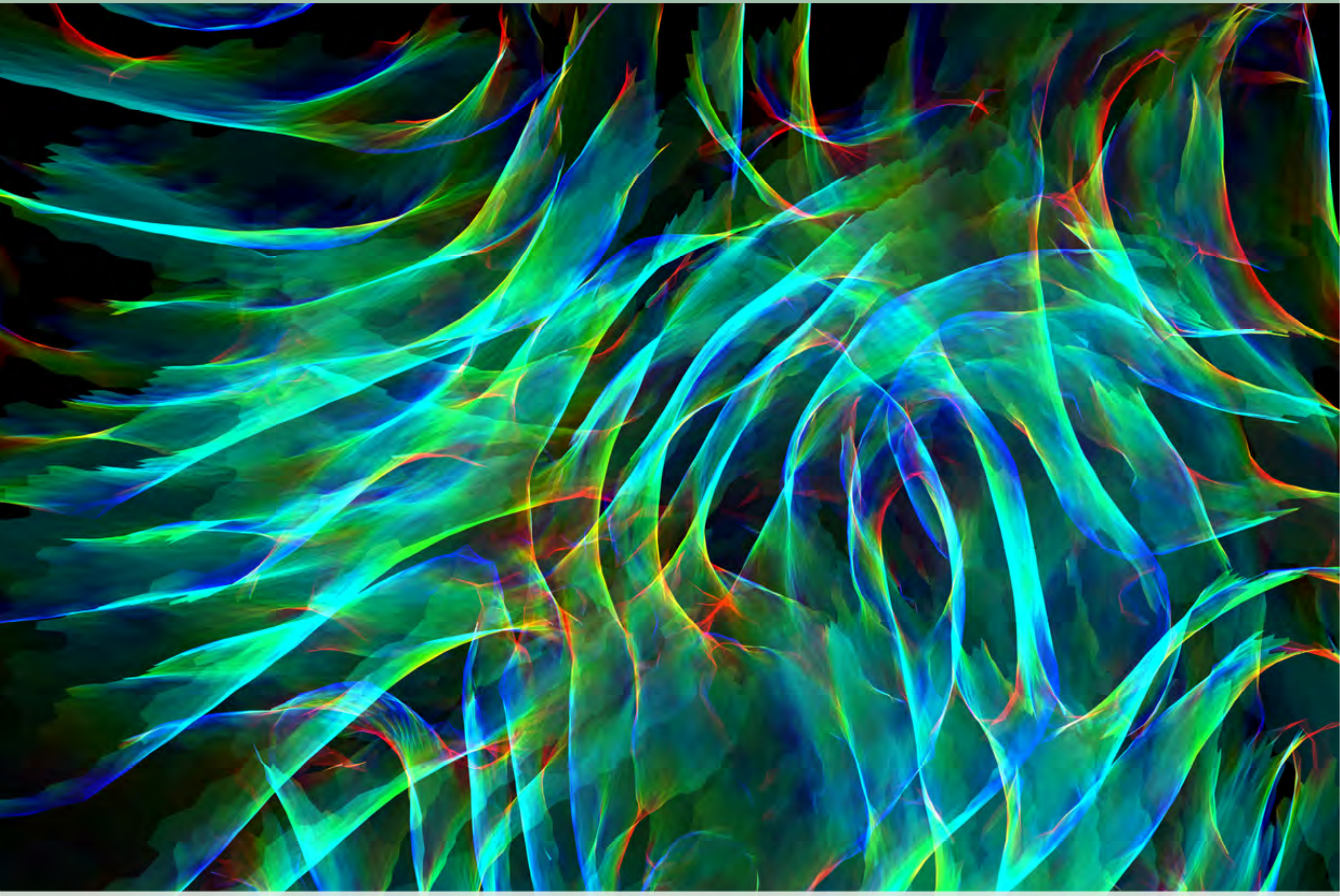
CAMBRIDGE **CARES**

A COLLABORATION BETWEEN THE UNIVERSITY OF CAMBRIDGE,
NANYANG TECHNOLOGICAL UNIVERSITY & NATIONAL UNIVERSITY OF SINGAPORE



Biannual Research Report

April - October 2019

CAMBRIDGE
CARES

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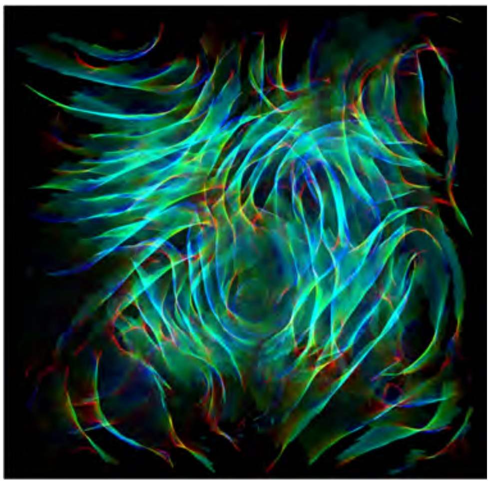

Disordered 3D graphene network shown as a surface mesh constructed from the graphene rings with the curvature coloured saddle-shape red, bowl-shape blue.

Image by Jacob MARTIN, PhD student, IRP3.

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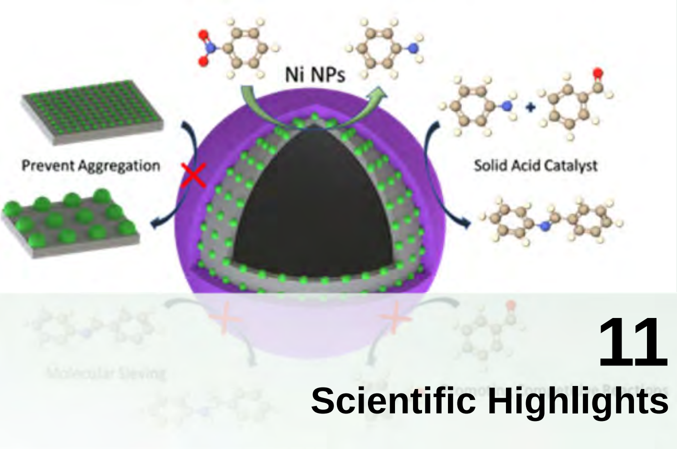
Focus on Impact



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FOREWORD

I am very pleased to present the 11th Biannual Research Report of the Cambridge Centre for Advanced Research and Education in Singapore (Cambridge CARES). We are one year into the second research phase of our flagship programme Cambridge Centre for Carbon Reduction in Chemical Technology (C4T) and several new projects are also in full swing. As well as the latest C4T research, this report contains an update on the progress of our first Intra-CREATE programme, eCO$_2$EP. There are also two articles on some of the practical impacts of our work, which I hope you will enjoy.

INTRA-CREATE

Our current Intra-CREATE programmes are eCO$_2$EP and the smaller, seed-funded ‘An intelligent platform for efficient energy management in an eco-industrial park.’ These are progressing well. We are also happy to have one application in the final selection for a large Intra-CREATE *Cities* grant. The proposed work involves fellow CREATE entity the Singapore-ETH Centre and Singapore’s Urban Redevelopment Authority, and would explore applications of the J-Park Simulator and knowledge graph with regard to city planning.

SMALL PROJECTS

Several smaller projects have started in 2019, most of which are being undertaken by our existing researchers. The RINGs project, which was first reported in the previous Biannual Report, is being run by former Cambridge-CARES PhD student Nick Jose. Nick has now employed all of his researchers and recently attended a bootcamp run by funder the SMART Innovation Centre.

EMERGING OPPORTUNITIES FUND

The C4T Emerging Opportunities Fund will support exciting new ideas that have arisen since the start of Phase 2. We received many excellent proposals, of which ten have been shortlisted. Following the Scientific Advisory Committee’s approval of these in December, funding will commence in January.

HIGHLIGHTS

Cambridge CARES was honoured to host a visit of the new British High Commissioner to Singapore, Kara Owen, in August. The High Commissioner was very interested to learn more about our work and had already met some of our researchers during an earlier visit to Cambridge.

CAMBRIDGE-CARES STUDENTS

The new academic year is underway in Cambridge and there are two new students commencing their PhDs as part of the Cambridge-CARES studentship scheme. One is funded by Syngenta (IRP2) and one by CMCL Innovations (IRP JPS). A further PhD student will start his time in Singapore in October, with funding from UCB Pharma (IRP1). We are looking forward to having them join us.

I hope I have encouraged you to read more about CARES’ latest work and achievements in this report. As ever, please do get in touch if you would like to know more about our work or have ideas for collaboration.

Professor Markus Kraft, CARES Director
October 2019

ABOUT US

Cambridge CARES is the University of Cambridge's presence in Singapore

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

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 on Singapore's Jurong Island. 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. Our six collaborative Interdisciplinary Research Programmes (IRPs) combine state-of-the-art experimental analysis with advanced modelling research from Cambridge and Singapore. Whilst each IRP has clearly defined milestones and deliverables, denoted as work packages (WPs), there is significant interaction between the IRPs.

The first five-year research phase of C4T came to an end in October 2018. The programme received a further five years of funding for Phase 2, which commenced in November 2018.

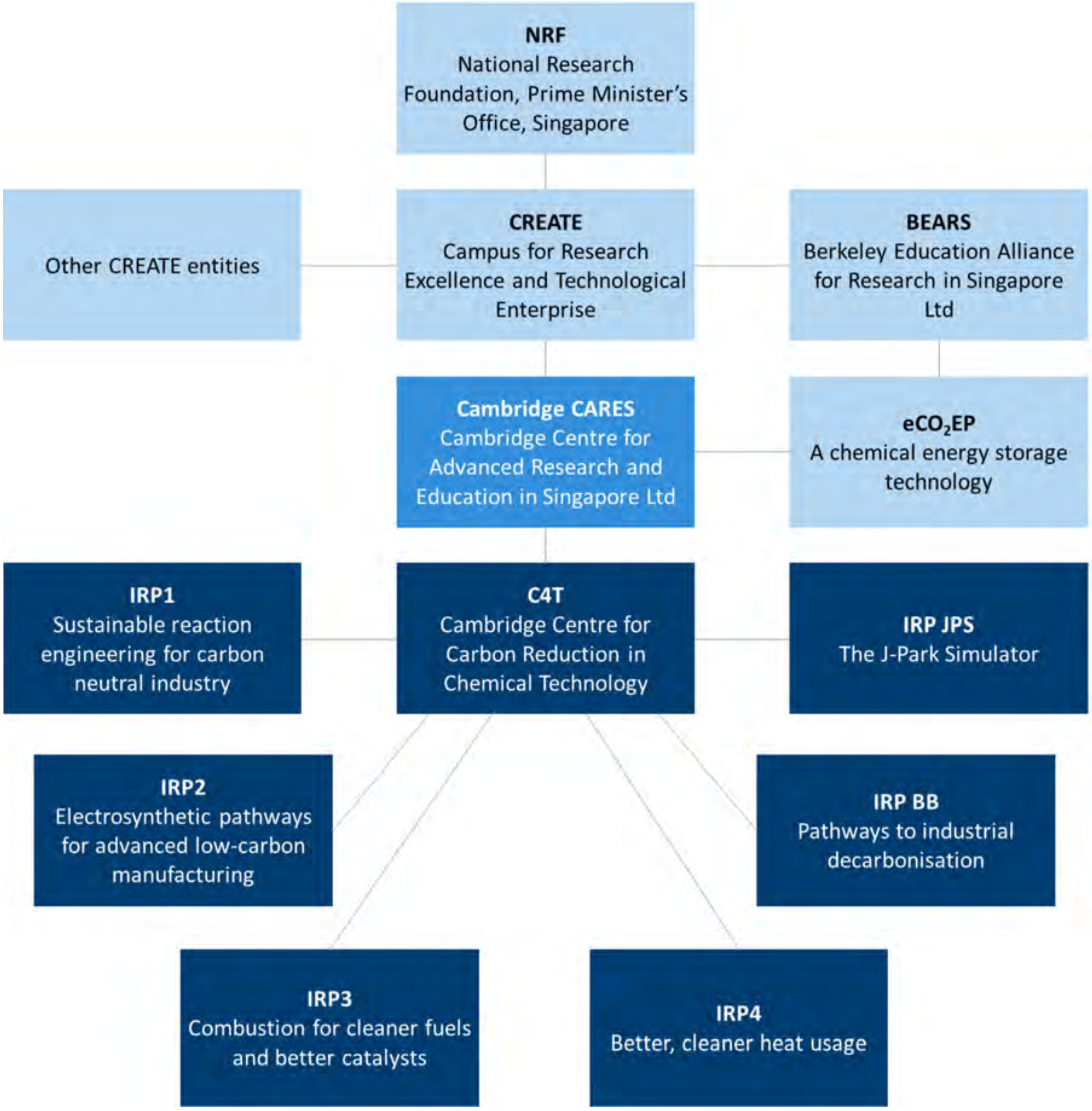
This report is a summary of our last half-year of research progress. It includes scientific updates from each of our researchers, along with abstracts and figures from our recent publications. There are also several articles that explain the fundamental science behind some of our work, and the impact this can have on carbon reduction.

C4T Cambridge Centre for Carbon Reduction in Chemical Technology

eCO_2EP A Chemical Energy Storage Technology

C4T answers the question of how to positively contribute to Singapore's ratification of the Paris Agreement on climate change while ensuring the country's progress and prowess in economic, technological, environmental and social dimensions. C4T Phase 2 systematically investigates the raw materials, processes and products of the local chemical industry and investigates technologies to lower the carbon footprint of this major pillar of Singapore's economy.

The second large programme administered by CARES is eCO_2EP. This is a three-year programme that brings together researchers from the University of Cambridge, the University of California, Berkeley, the National University of Singapore and Nanyang Technological University to develop ways of transforming carbon dioxide emitted as part of the industrial process into compounds that are useful in the chemical industry supply chain.



HIGHLIGHTS

OUTSTANDING WORK FROM THE LAST SIX MONTHS OF CAMBRIDGE CARES RESEARCH

ARTICLES

nature energy

Coupling orientation and mediation strategies for efficient electron transfer in hybrid biofuel cells

Kamal Elouarzaki, Daojian Cheng, Adrian C. Fisher and Jong-Min Lee

THE JOURNAL OF PHYSICAL CHEMISTRY C

Flexoelectricity and the Formation of Carbon Nanoparticles in Flames

Jacob W. Martin, Maria Botero, Radomir I. Slavchov, Kimberly Bowal, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-018-06269-z

OPEN

Hydrogen spillover through Matryoshka-type (ZIFs@)

Energy 150 (2018) 1039–1057

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

environmental power dispatch with small hydro power

B.Y. Qu, Gehan A.J. Amaratunga

REVIEW

H_2O_2 Production

Selective Electrochemical H_2O_2 Production through Two-Electron Oxygen Electrochemistry

Yuanyuan Jiang, Pengjuan Ni, Chuanxia Chen, Yizhong Lu, Biao Kong, Adrian Fisher, and Xin Wang*

Direct electrochemical production of hydrogen peroxide (H_2O_2) through two-electron oxygen electrochemistry, for example, the oxygen reduction in fuel cells or water oxidation in water electrolyzers, could provide an attractive alternative to locally produce this chemical on demand. The efficiency of these processes depends greatly on the availability of cost-effective catalysts with high selectivity, activity, and stability. In recent years, various novel nanostructured materials have been reported to selectively produce H_2O_2. Through combined experimental and theoretical approaches, underlying mechanisms in the electrochemical synthesis of H_2O_2 via oxygen electrochemistry have been unveiled. Considering the remarkable progress in this area, the authors summarize recent developments regarding the direct production of H_2O_2 through two-electron electrochemical oxygen reactions. The fundamental aspects of electrochemical oxygen reactions are first introduced. Various types of catalysts that can effectively produce H_2O_2 via two-electron oxygen electrochemistry are then presented. In parallel, the unique structure-, component-, and composition-dependent electrochemical performance together with the underlying catalytic mechanisms are discussed. Finally, a brief conclusion about the recent progress achieved in electrochemical generation of H_2O_2 and an outlook on future research challenges are given.

Eliminating soot formation with multiscale modelling

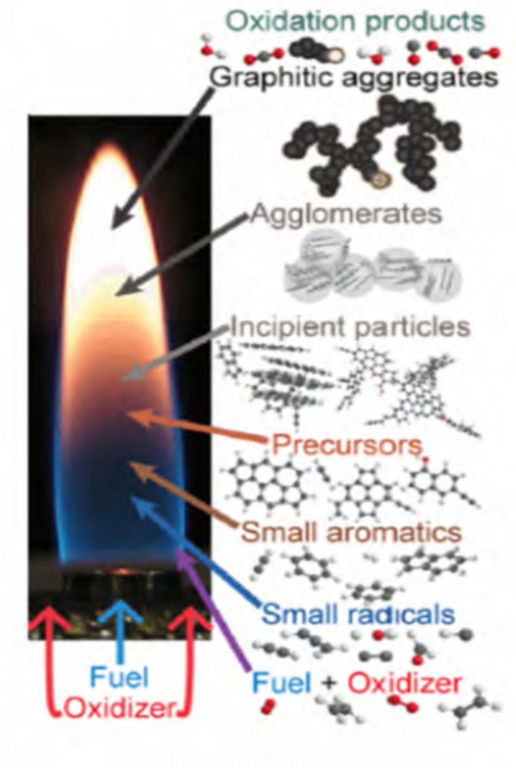
Angiras MENON, PhD student, IRP3

The generation of energy relies heavily on the combustion of fossil fuels, with nearly 85% of the world's primary energy sources coming from consumption of these fuels. Even with the increasing role of renewables in energy generation, curtailing emissions from combustion processes must be prioritised if countries such as Singapore are going to meet the stipulations of international agreements on climate change such as the 2016 Paris Agreement. The main emissions from combustion that contribute to radiative forcing and global climate change are gaseous products, for example CO_2, NO_x and methane. However, the second largest major contributor to global climate change is soot, the solid particulate matter that forms during combustion. Newer emission regulations, such as Euro 6, are recognising the importance of soot and are now also placing restrictions on the size and number of soot particles that can be emitted from engines. In order to meet these agreements and regulations, we require a deeper understanding of how soot forms. Here at CARES, we make use of a variety of computational and experimental techniques to develop multiscale mathematical models of soot formation in flames. These models will help guide the design of cleaner fuels and more efficient engines.

