can make previously uneconomic resources and/or feedstock available within significantly reduced timeframes. This can will further transform the global energy landscape and moreover, will impact the mix of feedstock we use for energy provision and material production—the so-called Feedstock Curve. During the presentation, three current examples are assessed to illustrate that this restructuring has by far wider reaching implications. Firstly, we examine how unconventional resources—mainly produced using fractured cracking techniques—have restructured the US energy landscape, are now fuelling the US economic recovery and will impact the geopolitical balance. Secondly, we assess how unconventional resources could impact European energy security, the Crimean crisis and redirect global cash flows. Thirdly, we analyse the potential impact of so-called methane hydrates deposited off the shores of Japan on the energy transition of the Island nation and how they might impact its trade deficit and long-term economic outlook. Last but not least, we will assess arguments that unconventional resources, when regulated properly, may be a blessing for the environment. With these examples, this presentation will illustrate the interconnectedness of economics, politics, environmental conservation and technology.

Biography: Dr Inderwildi serves as Advisory Board member for Energy & Environmental Science, a high-impact journal published by the Royal Society of Chemistry and the Energy Advisory Board of the Council of Canadian Academies. Dr. Inderwildi was educated in science and engineering at the University of Heidelberg, the Swiss Institure of Technology, and the University of Amsterdam. He received additional training in economics and policy at the Massachusetts Institute of Technology and the London School of Economics and Political Science and is currently pursuing an MBA at ESSEC Business School.

Assoc. Prof. Zdenek Sofer University of Chemistry and Technology, Prague

November 2016

Assoc. Prof. Zdenek Sofer, University of Chemistry and Technology Prague, Layered materials for energy related applications, November 2016

Abstract: The graphene and its inorganic analogues attract great attention in last decade due to its outstanding properties. These materials offer huge opportunities in several energy-related applications like energy storage and conversion, gas sorption and separation of CO2. The energy-related application of layered materials currently focuses on electrocatalysis such as hydrogen evolution reaction and oxygen reduction reaction which are crucial for hydrogen economics. The graphene-based materials, as well as transition metal dichalcogenides, can be applied as an effective electrocatalytic material. This topic is strongly related hydrogen storage using graphene and its derivatives. The modification of graphene can be applied for CO2 capture and also for gas separation using graphene based membranes and foils. These applications will be discussed in the presented talk.

Biography: Assoc. Prof Zdenek Sofer (born in 1981 in Plzen, Czech Republic) received his Ph.D. in Inorganic Chemistry, UCT Prague in 2013. He currently leads a research group concerning on 2D nanomaterials (6 Ph.D., 2 MSc.) His laboratory is equipped for synthesis and characterization of graphene and other 2D nanomaterials like transition metal dichalcogenides.

A.2 CARES C4T Visiting Scientists Programme

Emeritus Professor Karl Johan Åström Department of Automatic Control, LTH, Lund University, Sweden

March 2017

Emeritus Professor Karl Johan Åström Department of Automatic Control, LTH, Lund University, Sweden, A perspective on the Field of Automatic Control, March 2017

Abstract: This lecture presents a personal perspective on the young field of control. Extensive use of control appeared with the development of industry: steam, electricity, transportation and communication. Control was established as a field from 1940 to 1960, creating a paradigm shift as it cut across the traditional engineering disciplines: civil, mechanical, electrical, chemical and aerospace. A holistic view of control systems with a unified theory emerged in the 1950s, when similarities in widely different fields were recognized. The military efforts during the Second World War was a strong driver. Education spread rapidly to practically all engineering disciplines. An interna-tional organization (IFAC) was established in 1956 and the first IFAC World Congress was held in 1960. A second phase, often called the Golden Age, started around 1960. It was driven by the space race, computer control and a strong influx of mathematics. A large number of sub specialties emerged, but the holistic view of the field was unfor-tunately lost. We are now entering a third phase driven by the ubiquitous use of control practically everywhere in-cluding fields like physics and biology. New exciting areas are: networked systems, autonomy and safe design of large complex systems. The new challenges will require strong interactions with computing and communication. Education is critical for the future development. To meet the challenges it is particularly important to educate a new generation of engineers and researchers who will make it possible to do work individually and in teams combining deep theoretical knowledge with strong engineering skills.

Biography: Karl Johan Åström was educated at the Royal Institute of Technology (KTH) in Stockholm. From 1960 to 1965 he worked for IBM on computer control. In 1965 he was appointed Professor at Lund University, where he founded the new department of Automatic Control. Åström has broad in-terests covering theory and applications. He has supervised more than 65 PhD students, authored 10 books, published extensively in archival journals and he holds several patents. Åström is a member of the Royal Swedish Academy of Engineering Sciences (IVA), the Royal Swedish Academy of Sciences (KVA) and a foreign member of the US National Academy of Engineering. He has received many hon-ors, among them six honorary doctorates, the 1987 IFAC Quazza Medal, the 1990 IEEE Control Sys-tems Award, the 1993 IEEE Medal of Honor and the 2002 Great Gold Medal of IVA. In 2003 he was inducted in the Process Control Hall of Fame.

Dr. Peter Bishop, Johnson Matthey Technology Centre.

March 2017

Dr. Peter Bishop, Johnson Matthey Technology Center, Use of Advanced Materials in Johnson Matthey, Catalysis and Functional Film Application, March 2017

Abstract: An overview of Johnson Matthey and how divisional structure relates to research at the Johnson Matthey Technology Centre (JMTC) will be given. Heterogeneous catalysis ranging from gas/solution phase and fine chemical synthesis form a strong core within JM products. Underpinning research in materi-als chemistry relating to inorganic supports and metal nanoparticle synthesis for these transformation will be discussed. Key reactions such as Fischer Tropsch and selective hydrogenation will highlight guiding prin-ciples for optimization of product activity and selectivity. The presentation will move onto other product areas for JM namely glass and electro ceramic applications where materials chemistry underpins the performance of thick film coatings such as obscuration enamels and silver conductors on glass for the automotive industry. The latter part of the presentation will move onto new thin film conducting track technologies for paper and plastic substrates using gold nanoparticles. Relevant TEM/SEM, XRD, ssNMR will be used to support concepts discussed above.

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