Soot formation involves several complex chemical and physical processes. First, the fuel breaks down into smaller molecules in pyrolysis, before a sequence of chemical reactions generates polyaromatic hydrocarbons (PAHs). These PAHs then come together to form the first soot particles, which then undergo various particle processes before being emitted. Our research group at CARES and Cambridge has developed a comprehensive particle model that describes how soot grows once it forms, but the mechanism of inception where the PAHs actually form soot has been an open question for decades. This is a key problem, as most models are highly sensitive to how the soot formation is described.

Angiras Menon received his B.A. and M.Eng. degrees in chemical engineering from the University of Cambridge in June 2016. He joined the Computational Modelling group in Cambridge in October 2016 as a PhD student under Prof. Markus Kraft. Angiras's research project involves using computational chemistry tools, particularly density functional theory, to study the gas-phase chemistry leading to the formation of carbonaceous nanoparticles formed in flames and engines. He is also interested in reaction kinetics, molecular dynamics and optimisation techniques as applied to problems in combustion and renewable energy.

As such, recent work at CARES has focused on discovering how inception of soot occurs by trying to identify what types of PAHs are most important in the process. At CARES, we have shown that curved PAHs are able to interact with each other as well as with charged molecules in the flame, thereby stabilising them. Recent work in the community has also highlighted the role of radical PAHs, which are able to grow quickly by rapid chain reactions. Our work at CARES applies computational chemistry methods to test these various hypotheses of how soot forms. By computing the optical properties of PAHs, we have shown that only a narrow range of PAH sizes are likely to form soot. We are also developing kinetic and thermodynamic models to describe how fast and how likely these different PAHs form, and comparing them to our flame experiments from the laboratory. By researching soot formation, we hope to be able to identify a range of operating conditions (temperature, pressure, type of fuel) where soot formation is unfavoured, so that particulate emissions from combustion can be reduced in the future.



Credit: Hope A. Michelsen

Combustion Energy Frontier Research Centre, 2016

FOCUS ON

IMPACT

Unlocking a pathway to a sustainable resource economy

Dr SEE Jie Yang, Research Fellow, IRP1

Rising global temperatures due to increasing greenhouse gas levels amidst the rapid depletion of the earth's resources have sparked intense worries regarding the future of our environment. Such mounting concerns have led to efforts by scientists and researchers to spearhead research for developing and discovering environmentally friendly and sustainable global energy resources. Crop waste, a by-product of agricultural activities, is a highly apt target for energy and resource extraction research.

For the past few years, our lab has performed extensive research on the extraction of utility chemicals from agricultural waste. Examples include the production of terephthalic acid from corn stover lignin and amino acid from biomass. [1-2] In this work, environmentally friendly strategies are being developed to generate a class of UV filters commonly adopted in the cosmetics industry. This is accomplished through the adept use of chemical transformations on corn stover derived intermediates. Most of these platform chemicals were synthesised through a short two-step protocol. Commercially available, recyclable and economical catalysts were adopted in our efforts. Our success in this direction brings to fruition the formation of a recyclable resource economy co-existing in a harmonious relationship with the environment. Further work on this project is underway and is foreseen to be published in the near future.

Referenced publications

[1] Song, Song, et al. 2019. "Production of terephthalic acid from corn stover lignin." *Angewandte Chemie International Edition*. https://doi.org/10.1002/anie.201814284.

[2] Deng, Weiping, et al. 2018. "Catalytic amino acid production from biomass-derived intermediates." *Proceedings of the National Academy of Sciences*. https://doi.org/10.1073/pnas.1800272115.

Dr See Jie Yang undertook his Bachelor's degree in Chemistry at NUS, graduating in 2015. His fourth year project was titled "Metal Organic Frameworks for CO_2 Capture" and completed under the guidance of Prof. Andy Hor Tzi Sum. Dr See undertook his PhD in Chemistry (2015 – 2018) under Assoc. Prof. Zhao Yu and Prof. Yeung Ying Yeung focusing on group 7 elements, the chalcogens, and their utility in organic synthesis and catalysis. He is genetically programmed to carry an intrinsic love for organic synthesis and chocolate.

Highlighted research outputs from April - October 2019

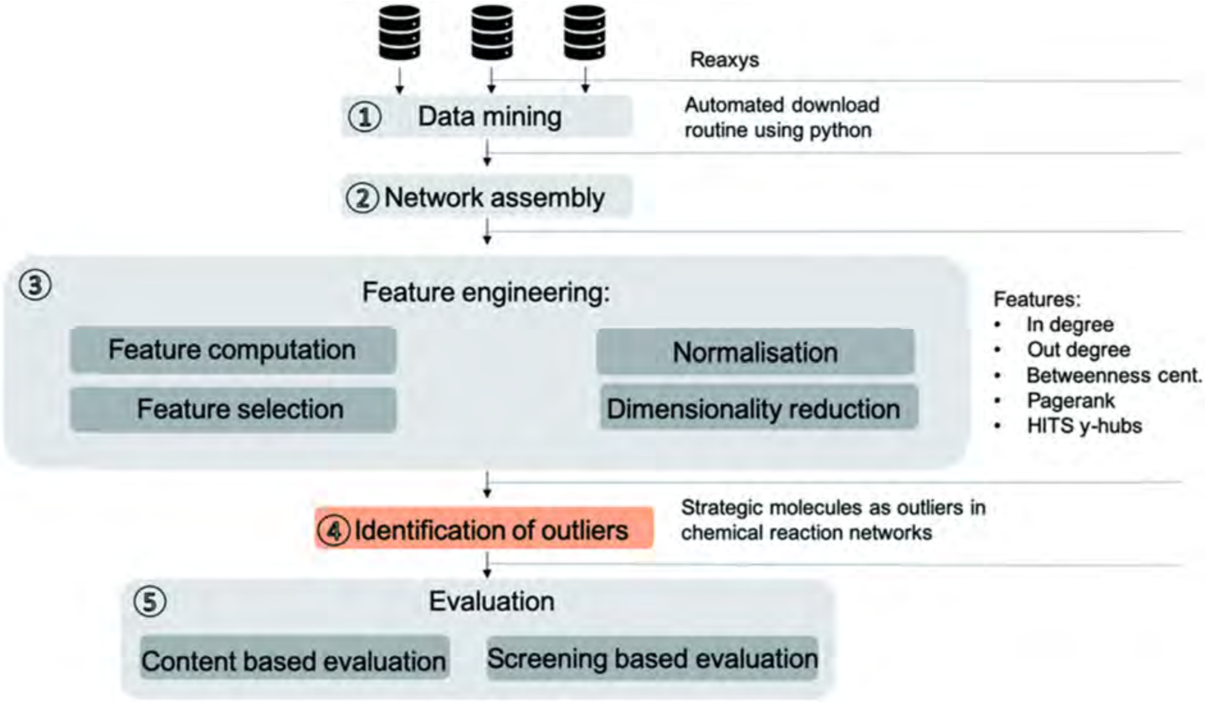
A selection of our top publications and research highlights from across the programme.

IRP1: Identification of strategic molecules for future circular supply chains using large reaction networks

Jana Weber, Pietro Lió and Alexei Lapkin, *Reaction Chemistry & Engineering*

DOI: 10.1039/C9RE00213H

Networks of chemical reactions represent relationships between molecules within chemical supply chains and promise to enhance planning of multi-step synthesis routes from bio-renewable feedstocks. This study aims to identify strategic molecules in chemical reaction networks that may potentially play a significant role within the future circular economy. We mine Reaxys® database in order to assemble a network of chemical reactions. We describe molecules within the network by a portfolio of graph theoretical features, and identify strategic molecules with an isolation forest search algorithm. In this work we have identified a list of potential strategic molecules and indicated possibilities for reaction planning using these. This is exemplified by a potential supply chain of functional molecules from bio-waste streams that could be used as feedstocks without being converted to syngas. This work extends the methodology of analysis of reaction networks to the generic problem of development of new reaction pathways based on novel feedstocks.



IRP1: Confined transformation of UiO-66 nanocrystals to yttria-stabilised zirconia with hierarchical pore structures for catalytic applications

Runze Qin and Hua Chun Zeng, *Advanced Functional Materials*

DOI: 10.1002/adfm.201903264

Solid acids as a substitution for hazardous liquid acids (e.g., HF and H_2SO_4) can promote many important reactions in the industry, such as carbon cracking, to proceed in a more sustainable way. Starting from a zirconium-based metal-organic framework (UiO-66 nanocrystals), herein a transformative method is reported to prepare micro/mesoporous yttria-stabilised zirconia (YSZ) encapsulated inside a mesoporous silica shell. It is then further demonstrated that the resultant reactor-like catalysts can be used for a wide range of catalytic reactions. The acidity of the YSZ phase is found with rich accessible Lewis acid and Brønsted acid sites and they display superior performances for esterification (acetic acid and ethanol) and Friedel-Crafts alkylation (benzylation of toluene). After being loaded with different noble metals, furthermore, hydrogenation of CO_2 and a one-pot cascade reaction (nitrobenzene and benzaldehyde to *N*-benzylaniline) are used as model reactions to prove the versatility and stability of catalysts. Based on the findings of this work, it is believed that this class of reactor-like catalysts can meet future challenges in the development of new catalyst technology for greener heterogeneous catalysis.

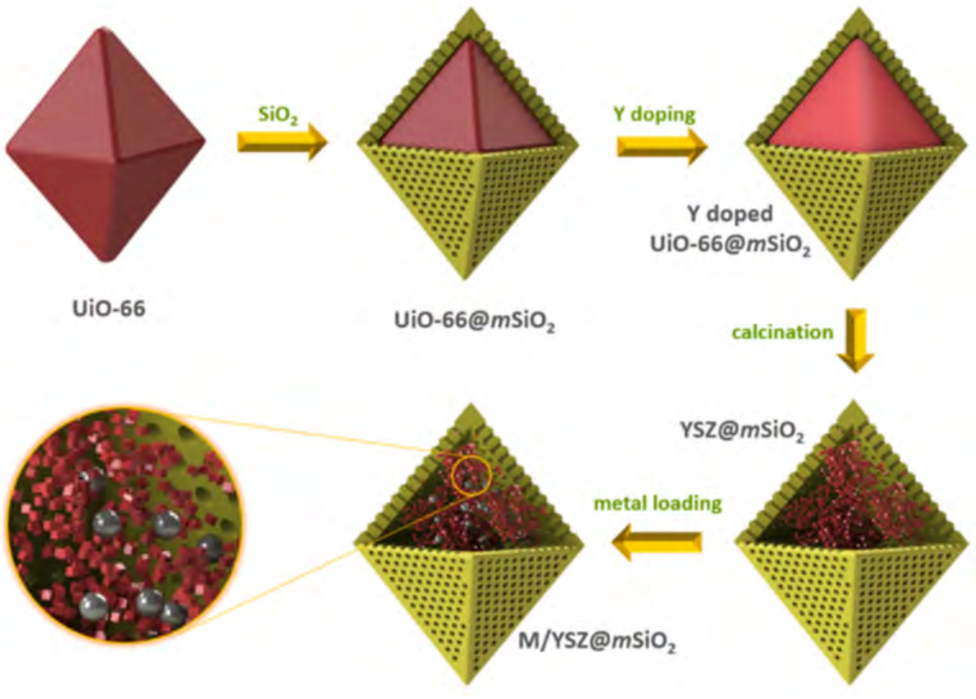


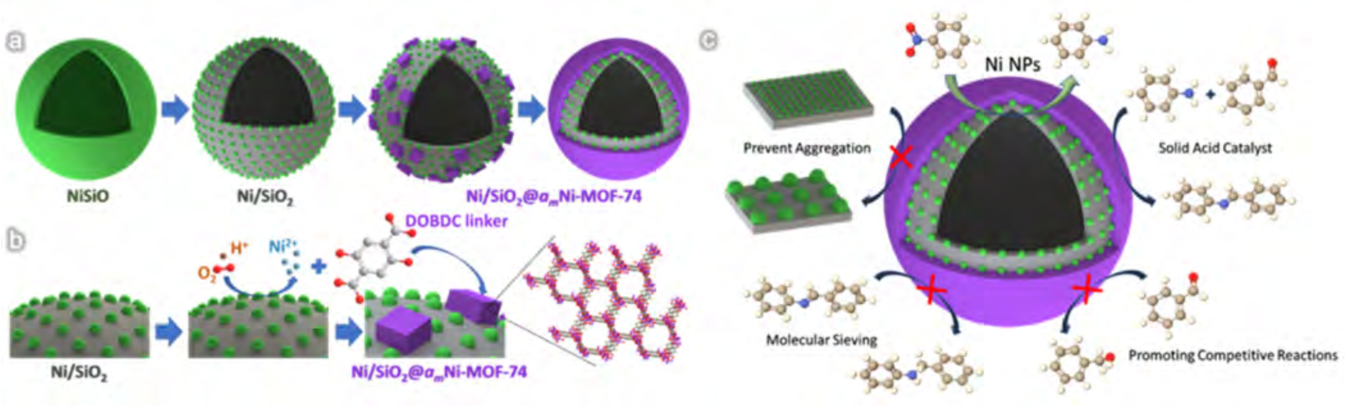
*Illustration of the stepwise preparation of the M/YSZ@*mSiO_2* nanoreactors in this work (UiO-66, starting nanocrystals; SiO_2, silica precursors; *mSiO_2*, mesoporous silica shell; Y, yttrium; M = catalytic metal nanoparticles depicted as small shining spheres).*

IRP1: Synthetic chemistry and multifunctionality of an amorphous Ni-MOF-74 shell on a Ni/SiO$_2$ hollow catalyst for efficient tandem reactions

Bowen Li and Hua Chun Zeng, *Chemistry of Materials*

DOI: 10.1021/acs.chemmater.9b02070

Core–shell particles, a unique class of functional materials, have received increasing research interest for the past two decades owing to their exceptional performance in many technological fields. For catalysis, coating a core catalyst with a shell could effectively enhance core stability and catalytic activity, provide reactant/product selectivity, add stimuli-responsive smart features, and so forth. Despite the rapid advancement made for core–shell materials, it is rare to see such shells displaying more than one or two functional roles in a single reaction system. Herein, we have developed an amorphous Ni-MOF-74 coating process for a hollow sphere made of silica-supported Ni nanoparticles. Multifunctional catalysts prepared by integration of metal–organic frameworks (MOFs) and metals were mainly limited to noble metals, whereas our catalyst successfully integrates highly dispersed transition-metal nanoparticles with MOFs. Our MOF shell possesses four distinct functionalities for tandem imination: to prevent detachment and segregation of catalytic Ni nanoparticles, to act as an acid catalyst, to avoid over-hydrogenation of the desired product via molecular sieving, and to suppress the undesired byproduct via promoting competitive reaction with a size-sieveable product. As a result, this MOF shell enables Ni/SiO$_2$ to serve as a potential alternative to noble metal catalysts in this tandem reaction, and chemical transformation of the reactant substrate to a targeted product can be achieved more effectively.



(a) Stepwise synthesis of Ni/SiO$_2$@a_mNi-MOF-74 hollow spheres, (b) a_mNi-MOF-74 formation via oxidation–etching–coordination process using a Ni NP solid precursor, and (c) illustration for multifunctionality of a_mNi-MOF-74 in tandem imination of nitrobenzene with benzaldehyde.

IRP2: Transition metal oxides for water oxidation: All about oxyhydroxides?

Zhichuan J. Xu, Perspective in *Science China Materials*

DOI: 10.1007/s40843-019-9588-5

1. Is the surface reconstruction of an oxyhydroxide surface under the oxygen evolution reaction (OER) a general phenomenon for all transition metal oxides? As stated above, a few oxides, like BSCF, have been found to undergo surface reconstruction to an oxyhydroxide surface under OER conditions. However, the investigation is limited to only a few oxides so far. The effect of OER conditions on the surfaces of oxides with stable performance upon cycling, such as $LaCoO_3$ and $ZnCo_2O_4$, remains unknown. In addition, for simple oxides such as CoO, MnO, etc., there is no study to investigate if they will form an oxyhydroxide surface under OER too. The only known fact is that they usually show lower activity towards OER as compared with perovskite and spinel oxides. One exception is NiO, which is not stable upon cycling and will transform to NiOOH under OER conditions. More effort may be needed in future to investigate the surface of all transition metal oxides under OER conditions, regardless of whether the oxides to be investigated exhibit stable cycling performance or not, and whether the oxides exhibit high or low OER activity.

2. Do all oxyhydroxide surfaces give the same activity? If the answer is yes, oxyhydroxides should be used directly as the catalyst, instead of starting with the pre-catalysts. Based on the reported results to date, the answer most likely will be no. The activity difference among several reconstructed surfaces and directly synthesised oxyhydroxides can be found in literature. For the same oxyhydroxides, it has been found that the reaction pathway depends on oxygen vacancy level, metal-oxygen covalency, cation-doping and other factors around the electronic structure of oxyhydroxides. One may expect that the oxyhydroxide surface with a desired electronic structure can result from carefully selected pre-catalysts.

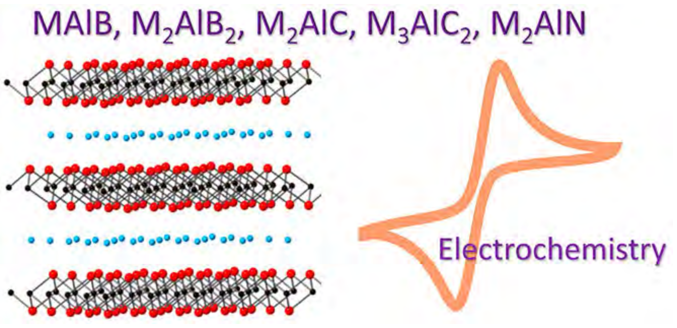
3. What are key factors to be considered in designing oxide pre-catalysts, which may result in a highly active oxyhydroxide surface? This could be one of the important topics in future for developing OER catalysts based on transition metals. At present, most research is aimed at investigating the surface reconstruction and the resulting surface. Less is about how to promote reconstruction towards the desired surface for OER. There is a lot of room for future research that aims to understand the relationship between pre-catalyst structure and the resulting surface, as well as to establish the design principles of pre-catalysts.

IRP2: MAX and MAB phases: two-dimensional layered carbide and boride nanomaterials for electrochemical applications

Nur Farhanah Rosli, Muhammad Zafir Mohamad Nasir, Nikolas Antonatos, Zdeněk Sofer, Apurv Dash, Jesus Gonzalez-Julian, Adrian C. Fisher, Richard D. Webster and Martin Pumera*, *ACS Applied Nano Materials*

DOI: 10.1021/acsanm.9b01526

Electrochemical and electrocatalytic properties of a class of layered materials known as MAX and MAB phases have yet to gain interest in the scientific community. Herein, electrochemical and toxicity studies of six MAX and MAB phases (Ti_2AlC, Ti_2AlN, Ti_3AlC_2, Ti_3SiC_2, Cr_2AlB_2, and MoAlB) were explored. The materials were found to possess high heterogeneous electron transfer (HET) rates, enhanced electrochemical sensing of ascorbic acid and uric acid, and promising electrocatalytic performances toward hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). MAB phases possessed better electrochemical properties than did MAX phases. In addition, *in vitro* cytotoxicity studies toward various human cells found near negligible toxicity toward the cells tested deeming them safe for handling and biocompatible for future biological applications. Therefore, MAX and MAB phases can be regarded as safe layered materials for potential electrochemical applications.

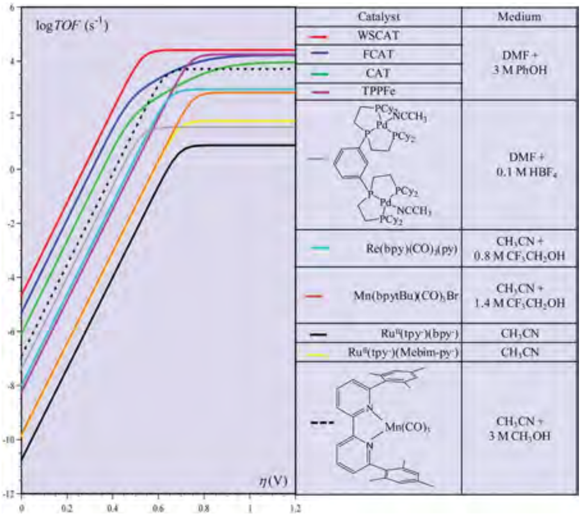


IRP2: Recent trends, benchmarking, and challenges of electrochemical reduction of CO_2 by molecular catalysts

Kamal Elouarzaki, Vishvak Kannan, Vishal Jose, Harshjyot Singh Sabharwal and Jong-Min Lee, *Advanced Energy Materials*

DOI: 10.1002/aenm.201900090

CO_2 reduction using molecular catalysts is a key area of study for achieving electrical-to-chemical energy storage and feedstock chemical synthesis. Compared to classical metallic solid-state catalysts, these molecular catalysts often result in high performance and selectivity, even under unfavorable aqueous environments. This review considers the recent state-of-the-art molecular catalysts for CO_2 electroreduction and explains the observed performance, therefore guiding the design principles for the next generation of molecules and material/molecule hybrid electrodes. The most recent advances related to these issues are discussed.

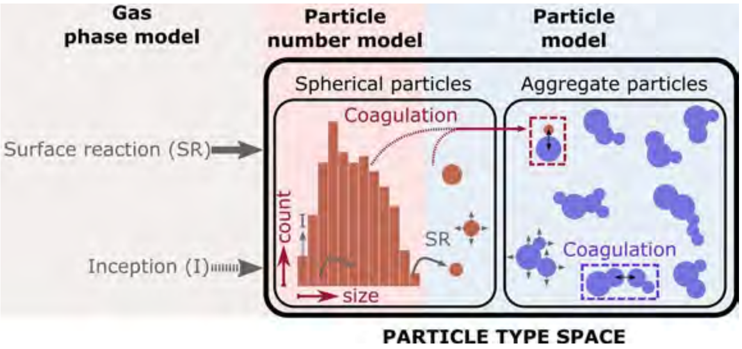


IRP3: A hybrid particle-number and particle model for efficient solution of population balance equations

Astrid Boje, Jethro Akroyd and Markus Kraft, *Journal of Computational Physics*

DOI: 10.1016/j.jcp.2019.03.033

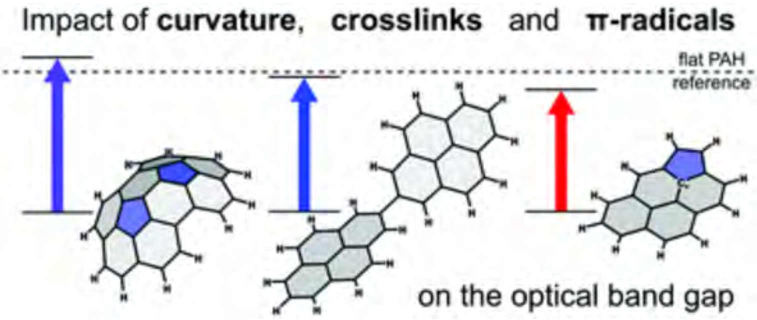
This work presents a hybrid particle-number and particle model to improve efficiency in solving population balance equations for type spaces spanning spherical and aggregate particles. The particle-number model tracks simpler, spherical particles cheaply by storing only the number of particles with a given one-dimensional internal coordinate, while the particle model allows resolution of the detailed aggregate structure that occurs due to collision and coagulation between particles by storing distinct computational entries for each particle. This approach is exact if primary particles are defined by their monomer count and the particle-number model increments in single monomers. A stochastic method is used to solve the population balance equations for the combined type space. The hybrid method works well for large ensembles (> 2^{12} particles) with a detailed particle model, where performing a finite number of particle-number updates is demonstrated to be 40–50% cheaper than updating an equivalent ensemble of discrete particles. These savings can be traded for a larger sample volume to increase the resolution in the particle size distribution or more repeat runs to reduce the total error. Run time improvements are curtailed at very high surface growth and coagulation rates due to the fixed cost of growth updates on the large aggregates formed; however, the hybrid method is still attractive in this case as its primary purpose is to reduce error by preventing saturation of the ensemble with simple particles at high inception rates.



IRP3: Optical band gap of cross-linked, curved, and radical polyaromatic hydrocarbons

Angiras Menon, Jochen Dreyer, Jacob Martin, Jethro Akroyd, John Robertson and Markus Kraft, *Physical Chemistry Chemical Physics*

DOI: 10.1039/C9CP02363A



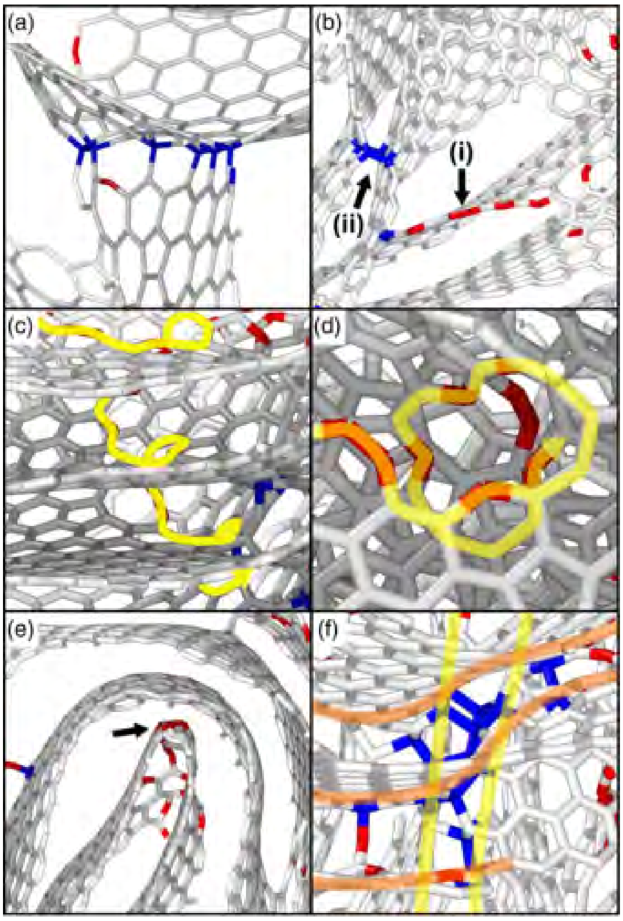
In this work, the optical band gaps of polycyclic aromatic hydrocarbons (PAHs) crosslinked via an aliphatic bond, curved via pentagon integration and with radical character were computed using density functional theory. A variety of different functionals were benchmarked against optical band gaps (OBGs) measured by ultraviolet-visible spectroscopy with HSE06 being most accurate with a percentage error of 6% for a moderate basis set. Pericondensed aromatics with different symmetries were calculated with this improved functional providing new scaling relationships for the OBG versus size. Further calculations showed crosslinks cause a small decrease in the OBG of the monomers which saturates after 3–4 crosslinks. Curvature in PAHs was shown to increase the optical band gap due to the resulting change in hybridisation of the system, but this increase saturated at larger sizes. The increase in OBG between a flat PAH and a strained curved one was shown to be equivalent to a difference of several rings in size for pericondensed aromatic systems. The effect of σ-radicals on the optical band gap was also shown to be negligible, however, π-radicals were found to decrease the band gap by ~0.5 eV. These findings have applications in understanding the molecular species involved in soot formation.

IRP3: Topology of disordered 3D graphene networks

Jacob Martin, Carla de Tomas, Irene Suarez-Martinez, Markus Kraft and Nigel Marks, *Physical Review Letters*

DOI: 10.1103/PhysRevLett.123.116105

Disordered carbons comprise graphene fragments assembled into three-dimensional networks. It has long been debated whether these networks contain positive curvature, as seen in fullerenes, negative curvature, as proposed for the schwarzite structures, or zero curvature, as in ribbons. We present a mesh-based approach to analyze the topology of a set of nanoporous and glassy carbon models that accurately reproduce experimental properties. Although all three topological elements are present, negatively curved structures dominate. At the atomic level, analysis of local environments shows that sp- and sp^3-bonded atoms are associated with line defects and screw dislocations that resolve topological complexities such as termination of free edges and stacking of low curvature regions into ribbons. These results provide insight into the synthesis of porous carbon materials, glassy carbon and the graphitisability of carbon materials.

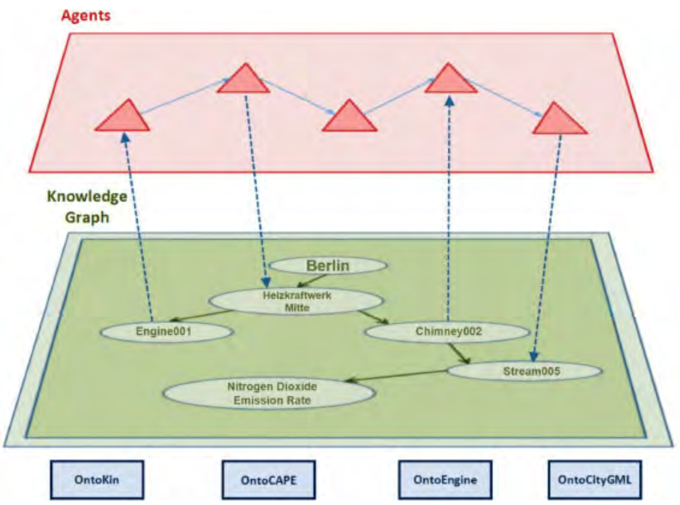


IRP JPS: An agent composition framework for the J-Park Simulator - A knowledge graph for the process industry

Xiaochi Zhou, Andreas Eibeck, Mei Qi Lim, Nenad Krdzavac and Markus Kraft, *Computers & Chemical Engineering*

DOI: 10.1016/j.compchemeng.2019.106577

Digital twins, Industry 4.0 and Industrial Internet of Things are becoming ever more important in the process industry. The Semantic Web, linked data, knowledge graphs and web services/agents are key technologies for implementing the above concepts. In this paper, we present a comprehensive semantic agent composition framework. It enables automatic agent discovery and composition to generate cross-domain applications. This framework is based on a light-weight agent ontology, OntoAgent, which is an adaptation of the Minimal Service Model (MSM) ontology. The MSM ontology was extended with grounding components to support the execution of an agent while keeping the compatibility with other existing web service description standards and extensibility. We illustrate how the comprehensive agent composition framework can be integrated into the J-Park Simulator (JPS) knowledge graph, for the automatic creation of a composite agent that simulates the dispersion of the emissions of a power plant within a selected spatial area.

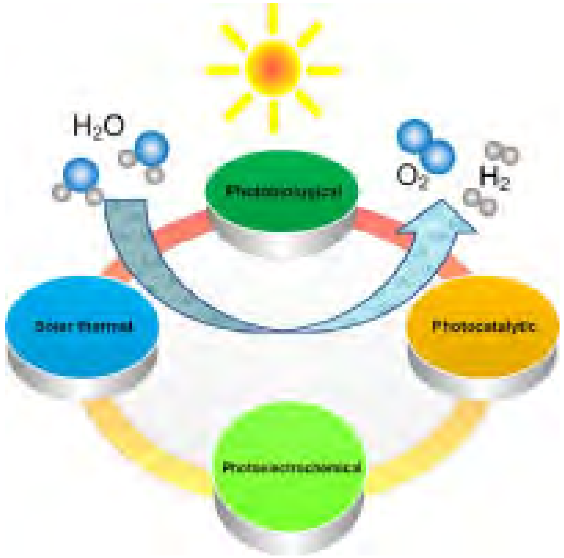


eCO_2EP: Research advances towards large-scale solar hydrogen production from water

Guanyu Liu, Yuan Sheng, Joel Ager, Markus Kraft and Rong Xu, *EnergyChem*

DOI: 10.1016/j.enchem.2019.100014

Solar hydrogen production from water is a sustainable alternative to traditional hydrogen production route using fossil fuels. However, there is still no existing large-scale solar hydrogen production system to compete with its counterpart. In this Review, recent developments of four potentially cost-effective pathways towards large-scale solar hydrogen production, viz. photocatalytic, photobiological, solar thermal and photoelectrochemical routes, are discussed, respectively. The limiting factors including efficiency, scalability and durability for scale-up are assessed along with the field performance of the selected systems. Some benchmark studies are highlighted, mostly addressing one or two of the limiting factors, as well as a few recent examples demonstrating upscaled solar hydrogen production systems and emerging trends towards large-scale hydrogen production. A techno-economic analysis provides a critical comparison of the levelised cost of hydrogen output via each of the four solar-to-hydrogen conversion pathways.



IRP1

SUSTAINABLE REACTION ENGINEERING FOR CARBON NEUTRAL INDUSTRY

IRP1 is focused on chemical technologies that allow rapid decarbonisation of chemical industry and the chemical supply chain. Our target is to deliver innovative solutions to direct utilisation of carbon dioxide as a feedstock, as well as to significantly increase the efficiency in conversion of methane to bulk intermediates. We are also exploring the options for the emerging circular economy, by developing new transformations of molecules available in different bio-waste resources into high-value functional molecules. Potential impact on carbon emissions reduction is evaluated by life cycle assessment tools.

IRP1 Principal Investigators:

Professor Alexei LAPKIN
University of Cambridge

Asst Professor Paul LIU Wen
Nanyang Technological University

Professor ZENG Hua Chun
National University of Singapore

OVERVIEW

Phase 2 of IRP1 is developing along three main directions: new structured nanomaterials for C1 feedstocks conversion and their scale up to industrially-relevant catalytic systems, development of new transformations for conversion of bio-waste streams into higher-value products, and engineering of catalytic processes for reduction of carbon emissions.

In the first part of Phase 2 the work is focusing on generation of new materials, scoping reactions for the bio-waste transformation and continuing the work on chemical looping technology. Some of the work in the IRP is also delving into machine learning and process development methodology. This aspect of the IRP is building a new platform for innovative research methods that incorporate elements of data science and machine learning into the design of new materials and processes.

Professor Alexei Lapkin, PI
University of Cambridge

Update on work package 1.1

Design of nano-structured catalysts

In recent years, one of the major directions for the development of integrated nanocatalysts (INCs) has been to integrate catalysts with different functionalities so that complex reaction systems could be carried out in one step with desired product yield. Synthesis of core-shell structured INCs is a commonly adopted strategy as it allows easy integration of core and shell materials with controlled compositions and functionalities to produce various INCs targeting individual reaction systems.

In the past six months, **LI Bowen (PhD student, NUS)** along with his supervisor Prof. ZENG Hua Chun (PI, NUS) has developed a general synthetic approach to produce organic-inorganic hybrid silica (HS) coating shell with homogeneously distributed organic functional groups using a mixture of tetraethyl orthosilicate (TEOS) and non-bridged organosilica precursor 3-mercaptopropyltrimethoxysilane (MPTMS, R-Si (R'O)$_3$). Adoption of such a non-bridged organosilica precursor has demonstrated the possibility of greatly extending the range of organic functional groups that could be incorporated into the organic-inorganic silica structure at a much lower cost. The versatility of this shell coating approach has been demonstrated with two different core materials, namely solid silica spheres (SiO_2) and hollow nickel silicate spheres (NiSiO), forming core-shell (SiO_2@HS) and hollow core-shell (NiSiO@HS) morphologies respectively (Figure 1.1).

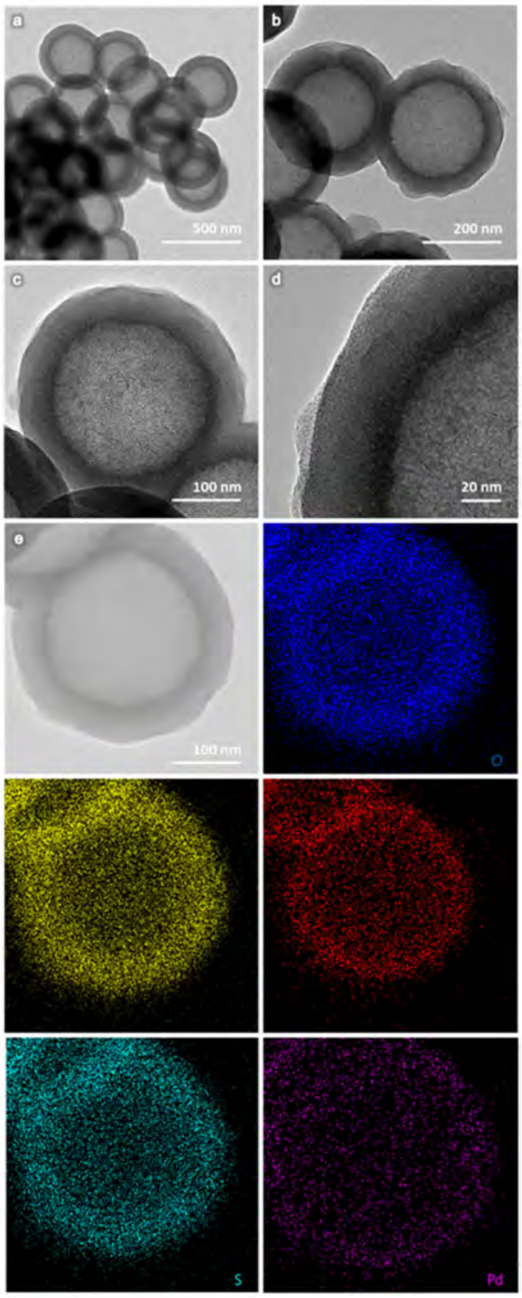


Fig. 1.1: Representative (a-d) TEM images and (e) STEM image and corresponding line scans of NiSiO@HS-Pd hollow sphere sample.

Bowen LI

Subsequently, Bowen has illustrated that these incorporated organic groups could immobilise noble metal ions the same way as pure organosilica synthesised using only MPTMS. By imprinting CTA$^+$ ions during the shell synthesis, additional functionality has been introduced of accommodating transition metal ion deposition via cationic exchange to the as-formed hybrid silica shell. The metal ion-deposited samples could also been calcined to produce metal nanoparticles for heterogeneous catalysis. By tailoring the composition of metal nanoparticles, specific catalysts targeting various CO_2 related reactions could be developed (e.g., Ni based catalyst for dry reforming of CO_2 with CH_4 and Cu based catalyst for CO_2 hydrogenation).

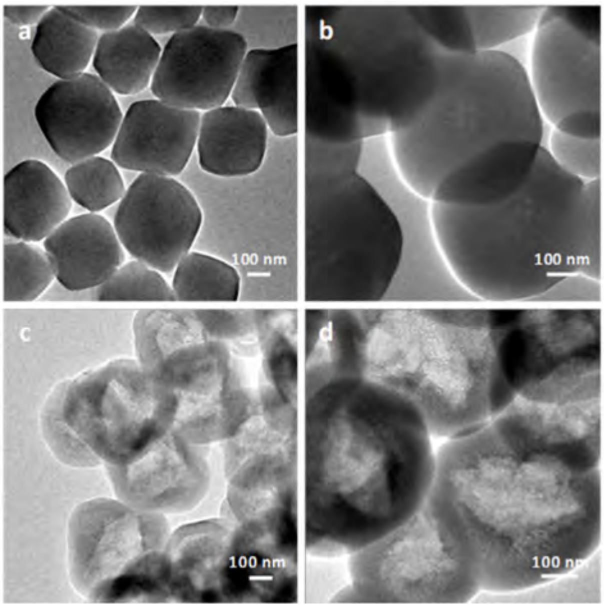


Fig. 1.2: TEM images of (a) Al-MIL-96, (b) Al-MIL-96@mSiO$_2$, and (c & d) porous Al$_2$O$_3$@mSiO$_2$.

Runze QIN

Metal-organic frameworks (MOFs) have raised enormous attention for their high specific surface areas and tunable pore sizes. Employing MOFs as catalyst precursors, **QIN Runze (PhD student, NUS)** synthesised porous aluminium oxide inside a mesoporous silica shell. After loading with Cu and Zn, the resultant nanoreactors demonstrated superior catalytic performance for CO$_2$ conversion to methanol over industrial catalysts. The good distribution of metal nanoparticles inside the porous Al$_2$O$_3$ pore channels also prevents active nanoparticles from the sintering process, showing consistent activity over a long period of reaction run time without particulate agglomeration of working metal catalysts (Figures 1.2, 1.3).

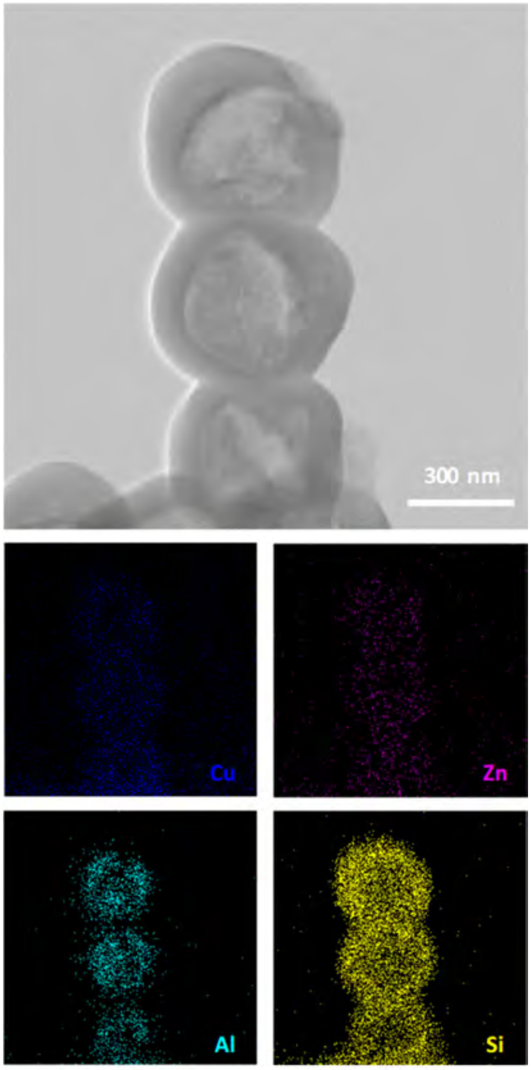


Fig. 1.3: HRTEM-EDX elemental mappings of CuZn/Al$_2$O$_3$@mSiO$_2$ catalyst.

Runze QIN

WANG Jingjing (PhD student, NUS) reports that the electrochemical oxygen reduction reaction (ORR) is one of the key processes for various energy storage and conversion systems, such as fuel cells and rechargeable metal-air batteries. To date, Pt and Pt-based catalysts are still the state-of-the-art ORR electrocatalysts, but their high cost and scarcity largely restrict their practical application. Therefore, exploring nonprecious metal catalysts with comparable ORR performance is highly desired. Recently, a number of alternatives have been constructed, such as metal alloys (Pd-Cu), doped carbon materials (N, P, S or co-doped carbon), metal oxides (Co$_3$O$_4$, MnO$_2$ etc.), chalcogenides and polypyrrole composites as well as newly developed metal–organic frameworks (MOFs).

Among these materials, the metal-nitrogen-carbon catalysts, where the metal usually presented as isolated atoms, have been demonstrated as promising electrocatalysts. However, the tunability of the metal species is still far from adequate. Low content of metals and the lack of coupling between multimetal atoms also affect the ORR kinetics. Moreover, the dense structures reported by most studies severely impede the exposure of active sites, and hamper their further improvement of ORR performance.

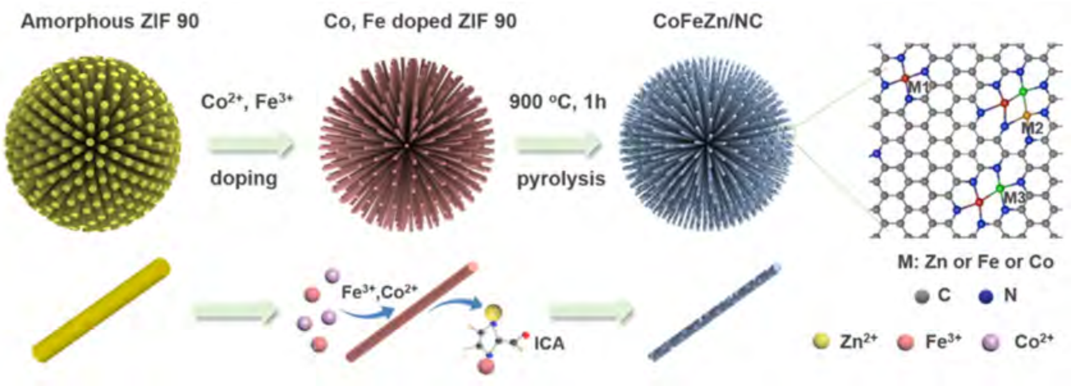


Fig. 1.4: Schematic illustration for the growth process of CoFeZn/NC. *Jingjing WANG*

Over this review period, atomically dispersed trimetal (Co, Fe and Zn) clusters were constructed, confined in N doped carbon with excellent ORR performance. The as-obtained catalyst possessed an open hierarchical structure and abundant mesopores, which efficiently improves the exposure of active sites. More importantly, the metal content of this CoFeZn/NC catalyst is relatively high (totally 5.512 wt%) compared to reported works. Benefiting from the structural and compositional merits of CoFeZn/NC catalyst, it exhibited highly efficient ORR activity, which is better than the commercial Pt/C, as well as good methanol tolerance and excellent working stability (Figure 1.4).

Alvin LIM Ming Hao (PhD student, NUS) reports that catalytic hydrogenation of carbon dioxide to methanol has been a promising approach to tap into CO_2 utilisation as well as producing a liquid fuel or a raw material in the petrochemical industry. Copper and zinc have been the two transitional metals that are commonly incorporated as the tandem active catalytic sites to achieve high methanol selectivity and catalytic performance. However as reported in this work package's previous update, ZnAl-LDH and CuZnAl-LDH, when synthesised, preferentially form dense microspheres instead of flower-like structures (unlike their counterparts CuAl-LDH and MgAl-LDH). In this work, therefore, a series of facile post-synthesis treatment was developed to circumvent this problem by forming a mixed metal–LDH (MM-LDH) with 3D flower-like petals that incorporates both copper and zinc at controlled atomic ratio (Figure 1.5). This was accomplished by utilising the unique "memory effect" property of annealed LDH or Layered Double Oxide (LDO). Taking advantage of this phenomenon, MgAl-LDO was reintroduced into aqueous metal precursor solution, forming well-dispersed copper and zinc onto the petals of the nanoflower (NF), resulting in MM-LDH-NF. The as-synthesised unoptimised MM-LDH were evaluated through high pressure CO_2 hydrogenation experiments and some promising results have been found.

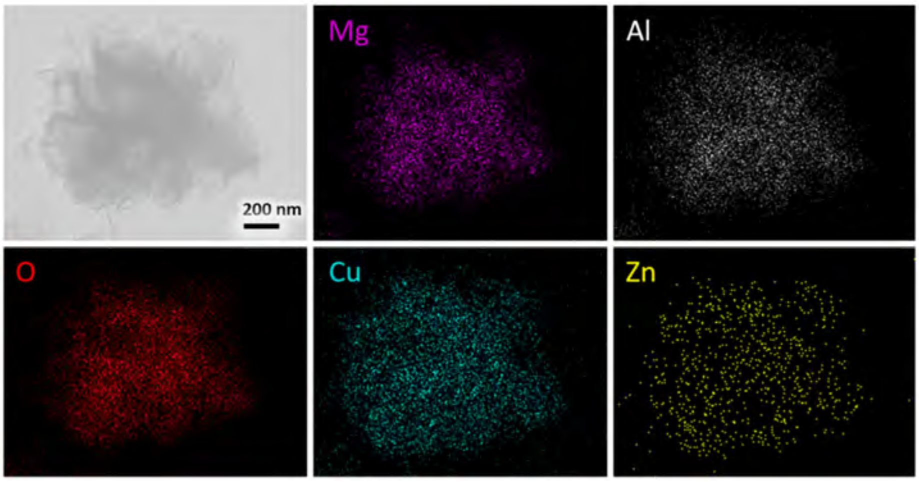


Fig. 1.5: HR-TEM and elemental mapping of MM-LDH with flower-like structure. *Alvin LIM Ming Hao*

Update on work package 1.2

Novel reactions and functional molecules

Within work package 1.2, the Cambridge team is working on developing the data-science approach to solving the problem of exploitation of bio-waste as a source of molecules. Our initial approach is to identify the potential "strategic" molecules – molecules that are important in the network of chemical transformations due to their connectivity to feedstocks and to useful products. Building on this work, the team will now proceed to develop a case study of analysing potential routes for utilisation of a bio-waste stream to produce a high-value functional product.

Dr SEE Jie Yang (Research Fellow, NUS) reports that the growing importance of a sustainable atom economy has led to a corresponding spike in the research on green or environmentally sustainable feedstock for the production of platform chemicals. Of particular attention and importance would be the generation of platform chemicals from agricultural waste, specifically crop waste such as corn stover and sugarcane bagasse. Crop wastes have a high content of lignocellulose, which is a polymer comprising useful aromatic subunits such as ferulic acid, steryl acid and p-coumaric acid. Recent advances in biorefinery technologies and synthesis processes have allowed for the extraction of several of these platform chemicals in viable yields. Of particular importance is p-coumaric acid and its related methyl p-coumarate, which could be chemically transformed into several high value added chemicals commonly found in the cosmetics and pharmaceutical industries.

In this research, Dr See has worked on the design of greener synthesis routes for these high value added chemicals using cheap and/or recyclable catalysts and chemicals. The utilisation of commercially available and economical catalysts allowed us to synthesise several useful UV filters in three or fewer steps using platform chemicals extracted from crop wastes. The development of a methylation protocol using commercially available, economical and environmentally benign reagents in potassium carbonate and dimethyl carbonate allowed for the synthesis of an intermediate for a drug (esmolol) and several useful UV filters. The protocol could also be readily extended to other analogues of p-coumaric acid (i.e., ferulic acid), achieving similar yields. The project is ongoing and is expected to be published shortly.

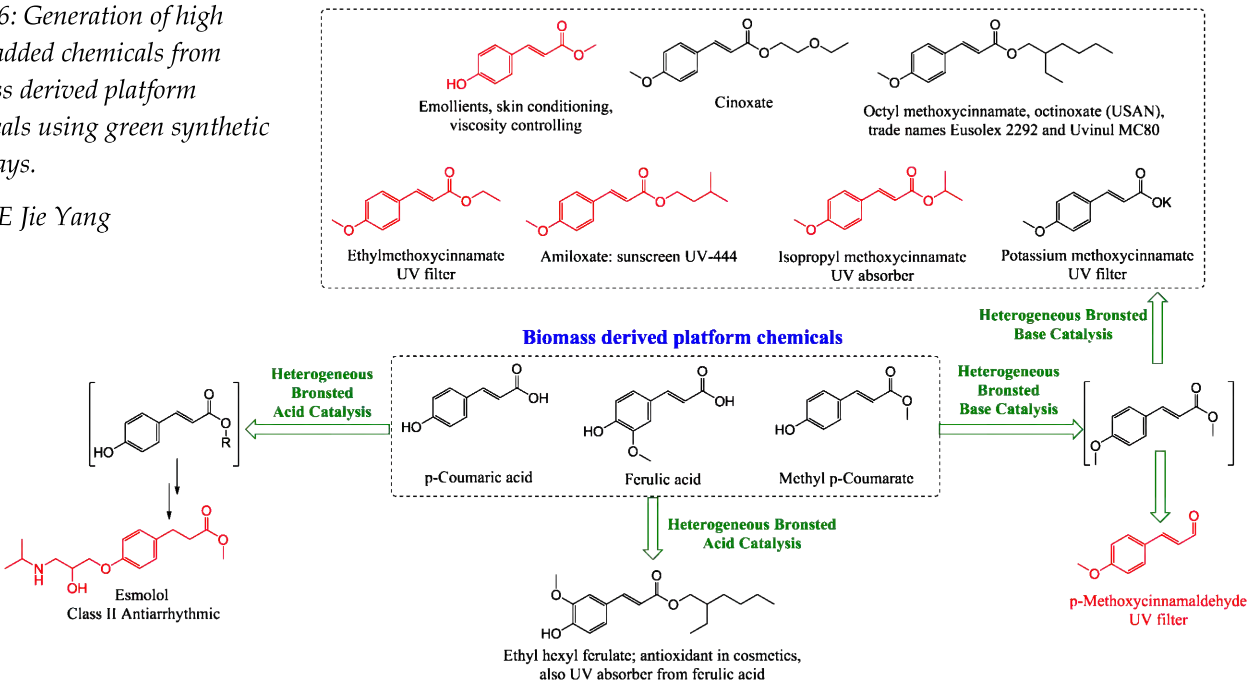


Fig. 1.6: Generation of high value added chemicals from biomass derived platform chemicals using green synthetic pathways.

Dr SEE Jie Yang

Dr CAO Liwei's (Research Fellow, CAM) research topic lies in accelerating formulated product design by combining artificial intelligence and a robotic experimental platform. An automated experimental platform was assembled in the lab in Cambridge with two main parts. One is for sample preparation, which can have at most 21 input ingredients. The other part of the wheel system is for analysis, which can record pH value, conductivity and turbidity as well as image analysis. An algorithm based on machine learning methods was also developed to guide the robotic system in order to achieve an optimal product design. As the proof of concept, a shampoo product was chosen as the case study. This part of the work is also funded by BASF SE.

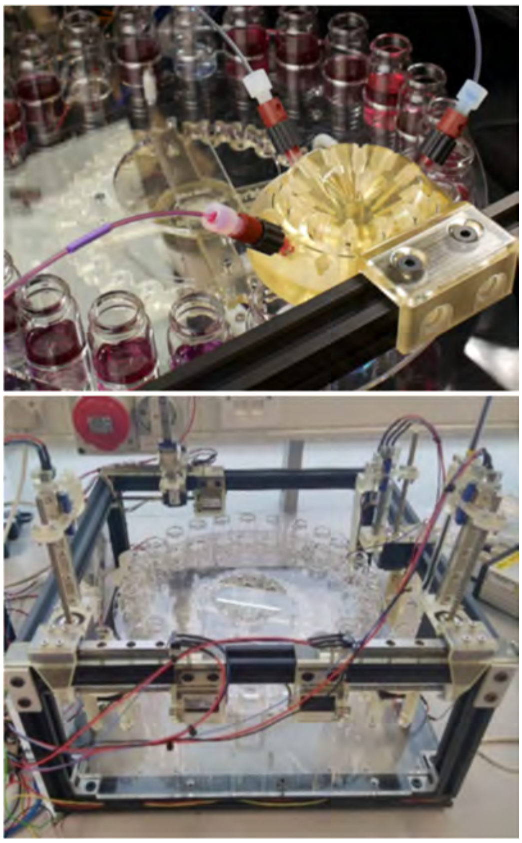


Fig. 1.7: Picture of the robotic system.

Top: wheel system for sample preparation. Bottom: robotic system for sample analysis.

Dr CAO Liwei

Update on work package 1.3

Novel reactors and process technology

Dr YAN Yong (Research Fellow, NTU) as been working on the modification of Cu supported on CeO_2 catalysts for the heterogeneous conversion of CO_2 into methanol. The pivotal role of Ce^{3+} species in the adsorption and activation of key surface intermediates has been revealed by incorporating proper dopants. *In situ* X-ray adsorption spectroscopy suggested the amount of Ce^{4+}/Ce^{3+} redox pairs was not affected by the doping while the relative amount of Ce^{3+} was drastically increased. The same trend has also been observed by X-ray photoelectron spectroscopy. The adsorption of CO, key intermediates for CO_2 hydrogenation into methanol, was strengthened with enriched Ce^{3+} species. Using *in situ* diffuse reflectance Fourier transform spectroscopy studies, Dr Yan further uncovered the promoted reactivity of carboxylate species over the doped catalysts. To provide theoretical evidence, density functional theory calculation was carried out. The adsorption of CO was stronger on Ce^{3+} than Ce^{4+}, which hindered the direct desorption of CO as a by-product. On the contrary, the adsorption of CH_3O^* was weakened on Ce^{3+}, which allowed it to desorb as final product CH_3OH and evacuate the active sites for subsequent reactions. These findings demonstrated that Ce^{3+}, rather than the Ce^{4+}/Ce^{3+} redox pair, determined the reactivity of Cu/CeO_2 catalysts for the hydrogenation of CO_2.

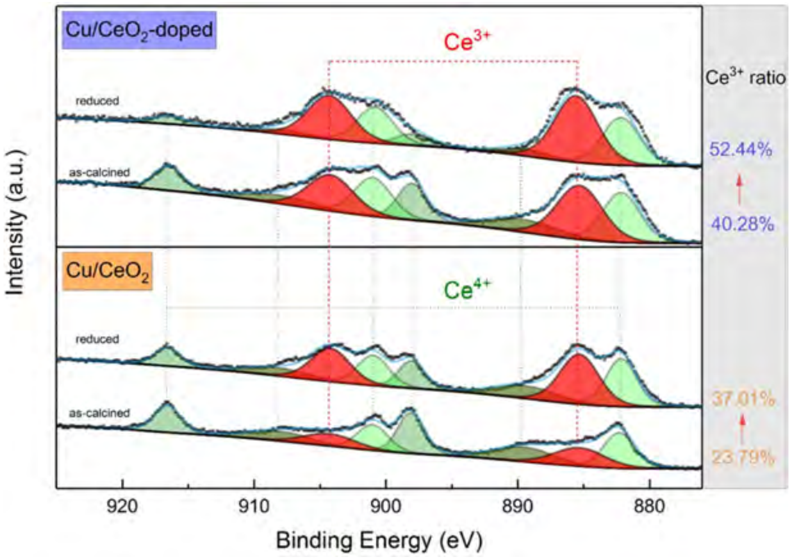


Fig. 1.8: Ce XPS spectra of as-calcined vs reduced Cu-CeO$_2$ series catalysts showing the comparable amount of Ce^{3+}/Ce^{4+} redox couples and the significantly enhanced quantity of Ce^{3+} after doping.

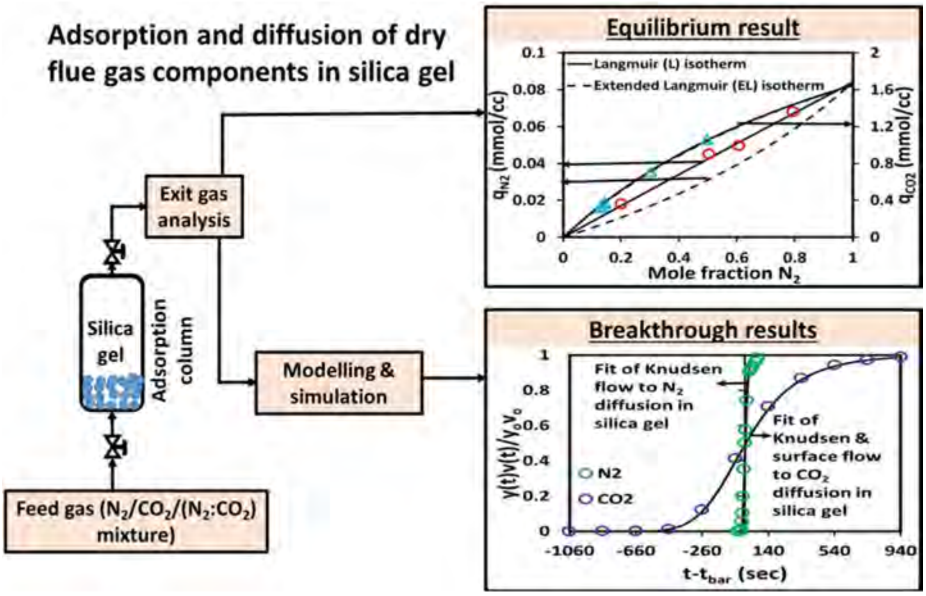
Dr YAN Yong

Nicholas JOSE (Research Assistant, CARES) successfully defended his thesis, titled "Annular Flow Synthesis and Assembly of Two-Dimensional Materials." This thesis was completed in CARES, and encompasses the work on flow synthesis of layered double hydroxides and metal organic frameworks for applications in energy storage, catalysis and separation.

Nick is now running a new CARES project (RINGs) with funding from CREATE's SMART Innovation Centre. More information on RINGs can be found on page 102.

Prerna GOYAL's (PhD student, NUS) research project aims to study drying of wet flue gas by Vacuum Swing Adsorption (VSA) on silica gel adsorbent. She has studied the adsorption and diffusion of pure CO$_2$/N$_2$ and their mixture in silica gel, and conducted breakthrough experiments on the adsorption and diffusion of moisture on silica gel. She found that the adsorption and desorption isotherms are independent of temperature and the desorption data showed hysteresis. She tried different desorption trajectories to ascertain the hysteresis path in the isotherm. Various isotherm models available in the literature were tried to fit the equilibrium data for moisture and the adsorption and desorption equilibrium data was fitted to a suitable isotherm model. Transport of moisture in silica gel pores was found to be governed by both Knudsen and surface flow. She further conducted moisture breakthrough runs at different temperatures to find out the activation energy for surface diffusion.

Prerna carried out ternary breakthrough experiments for understanding competitive adsorption of CO$_2$, N$_2$ and moisture after saturating the silica gel bed at different moisture levels and observed a reduction in CO$_2$ adsorption capacity with the increase in the relative humidity level in the bed. She will carry out further simulations to determine the isotherm model parameters for CO$_2$ and N$_2$ adsorption in the presence of moisture.



Scientific output

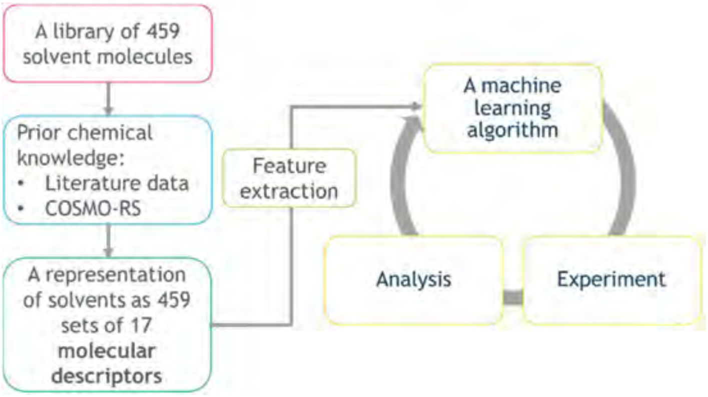
The following are the CREATE-acknowledged publications generated by IRP1 during the reporting period, excluding those already featured in the Scientific Highlights section on page 11.

Machine learning and molecular descriptors enable rational solvent selection in asymmetric catalysis

Yehia Amar, Artur Schweidtmann, Paul Deutsch, Liwei Cao and Alexei Lapkin, *Chemical Science*

DOI: 10.1039/C9SC01844A

Abstract: Disposal of nitrogen-containing sewage sludge (SS) via gasification leads to the formation of NO_x precursors and NO_x and ammonia emissions. Pretreatment of SS via hydrothermal carbonisation (HTC) was shown to improve coalification, desulfurisation, and deamination. In this study, we propose a combined hydrothermal pretreatment and CO_2 gasification process for removal of nitrogen from SS and production of energy via the gasification of the pretreated SS. In the HTC process, around 50% of nitrogen contained in the sludge was removed. The derived hydrochar (HC) was subsequently fed for gasification using CO_2 as a gasifying agent, which was characterised by the expected reduction in the formation of ammonia. We further improved the process by establishing cogasification of hydrochar with waste leaves. The improvement is believed to be due to the catalytic effect of Ca, present in plant leaves, on the gasification. Cold gas efficiency of the cogasification process of a 1/1 hydrochar/leaves blend by mass was enhanced to 66%. The combination of hydrothermal conversion of sewage sludge with CO_2 cogasification of hydrochar and waste leaves was shown to be a clean and efficient method for SS management and energy recovery.

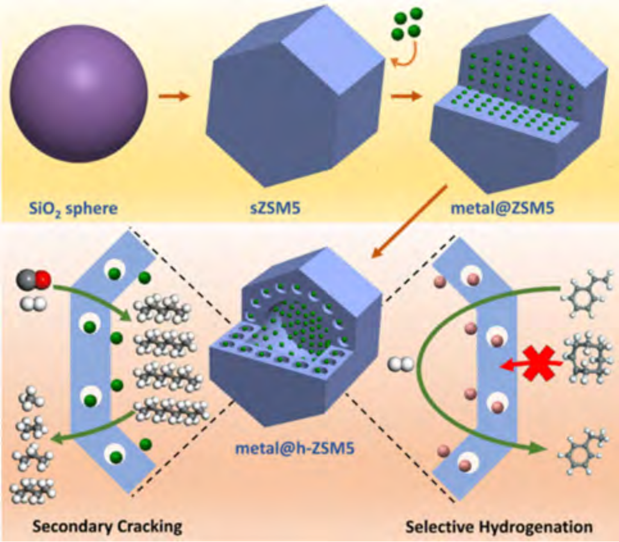


Transformation of Stöber silica spheres to hollow hierarchical single-crystal ZSM-5 zeolites with encapsulated metal nanocatalysts for selective catalysis

Kelvin Mingyao Kwok, Sze Wei Daniel Ong, Luwei Chen and Hua Chun Zeng, *ACS Applied Materials & Interfaces*

DOI: 10.1021/acsami.9b00630

Abstract: The activity of zeolite-supported nanocatalysts is dependent on both the dispersion, size, and location of metal nanoparticles around the zeolite and the size and pore structure of the zeolite. In this study, a synthetic approach was developed to encapsulate metal catalysts within hollow interiors of single-crystal ZSM-5. Briefly, Stöber silica spheres were synthesised and then transformed to single-crystal nano-ZSM-5 (Si/Al = 60), followed by growth of embedded metal nanoparticles and subsequently creation of a nanosized (30–50 nm shell thickness) hollow hierarchical zeolite structure. Metal nanoparticles such as Co, Cu, Cu–Zn, Fe, and Ni can be supported on the inner wall of the hollow zeolite and the surrounding satellite mesopores, without any particles present on the external zeolite surface. When evaluated as a catalyst for the Fischer–Trøpsch reaction, the Fe@h-ZSM5 catalyst shows high activity, sintering and coking resistance (50% longer stability than Fe@ZSM5), and secondary cracking reactions in the acid sites in the ZSM-5 shell, which reduce C_{5+} hydrocarbon selectivity and increase smaller-chain hydrocarbon selectivity. In addition, when Pt was further deposited inside the hollow structure, shape-selective alkene hydrogenation was demonstrated. These configured nanoscale zeolite catalysts have potential applications for reactions that involve supported metal nanoparticle catalysis, shape selectivity, or secondary cracking reactions.

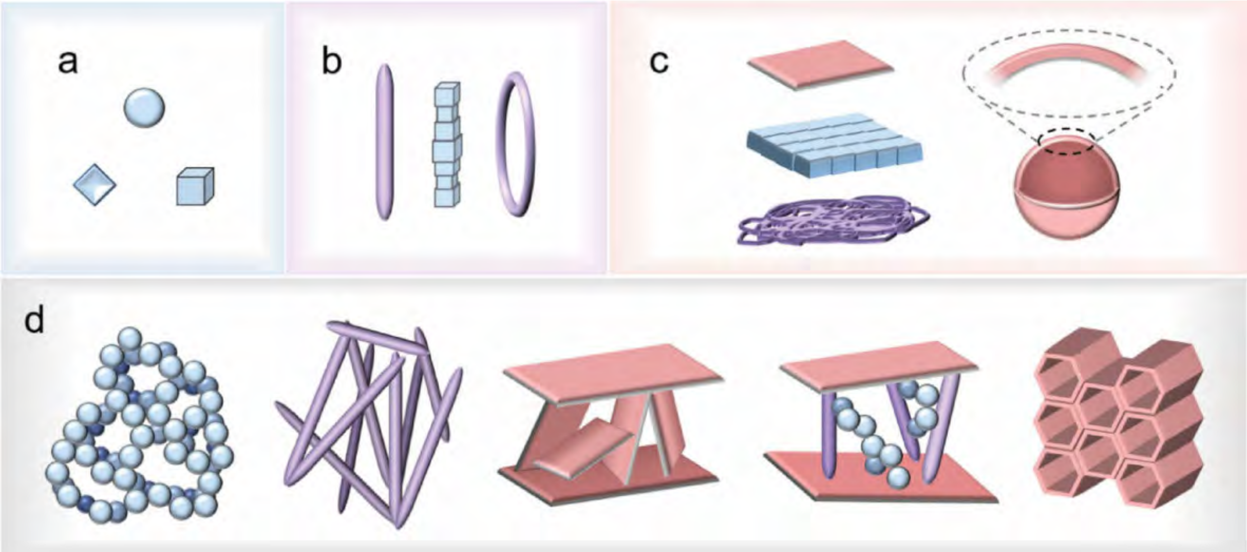


Low-dimensional metal-organic frameworks and their diverse functional roles in catalysis

Ying Chuan Tan and Hua Chun Zeng, *ChemCatChem*

DOI: 10.1002/cctc.201900191

Abstract: In recent years, metal-organic frameworks (MOFs) have gained tremendous attention as an emerging class of functional materials for the field of heterogeneous catalysis. In particular, low-dimensionality of these material-platforms can be singled out as an important structural parameter that endows unique or new functionalities and thus enables improved catalytic performance. Herein, firstly, this Review summarises important development of the synthetic preparation strategies of low-dimensional MOFs and their related composites. Next, effects of dimensionality on different catalytic roles of MOF platforms are highlighted and discussed. For instance, MOFs have been employed directly as heterogeneous catalysts, in which catalytic reactions take place within their pristine or deliberately created pores. Exploiting on the ordered pore structures, MOFs have also been integrated into reactor-like catalysts to act as a membrane for selective catalysis. MOFs have also demonstrated to be unique support materials for other catalyst components, of which enhancement in stability and catalytic performance have been addressed. Lastly, MOFs have also been extensively utilised as a sacrificial template to derive highly porous and catalytic active nanomaterials. On the basis of our personal perspectives, some future research directions are suggested in this review in order to further advance this class of emerging catalysts.

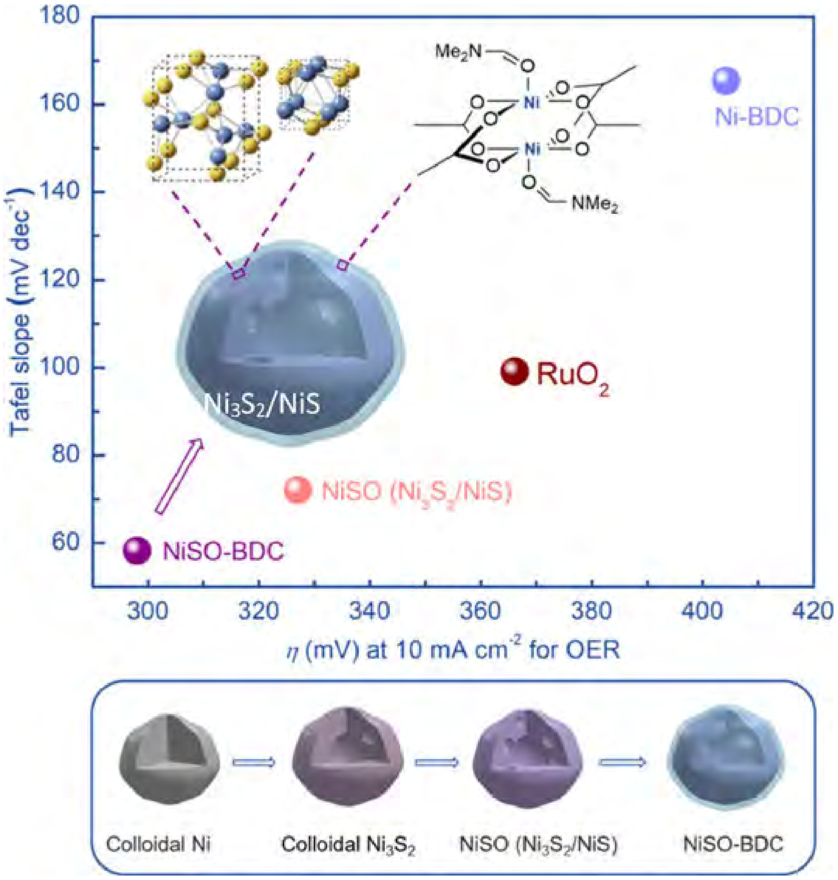


A hybrid electrocatalyst with a coordinatively unsaturated metal–organic framework shell and hollow Ni_3S_2/NiS core for oxygen evolution reaction applications

Jing Jing Wang and Hua Chun Zeng, *ACS Applied Materials & Interfaces*

DOI: 10.1021/acsami.9b04479

Abstract: Metal–organic frameworks (MOFs) have emerged as a promising class of materials. However, their insulating nature has limited their application as electrocatalysts. Herein, we report a heterogeneous nanostructure of a Ni-based MOF-modified Ni_3S_2/NiS hollow nanoparticle. The Ni_3S_2/NiS hollow core is prepared by a sulfuration process from a colloidal nickel nanoparticle using dodecanethiol followed by a low-temperature heat treatment in air to remove the adsorbed organic ligands. The thin shell of the Ni -based MOF (Ni-BDC) is synthesised using an in situ method in which the nickel sulfides supply the metal source and the additional terephthalic acid serves as the linker. Serving as an oxygen evolution reaction catalyst, this hybrid nanocomposite shows superior electrocatalytic performance with a low overpotential of 298 mV at 10 mA ·cm^{-2} without carbon addition and a long-time endurability with no detectable activity deterioration, which can be attributed to the synergistic effect of the advantageous heterogeneous structure, combining the good hydrophilicity and coordinative unsaturation of the Ni-BDC shell and the high conductivity and porosity of the Ni_3S_2/NiS core as well as the strongly coupled interface between them.



Other activities and achievements

PhD student Liwei CAO gave an oral presentation ‘Symbolic regression for automated physical model identification in reaction engineering’ in the conference *Machine Learning and AI in (bio)chemical engineering* in Cambridge, UK, July 2019.

PhD student Prerna GOYAL delivered a talk ‘Drying of wet flue gas by vacuum swing adsorption on silica gel’ at the *13th International Conference on the Fundamentals of Adsorption* held in Cairns, Australia in May.

Research Assistant Nicholas JOSE gave a flash talk on ‘A continuous annular microreactor for high shear synthesis of two-dimensional nanoparticles at *Continuous Flow Technology IV* in Manchester, UK, in May.

Research Fellow Dr YAN Yong, with **PI Prof. Paul LIU**, presented their research on ‘The disintegration of metal particles during CO_2 hydrogenation’ at the *26th Meeting of the North American Catalysis Society* in Chicago, US, 22-28 June.

Dr Yan was also the winner of the AIChE Singapore Local Section Outstanding Young Researcher Award 2019.

Prof. Liu gave a seminar titled ‘Carbon capture, storage and utilisation’, representing CARES, at the Science, Technology, Prototyping, Practice and Policy Workshop (STP^3) in June at SEC, CREATE.

Prof. Liu served as a panel number at the CCS Workshop at Innovate4Climate 2019, held at Marina Bay Sands in June.

PI Prof. Alexei LAPKIN gave a talk on ‘Circular economy’ at BASF SE, Ludwigshafen, in March.

Prof. Lapkin also gave a talk on ‘Emergence of digital molecular technology’ at UCB Pharma, Brussels, in October.

IRP2

ELECTROSYNTHETIC PATHWAYS FOR ADVANCED LOW-CARBON CHEMICAL MANUFACTURING

In IRP2, low carbon electrosynthetic processes and technologies are developed which target local, on-scale and on-demand conversion of electricity to commodity or specialty chemicals. As the contribution of renewables to the total electricity generation capacity continues to grow, novel technological opportunities arise for direct chemical conversion of the newly available low carbon electrons. This project addresses core challenges to the implementation of low carbon, on-demand driven advanced manufacturing of chemical targets via electrosynthesis.

IRP2 Principal Investigators:

Dr Adrian FISHER
University of Cambridge

Professor WANG Xin
Nanyang Technological University

Professor LEE Jim Yang
National University of Singapore

OVERVIEW

In the latest reporting period, IRP2 researchers have been developing the micro-variable pressure and temperature electrosynthesis plants. Research Fellows Dr Kamal Elouarzaki, Dr Minyu Zeng and Dr Chencheng Dai have designed and commissioned a new plant to operate in ultra high clean environments. This facility, once fully commissioned in early 2020, will be a world first. A current core focus of the team is the development of a fully operational sensing electrode for monitoring product generation within the micro-variable pressure and temperature electrosynthesis plant. Once operational the facility will be used to test and explore electrocatalytic reactions such as those reported by Dr Elouarzaki where a unique chemical inactivation/redox activation process (IAP) based on a non-enzymatic catalyst prepared by mixing rhodium-porphyrinic catalyst has been recently reported. The test facility will exploit the studies connecting electrochemical, mathematical models and DFT calculations to optimise synthesis performance.

The recently launched startup company Datum Electronix, between Dr Elouarzaki and Dr Adrian Fisher, has been active in developing industrial partnerships and has recently submitted an application to the MIT innovation call.

In collaboration with Prof. Xu Zhichuan (Co-I, NTU), Dr Chencheng Dai has reported advances in understanding in metal oxide electrocatalysts, more precisely assessment of their "intrinsic activity".

In collaboration with Prof. Erik Birgersson (Co-I, NUS), Dr Kuppa Ashoke Raman and Vishvak Kannan, work has continued in the area of advanced numerical analysis. Vishvak has been making progress in the sensitivity analysis of converting CO_2 to CO in a microfluidic cell (MFC) reactor. This MFC reactor is operated potentiostatically and is investigated at different operating cell potentials. Monte Carlo simulations (MCS) for the electrochemical reduction of CO_2 to CO was conducted based on a mechanistic mathematical model of the MFR.

In collaboration with Prof. Jim Yang Lee (PI, NUS), Dr Zhang Tianran and his colleagues have conjectured that the use of an electrode-integrated membrane and programmable electrical stimulus could reduce the frequency of membrane replacement. The approach works well for forward osmosis but runs into new operating issues when it is extended to reverse osmosis – the original placement of the embedded electrode was found to increase the membrane internal concentration polarisation and reduce the membrane salt rejection performance and water flux.

The development of the IRP2 international outreach programme has continued with an international programme delivered in Singapore in June 2019. Further programmes have been inititated with Project Dignity, Singapore, where IRP2 demonstrators have been working to deliver a demonstration of energy efficient technologies at their facilities in Singapore.

Dr Adrian Fisher, PI
University of Cambridge

Update on work package 2.1

Advanced electrode architectures

Dr Kamal ELOUARZAKI (Senior Research Fellow, NTU): With global energy demand on the rise, relying on non-renewable sources fossil fuels is no longer a viable option. Consequently, research directions have shifted towards technologies like hydrogen production, CO$_2$ reduction into value added chemical products, fuel cells, etc. Fuel cells offer much promise for replacing this colossal use of fossil fuels with renewables; the fuel cells produce negligible emissions. However, the fuel most often employed in fuel cells is hydrogen gas, which is largely produced from non-sustainable sources and is accompanied by carbon dioxide emissions. Therefore, the use of a renewable energy source such as biomass is becoming increasingly desirable. As one of the most abundant green sources of energy on the planet, carbohydrates, in particular glucose, is capable of producing 4430 Wh kg^{-1} (based on a thermodynamic calculation for its complete oxidation). This is on the same order as that of methanol, which has been considered as "dream fuel" capable of generating power densities that exceed lithium ion batteries with an easy storage and recharging of fuels. To derive useful energy from glucose, direct conversion of its chemical energy

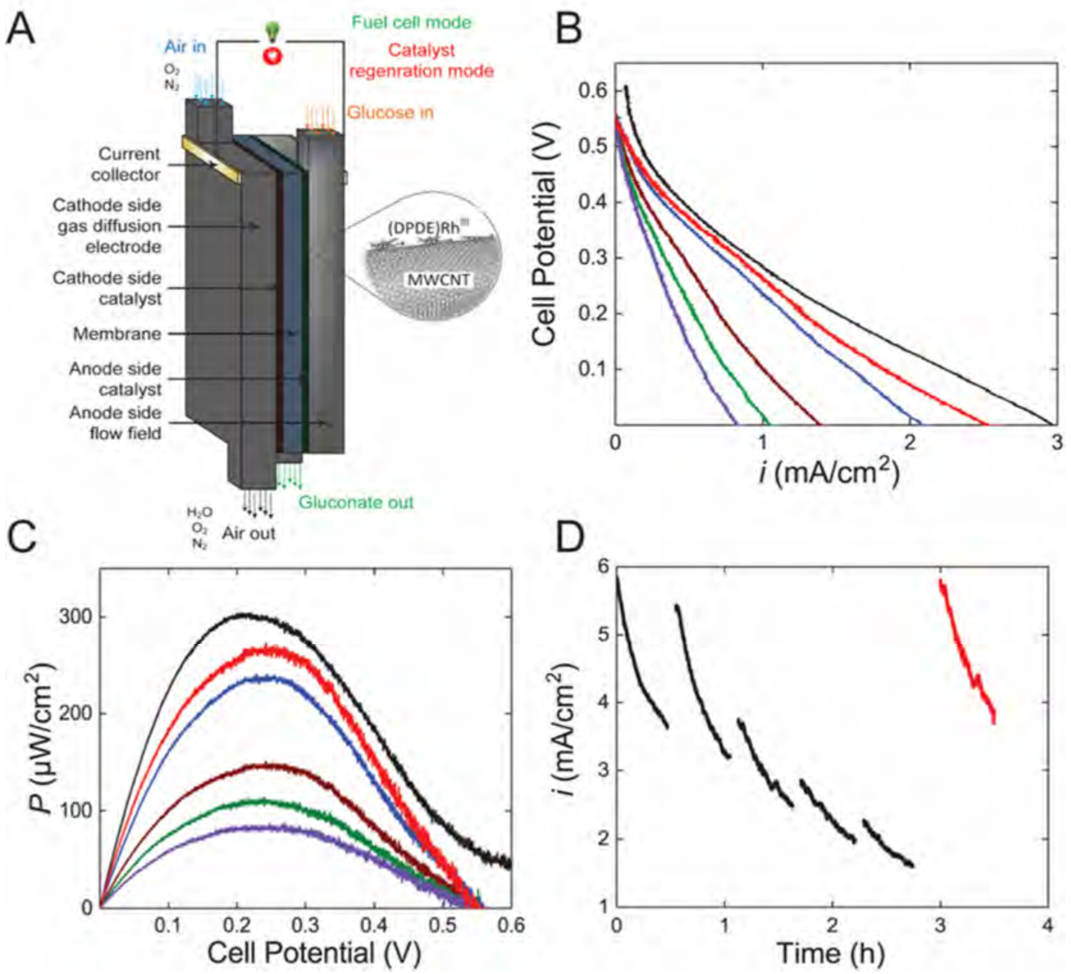


Fig. 2.1: (a) Schematic of the glucose fuel cell (GFC). (b) Polarisation curves measured at a scan rate of 2 mV s-1 with the initial measurement in black and the final measurement in purple; the red curve represents the polarisation curve after the application of -1.0 V. (c) Power curves corresponding to the polarisation curves with the red curve representing the measurement performed after applying -1.0 V. (d) Galvanostatic measurements recorded at 0.2 V for 30 minutes each with a relaxation time of 4 minutes; the red curve corresponds to the galvanostatic measurement recorded after the application of -1.0 V.

Dr Kamal ELOUARZAKI

to electrical energy is the best option. To produce electricity by electrochemically oxidising glucose and reducing oxygen into water, the anodic reaction is a key factor of the fuel cell performance. To construct fuel cells of practical significance, efficient catalysts are required to promote the glucose oxidation at low overpotential. Traditionally, platinum has been regarded as the best catalyst for fuel cells, although it still suffers from multiple drawbacks including its susceptibility to time-dependent drift and MeOH crossover and CO poisoning effects. In addition, the large-scale practical application of fuel cells cannot be realised if the expensive platinum-based electrocatalysts cannot be replaced by other efficient, low-cost, and durable electrodes.

To be economically attractive, the glucose fuel cell requires breakthroughs in anodic catalyst development and engineering. In this context, molecular catalysts represent a promising candidate to tackle the aforementioned challenges. The tuneable nature and electronic characteristics of molecular catalysts give access to a large variety of catalysts with high activity, selectivity and durability, as well as their ability to be integrated into sophisticated nano-assemblies. Rhodium based porphyrin complex was reported as glucose oxidation electrocatalyst in alkaline electrolytes. Despite the observed high performance, (DPDE)Rh^{III} suffers inactivation by OH^- ions, resulting in odd voltammetric traces with the shape similar to that exhibited by a hydrogenase enzyme. This inactivation dramatically changes the shape of the electrocatalytic cyclic voltamperograms, at the forward scan, the catalytic current due to glucose oxidation increases and considerably drops as the potential becomes more positive as a result of the oxidative formation of the inactive form. However, this behaviour is reversed on the subsequent sweep back to a more negative potential.

In this work, a surface confined rhodium(III) Deuteroporphine IX dimethyl ester complex ((DPDE)RhIII) on multi-walled carbon nanotube (MWCNT) network in the presence of glucose as a substrate is considered. Firstly, a "multi-step" CA method and is carried out and an irreversible loss in the catalytic current after the inactivation process is identified. Then, to probe into this loss, cyclic voltammetry (CV) is performed with a wide potential window to discern an irreversible wave which may be responsible for the loss of catalytic current. From this analysis a dimeric species was identified to be responsible for the current loss in the subsequent oxidation step. Secondly, the formation of dimeric species was included in a new EC'CECE catalytic scheme to derive its corresponding mathematical model and test its robustness. Following this, the model is validated with CV at different scan rates and multi-step CA. Finally, after establishing the mechanistic catalytic scheme, the (DPDE)RhIII complex was integrated in a fuel cell configuration. As shown in Figure 2.1, the resulting fuel cell exhibited a high power density associated with a loss in performance over time due to the irreversible formation of the dimeric species. By employing the multi-step CA during fuel cell tests, this loss was able to be recovered and thus the fuel cell can be termed "regenerative".

Dr Chencheng DAI (Research Fellow, NTU) has been looking at various aspects of electrocatalysis and water oxidation. Metal oxide electrocatalysts have recently received a lot of attention, but a more exact assessment of their "intrinsic activity" – current per unit catalyst surface area – is required. This calls for an experimental approach to determining the surface areas of metal oxide electrocatalysts, which was carried out by Dr Dai and his colleagues.

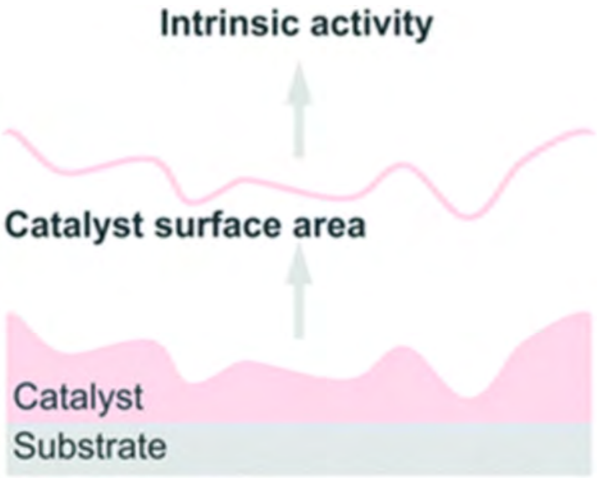


Fig. 2.2: Diagram of a metal oxide electrocatalyst.

Dr DAI Chencheng

Dr Dai also looked at cobalt spinel oxides, a class of promising transition metal oxides for the catalysing oxygen evolution reaction. Their structure affects their catalytic activity, so Dr Dai looked at the specific features of spinel oxide lattices. This work uncovered the influence of oxygen anion charge distribution on the electronic structure of the redox-active building block Co–O. The charge of oxygen anion tends to shift toward the octahedral-occupied Co instead of tetrahedral-occupied Co, which hence produces strong orbital interaction between octahedral Co and O. Thus, the OER activity can be promoted by pushing more Co into the octahedral site or shifting the oxygen charge towards the redox-active metal centre in CoO_6 octahedra. Spinel oxides are also widely studied with regard to their octahedral sites, which can act to promote fast oxygen evolution reaction kinetics that assist in hydrogen production by water electrolysis.

Nur Farhanah BTE ROSLI's (PhD student, NTU) recent work explores the electrochemical properties and applications of graphene analogues, specifically siloxane ($Si_6H_3(OH)_3$), germanane (Ge_6H_6) and methygermanane (Ge_6Me_6). Upon successful synthesis and characterisation of these layered materials, their sensing and electrocatalytic capabilities were studied. Specifically, studies to evaluate their capabilities to detect ascorbic acid, uric acid and dopamine as well as catalyse clean energy reactions such as hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) were carried out. In addition, toxic properties of these materials were studied to further understand the risks they may pose to human health. This toxicity study was extended to cells from different parts of a human body such as A549, MCF-7, HEK 293 and HepG2 cells. This research serves as a fundamental study to understand the properties and potential of new materials for various applications, including clean energy applications.

THAM Guo Xiong's (PhD student, NTU) main research lies in the study of electrode modifications via a range of electrochemical studies. In a study of the electrochemical polymerisation of aniline and melamine on COOH-functionalised multi-walled carbon nanotubes (fMWCNT) at a glassy carbon electrode (GCE) surface, electrochemical impedance spectroscopy (EIS) was performed. Further analysis of EIS results revealed that the relaxation time constant of the composite electrode PANIPMEL/fMWCNT/GCE was almost half of that of the composite electrode PMEL/fMWCNT/GCE but 300 times greater than PANI/fMWCNT/GCE. It is surmised that the diffusion paths of the electroactive species was somewhat obtrusive with the presence of the lesser resonant PMEL and the presence of the more resonant PANI facilitated a more efficient charge transfer to compensate for the poorer charge transfer by PMEL.

Problems have been reported in literature with the extremely poor dispersion of pristine carbon nanotubes (CNT), but there is not much information on their electrochemistry. In a separate study, Guo Xiong studied the electrochemistry of various solvents that have been commonly used to disperse pristine and chemically functionalised CNT. The drop cast of the dispersed CNT on a clean GCE surface was studied with the use of the ferrocyanide/ferricyanide redox couple. A study is currently underway which will hopefully offer better insights into the electrochemistry of the dispersed CNT in various solvents.

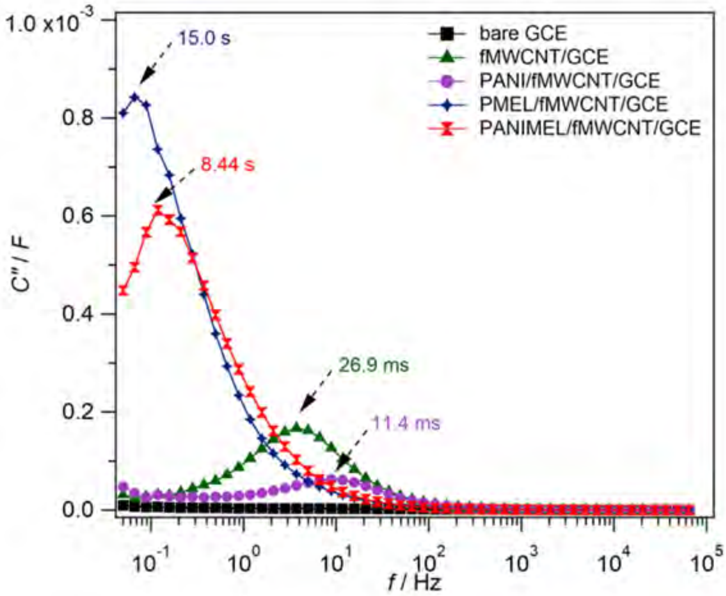


Fig. 2.3: Plot of imaginary capacitance (C") of various electrodes as a function of frequency.

THAM Guo Xiong

Update on work package 2.2

Co-generation and electrolytic synthesis reactor engineering

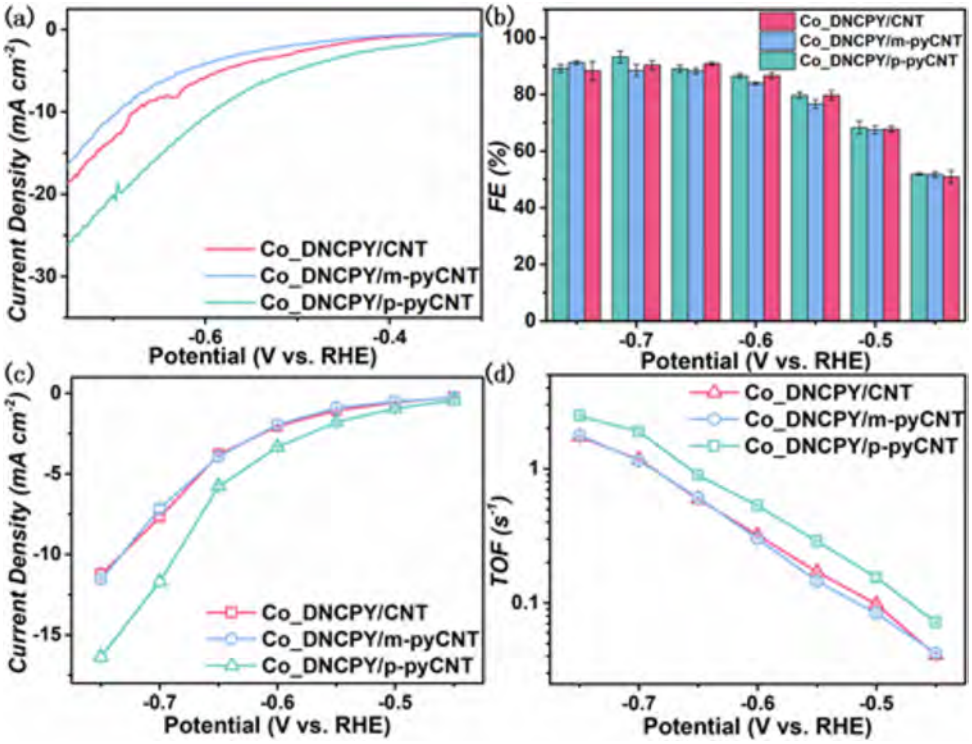
In the present work, **Dr SUN Libo (Research Fellow, NTU)** and colleagues have focused on the electrocatalytic CO_2 reduction in aqueous solution with Co_DNCPY loaded onto multi-walled carbon nanotube (CNT). The CNT was modified with aminopyridine to obtain meta-pyridine decorated CNT (m-pyCNT) and para-pyridine decorated CNT (p-pyCNT).

Through non-covalent pi-pi interaction with Co_DNCPY, three kinds of cobalt complexes, Co_DNCPY/CNT, Co_DNCPY/m-pyCNT and Co_DNCPY/p-pyCNT, could be obtained. As shown in Figure 2.4, it is found that due to the fifth ligand coordination from the p-pyCNT, Co_DNCPY/p-pyCNT exhibited increased current density and activity towards CO production than the other catalysts (for instance, when the applied voltage was at -0.75 V vs. RHE). The partial current density for CO production could reach 16.37 mA cm^{-1}, with a turnover frequency of 2.48 s^{-1}, and around 90% selectivity toward CO. The computational calculation is being processed to further support the results.

Dr ZHANG Tianran (Research Fellow, NUS) reports that fouling is a notable challenge for membrane applications in seawater treatment. He and his colleagues conjectured the use of an electrode-integrated membrane and programmable electrical stimulus to reduce the frequency of membrane replacement. The approach works well for forward osmosis but runs into new operating issues when it is extended to reverse osmosis – the original placement of the embedded electrode was found to increase the membrane internal concentration polarisation and reduce the membrane salt rejection performance and water flux. Dr Zhang designed a new device structure to overcome these issues (Figure 2.5). He used a porous titanium foil as the working electrode, which is placed at the back of membrane. A silver wire with a diameter of 0.25 mm is used as the counter electrode and is positioned above the membrane, while being separated from the latter with a polypropylene plastic spacer. The water flux through the membrane can then be unaffected. More importantly, with this design the salt

Fig. 2.4: (a) The LSV curves (b) faradaic efficiency of CO (c) partial current density of CO (d) turnover frequency of Co_DNCPY/CNT, Co_DNCPY/m-pyCNT and Co_DNCPY/p-pyCNT.

Dr SUN Libo



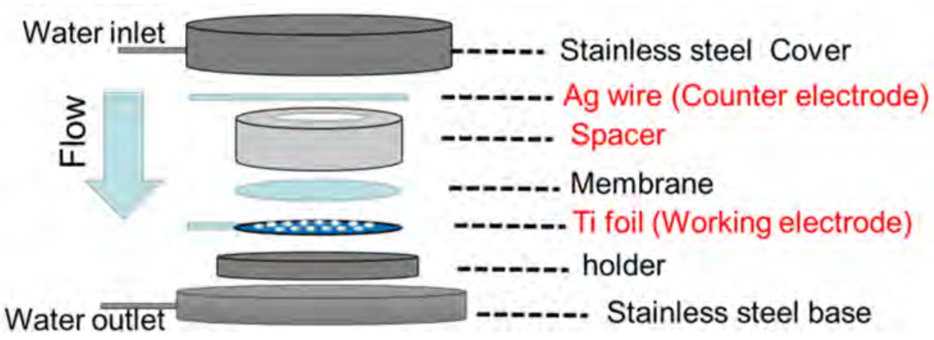


Fig. 2.5: The designed module for electrode-integrated membrane in Reverse Osmosis (RO) applications.

Dr ZHANG Tianran

rejection of the electrode-integrated membrane in reverse osmosis (RO) application is ~90% and comparable to a membrane without the electrode. With this design the electrode-integrated membrane for fouling reduction can be tested.

Vishvak KANNAN (PhD student, NUS) has been making progress in the sensitivity analysis of converting CO_2 to CO in a microfluidic cell (MFC) reactor. This MFC reactor is operated potentiostatically and is investigated at different operating cell potentials. Monte Carlo simulations (MCS) for the electrochemical reduction of CO_2 to CO was conducted based on a mechanistic mathematical model of the MFR.

Electrochemical conversion of CO_2 into useful chemicals in the MFC reactor depends not only on intrinsic electrochemical, physical and material parameters, but also on extrinsic operating conditions and cell design. Variations in these parameters significantly affect the overall performance of the MFC reactor. In this regard, to correlate the cell performance, conversion efficiency and selectivity of the MFC reactor with the variability of these input parameters, Vishvak carried out a Monte Carlo simulation (MCS) based on a mechanistic mathematical model for electrochemical conversion of CO_2 into CO in the MFC reactor. The MCS is conducted in two scenarios: first, by varying the stochastic parameters individually (IND), and second, by varying all the stochastic parameters simultaneously (SIM), at different cell potentials. These parameters are then ranked based on their contribution to the cell perfor-

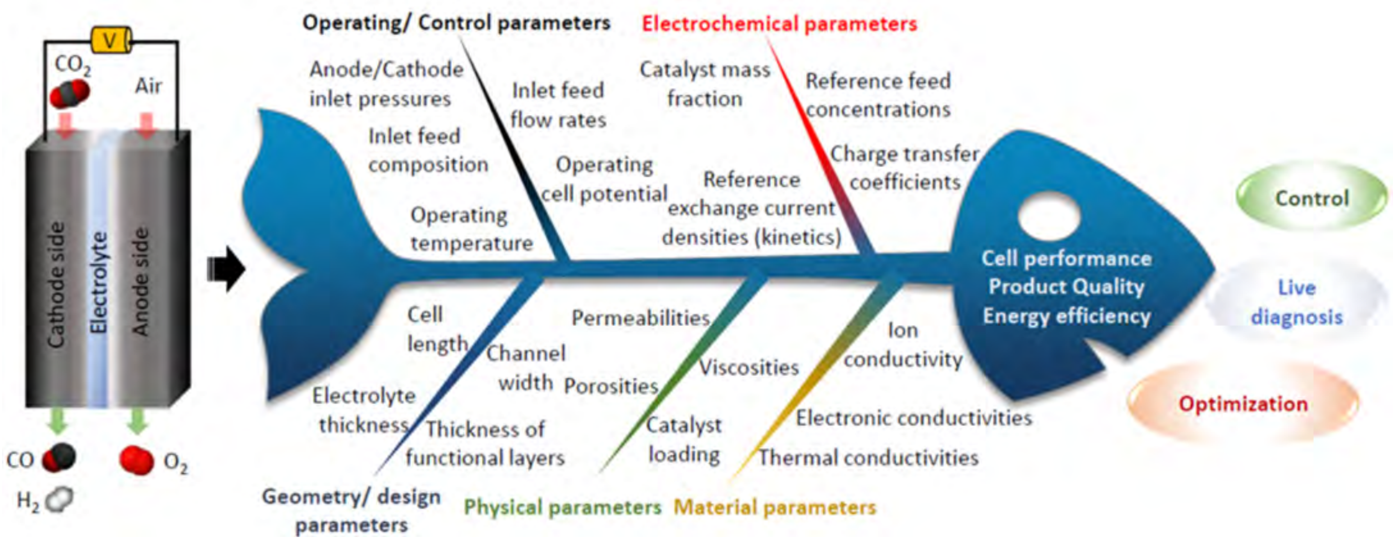


Fig. 2.6: A schematic of the MFC reactor for the electrochemical reduction of CO_2 and a cause-and-effect “fishbone” diagram illustrating the various stochastic input parameters and the response variables.

Vishvak KANNAN

mance, the conversion efficiency and the selectivity thereby, providing insights into optimum ranges of operation. The charge transfer coefficient towards CO and H_2 formation, catalyst properties, are the most sensitive parameters of the cell performance, conversion efficiency and selectivity, respectively, at all cell potentials. The thickness of the catalyst layer has a significant effect on the cell performance and conversion efficiency during the IND scenario but its relative effect during the SIM scenario is not significant at all the cell potentials. Furthermore, Vishvak derived reduced regression models based on supervised machine learning algorithms to predict the overall cell performance without having to solve the complete set of equations and also statistically discuss the distribution of overall cell performance at various cell potentials.

ZHANG Shengliang (PhD student, NUS) has been working on dual-band electrochromic smart windows with independent control of near-infrared (NIR) and visible (VIS) light transmittance. His most recent work was focused on addressing the anode issue in dual-band electrochromic devices (DBEDs). The common anode materials (e.g. NiO and polyaniline (PANI)) in conventional electrochromic devices without the dual-band control are not suitable for DBEDs because they are coloured when the dual-band electrochromic cathode operates in the NIR-selective modulation region. As a result, these anode materials will reduce the VIS light transmittance of the DBED operating in the cool mode (VIS transmitting and NIR-blocking). Shengliang considered the use of tin-doped indium oxide (ITO) nanocrystals (NCs) as a capacitive charge-balancing DBED anode for the following reasons: the ITO NCs are conductive, and VIS light transparent throughout the device operating voltage range. As a result, they would not interfere with the NIR -selective modulation of the DBED like most other anode materials. The high surface area and good electrical conductivity of the ITO NCs would facilitate rapid adsorption/desorption of anions and increase their effectiveness as a thin ion storage layer on the anode for cathode charge balancing. The optimised DBED prototype assembled from an ITO NC anode and a WO_{3-x} cathode was therefore able to deliver independent and efficient control of VIS light and NIR with high optical modulation, high coloration efficiency, fast switching speed, and good bistability and cyclability.

Update on work package 2.3

Micro-variable pressure and temperature electrosynthesis plant

Dr ZENG Minyu (Research Fellow, CAM) has designed a variable temperature/pressure flow rig which is currently under construction. This rig would act as the platform for the demonstration of clean and low carbon emission electrochemical synthesis processes. The rig will be able to withstand high temperature and high pressure with the capability to deal with multiphase reactions. It will be used as the platform to scale up various low carbon emission processes for chemical manufacturing which are currently under investigation in IRP2.

Scientific output

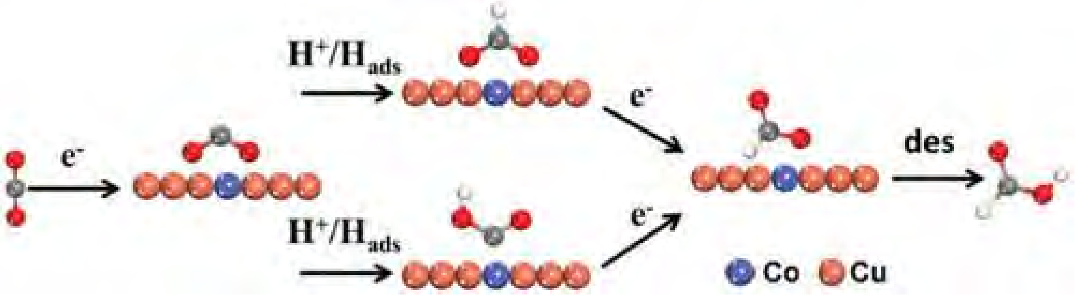
The following are the CREATE-acknowledged publications generated by IRP2 during the reporting period, excluding those already featured in the Scientific Highlights section on page 11.

Selective electroreduction of carbon dioxide to formic acid on cobalt-decorated copper thin films

Chencheng Dai, Libo Sun, Jiajia Song, Hanbin Liao, Adrian C. Fisher and Zhichuan J. Xu, *Small Methods*

DOI: 10.1002/smtd.201900362

Abstract: The development of highly efficient, selective, and economic approaches for electrochemical reduction of carbon dioxide to hydrocarbons is a promising way to promote the sustainable carbon cycle nowadays. Here, a stable cobalt-decorated copper catalyst is reported with significantly enhanced selectivity toward formic acid produced from CO_2 through electrochemical reduction. This catalyst is prepared through the electrodeposition of cobalt on the surface of copper, followed by Ar and air atmosphere treatment. The as-prepared catalyst exhibits selective conversion of CO_2 to formic acid with a Faradaic efficiency (FE) of ≈80% at an applied potential of −0.65 V versus reversible hydrogen electrode. Meanwhile, the copper electrode treated with the same conditions without cobalt decoration and the cobalt-decorated copper electrode without Ar treatment process only show an FE toward formic acid of ≈56% and ≈57% from CO_2 reduction, respectively. This study represents a facile decoration method to prepare highly selective electrocatalysts for the efficient reduction of CO_2 to value-added chemicals in aqueous electrolytes.

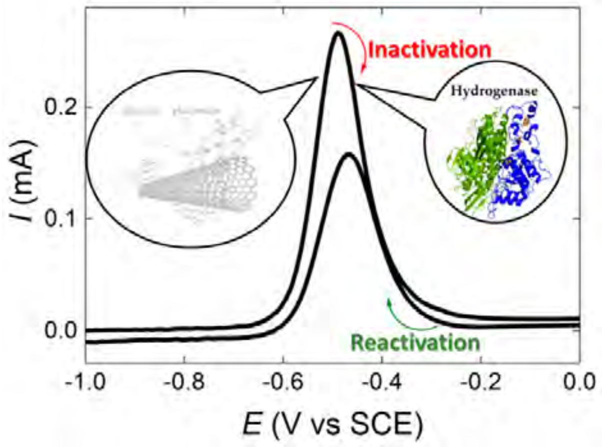


Hydrogenase-like electrocatalytic activation and inactivation mechanism by three-dimensional binderless molecular catalyst

Kamal Elouarzaki, Yian Wang, Vishvak Kannan, Haoxiang Xu, Daojian Cheng, Jong-Min Lee and Adrian C. Fisher, *ACS Applied Energy Materials*

DOI: 10.1021/acsaem.9b00203

Abstract: In response to issues raised by modern energy challenges, molecular electrocatalysis is currently attracting a lot of attention to the tailoring of “model” catalysts, notably understanding the mechanisms and kinetic and thermodynamic parameters that occur during a catalytic reaction. In this regard, nature offers extremely efficient enzymes called hydrogenases. These enzymes that catalyse the reversible interconversions between H_2 and H^+ at high turnover rates are inactivated by O_2. This inactivation yields odd cyclic voltammetric responses originating from a chemical inactivation–redox activation process (IAP). Although IAP has been extensively studied for hydrogenases, their catalytic mechanism is not fully understood because of the intricate but necessary electrical wiring, desorption, and complex biochemical environment required. Here, we report a unique example of IAP based on a nonenzymatic catalyst prepared by mixing rhodium-porphyrinic catalyst and an interconnected multiwalled carbon nanotubes matrix which presents an excellent and stable electron transfer. We com-



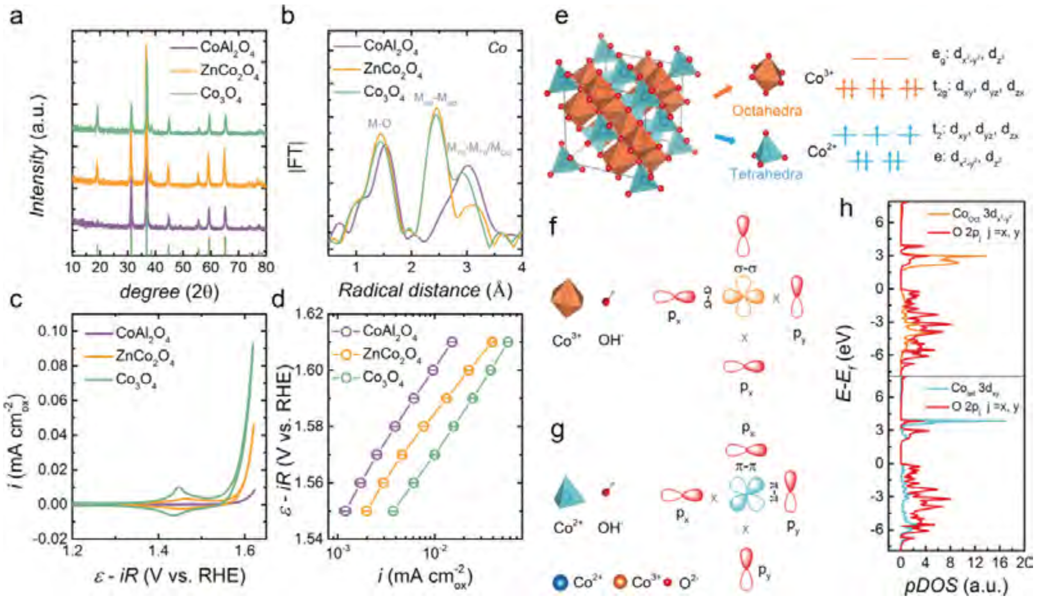
bined organic synthesis, electrochemistry, mathematical models, and density functional theory calculations to uncover the molecular IAP at the catalytic metallic site. We present a mechanistic analysis of the noncatalytic and catalytic responses exhibited by this complex, enabling a comprehensive understanding of the thermodynamic and kinetic parameters that govern the IAP. These stepwise studies support a mechanism for glucose oxidation that proceeds most likely through an EC'CE scheme with catalytic steps similar to the ones reported for NiFe hydrogenases. The overall mechanism of the molecular IAP was detailed on the basis of our experimentally validated models and compared to NiFe hydrogenase IAP. Our findings offer novel perspectives to design finely optimised catalysts by eliminating the inactivation phenomena.

Shifting oxygen charge towards octahedral metal: a way to promote water oxidation on cobalt spinel oxides

Shengnan Sun, Yuanmiao Sun, Ye Zhou, Shibo Xi, Xiao Ren, Bicheng Huang, Hanbin Liao, Luyuan Paul Wang, Yonghua Du and Zhichuan J. Xu, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.201902114

Abstract: Cobalt spinel oxides are a class of promising transition metal (TM) oxides for catalysing oxygen evolution reaction (OER). Their catalytic activity depends on the electronic structure. In a spinel oxide lattice, each oxygen anion is shared amongst its four nearest transition metal cations, of which one is located within the tetrahedral interstices and the remaining three cations are in the octahedral interstices. This work uncovered the influence of oxygen anion charge distribution on the electronic structure of the redox-active building block Co–O. The charge of oxygen anion tends to shift toward the octahedral-occupied Co instead of tetrahedral-occupied Co, which hence produces strong orbital interaction between octahedral Co and O. Thus, the OER activity can be promoted by pushing more Co into the octahedral site or shifting the oxygen charge towards the redox-active metal centre in CoO_6 octahedra.

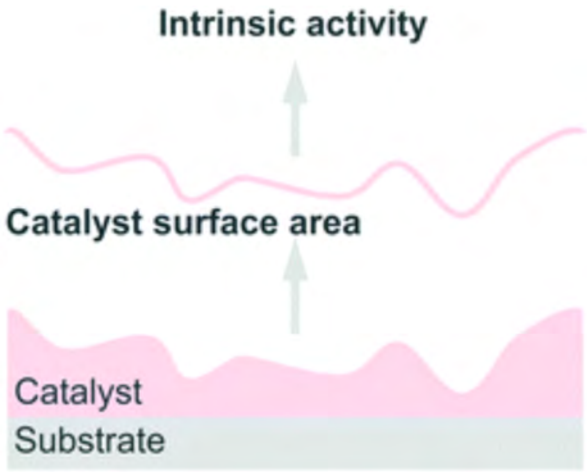


Approaches for measuring the surface areas of metal oxide electrocatalysts for determining their intrinsic electrocatalytic activity

Chao Wei, Shengnan Sun, Daniel Mandler, Xun Wang, Shi Zhang Qiao and Zhichuan J. Xu, *Chemical Society Reviews*

DOI: 10.1039/C8CS00848E

Abstract: Great attention has been recently drawn to metal oxide electrocatalysts for electrocatalysis -based energy storage and conversion devices. To find the optimal electrocatalyst, a prerequisite is an activity metric that reasonably evaluates the intrinsic electrocatalytic activity of a particular catalyst. The intrinsic activity is commonly defined as the specific activity which is the current per unit catalyst surface area. Thus, the precise assessment of intrinsic activity highly depends on the reliable measurement of catalyst surface area, which calls for the knowledge of experimental approaches for determining the surface areas of metal oxide electrocatalysts. This tutorial review aims to summarise and analyse the approaches for measuring the surface areas of metal oxide electrocatalysts for evaluating and comparing their intrinsic electrocatalytic activities. We start by comparing the popular metrics for activity estimation and highlighting the importance of surface-area-normalised activity (i.e. specific activity) for intrinsic chemistry analysis. Second, we provide some general guidelines for experimentally measuring the electrochemically active surface area (ECSA). Third, we review the methods for the surface area measurement of metal oxide electrocatalysts. The detailed procedure for each method is explicitly described to provide a step-by-step manual that guides researchers to perform the measurement; the rationales and uncertainties for each method are discussed to help readers justify the reliable assessment of surface area. Next, we give our recommendations on selecting a rational experimental approach for the surface area measurement of a particular metal oxide electrocatalyst. Lastly, we discuss the future challenges of ECSA measurement and present an exemplary novel ECSA technique.



Overcoming the technical challenges in Al anode–based electrochromic energy storage windows

Shengliang Zhang, Sheng Cao, Tianran Zhang, Qiaofeng Yao, Haibin Lin, Adrian C. Fisher and Jim Yang Lee, *Small Methods*

DOI: 10.1002/smtd.201900545

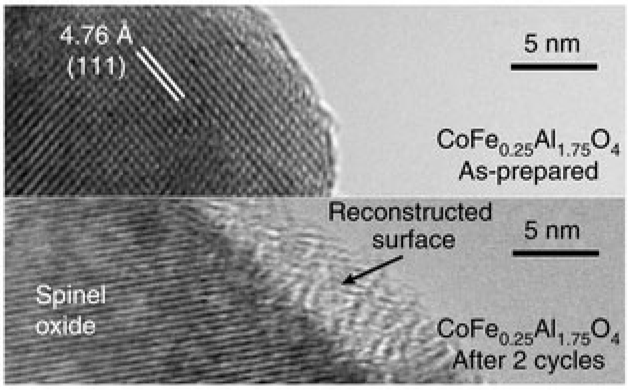
Abstract: A new variant of electrochromic energy storage (EES) windows is introduced recently by pairing an electrochromic cathode with an Al anode. Electrochromism in this case is driven by the built-in potential difference and chemical recharging (via oxidation by O_2 or H_2O_2) without the need for an external power source. However, the Al anode–based EES windows are adversely affected by the irreversibility of the Al anode reaction, the inconvenience of chemical recharging, and a short cycle life. An electrically rechargeable alternative based on a prelithiated Al anode and a WO_{3-x} cathode is presented here, which not only overcomes the operational difficulties of Al anode–based EES windows, but also allows for spectrally selective modulation of visible light and near-infrared and efficient energy recycling. This dual-band electrochromic energy storage (DEES) window upon assembly is able to self-colourise by its high built-in cell voltage (≈2.59 V) without any energy input, and to recycle a large fraction of the energy consumed in the bleaching operation. The DEES window, with its impressive dual-band electrochromic performance and low energy consumption in a round-trip electrochromic operation, can be an energy-saving technology for buildings.

Iron-facilitated dynamic active-site generation on spinel $CoAl_2O_4$ with self-termination of surface reconstruction for water oxidation

Tianze Wu, Shengnan Sun, Jiajia Song, Shibo Xi, Yong hua Du, Bo Chen, Wardhana Aji Sasangka, Hanbin Liao, Chee Lip Gan, Günther G. Scherer, Lin Zeng, Haijiang Wang, Hui Li, Alexis Grimaud and Zhichuan J. Xu , *Nature Catalysis*

DOI: 10.1038/s41929-019-0325-4

Abstract: The development of efficient and low-cost electrocatalysts for the oxygen evolution reaction (OER) is critical for improving the efficiency of water electrolysis. Here, we report a strategy using Fe substitution to enable the inactive spinel $CoAl_2O_4$ to become highly active and superior to the benchmark IrO_2. The Fe substitution is revealed to facilitate surface reconstruction into active Co oxyhydroxides under OER conditions. It also activates deprotonation on the reconstructed oxyhydroxide to induce negatively charged oxygen as an active site, thus significantly enhancing the OER activity of $CoAl_2O_4$. Furthermore, it promotes the pre-oxidation of Co and introduces great structural flexibility due to the uplift of the oxygen 2*p* levels. This results in the accumulation of surface oxygen vacancies along with lattice oxygen oxidation that terminates as Al^{3+} leaches, preventing further reconstruction. We showcase a promising way to achieve tunable electrochemical reconstruction by optimising the electronic structure for low-cost and robust spinel oxide OER catalysts.

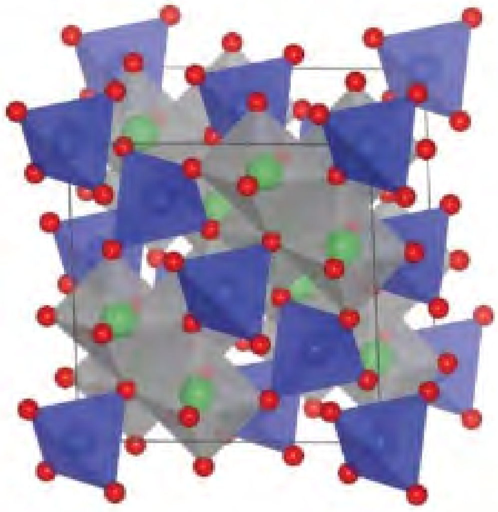


Significance of engineering the octahedral units to promote the oxygen evolution reaction of spinel oxides

Ye Zhou, Shengnan Sun, Chao Wei, Yuanmiao Sun, Pinxian Xi, Zhenxing Feng and Zhichuan J. Xu, *Advanced Materials*

DOI: 10.1002/adma.201902509

Abstract: The clean energy carrier, hydrogen, if efficiently produced by water electrolysis using renewable energy input, would revolutionise the energy landscape. It is the sluggish oxygen evolution reaction (OER) at the anode of water electrolyser that limits the overall efficiency. The large spinel oxide family is widely studied due to their low cost and promising OER activity. As the distribution of transition metal (TM) cations in octahedral and tetrahedral site is an important variable controlling the electronic structure of spinel oxides, the TM geometric effect on OER is discussed. The dominant role of octahedral sites is found experimentally and explained by computational studies. The redox-active TM locating at octahedral site guarantees an effective interaction with the oxygen at OER conditions. In addition, the adjacent octahedral centers in spinel act cooperatively in promoting the fast OER kinetics. In remarkable contrast, the isolated tetrahedral TM centers in spinel prohibit the OER mediated by dual-metal sites. Furthermore, various spinel oxides preferentially expose octahedral-occupied cations on the surface, making the octahedral cations easily accessible to the reactants. The future perspectives and challenges in advancing fundamental understanding and developing robust spinel catalysts are discussed.



Other activities and achievements

PhD student THAM Guo Xiong presented a poster with the title 'Carbon nanotube based electropolymerised conducting polymer films in potential applications of electrochemical energy storage' at the *Chemistry National Meeting Singapore (ChNMSG) 2019* in May.

PhD student Vishvak KANNAN gave the presentation 'Sensitivity analysis based on Monte Carlo simulations of a 1D accelerated mechanistic model of a proton exchange membrane fuel cell' at *The Electrochemical Society 235th ECS Meeting* in Dallas, Texas, US. The research is now in *Meeting Abstracts* no. 22 (authors: Kannan, V., Fisher, A. C. and Birgersson, E. K).

Research Fellow Dr ZENG Minyu was featured on BBC explaining the fundamentals of the fuel cell for the 50th anniversary series on Apollo 11.

Dr Zeng on BBC Breakfast in July.

The dye laser being operated by researchers from IRP3.

COMBUSTION FOR CLEANER FUELS AND BETTER CATALYSTS

To formulate the fuel of the future, IRP3 looks at new molecules that can be produced within the techno-economic constraints of a refinery and that have the potential to reduce pollutant emissions when added to fossil-derived fuels. This research will help to identify the best fuels (or fuel mixtures) for low-emission energy conversion, and to design and manufacture optimised cost-effective nanostructured materials for catalysis.

IRP3 Principal Investigators:


Professor Markus KRAFT
University of Cambridge


Professor XU Rong
Nanyang Technological University


Assoc Professor YANG Wenming
National University of Singapore

OVERVIEW

In this reporting period, the long-standing mystery of how the first soot particles are formed from the gas phase in a hydrocarbon combustion process has continued to attract much of our attention, both from an experimental and a computational point of view. In the lab, we have been studying the nanostructure of soot in flames of mixtures of n-heptane, cyclohexene, and cyclopentene. We have found that, confirming our expectation, the presence of cyclopentene in n-heptane flames increases the amount of curvature in the resulting soot particles, due to increased incorporation of 5-membered rings into Polycyclic Aromatic Hydrocarbons (PAHs) – the main constituent molecules of soot. Further, curvature in soot precursor molecules appears to increase the rate of nucleation. These findings represent an intriguing follow-up to our recent modelling studies of curved PAHs and their electric dipoles, which cause much stronger interactions than those between neutral, flat PAHs, and thus are promising candidates for explaining the soot inception process. Another mechanism potentially contributing a piece to the puzzle is the role of cross-linked, i.e. covalently bonded, PAHs. Our computations indicate that some of the bonds involved are of sufficient strength to withstand thermal breakdown in flames.

On the inorganic side, we have been continuing our efforts in investigating functional nanostructured materials, mainly flame-synthesised titanium dioxide (TiO_2) nanoparticles, again both experimentally and computationally. A new premixed stagnation flame burner system has been completed, including software for its operation and control, and is now in the process of being commissioned and tested. In addition, new laser-based diagnostic capabilities for combustion experiments are under development, namely an *in situ* Raman probe designed specifically to study the initial stages of particle formation. Alongside this experimental work, we have been developing for some time a hybrid particle-number/detailed particle model, which has now reached a level of maturity so that we have been able to apply it successfully to the high-rate conditions found in an industrial titania reactor.

Professor Markus Kraft, PI
University of Cambridge

Update on work package 3.1

Refinery, fuel and engine of the future — experimental

Properties of surrogate fuels, marine engine after-treatment

Dr Maurin SALAMANCA's (Research Fellow, CAM) main research interest lies in the study of the soot formation process and the effect of biofuels on reducing pollutant formation. She has carried out a series of experiments to study the correlation between the fuel structure of unsaturated fuel and the soot nanostructure.

In this case, the soot nanostructure was studied using high-resolution transmission electron microscopy (HRTEM). The samples were collected in an *n*-heptane laminar co-flow diffusion flame doped with cyclohexene (CHE) and cyclopentene (CPE). Figure 3.1 shows HRTEM images; an onion-like structure is recognisable in all the particles. An amorphous core and a shell composed by graphitic-like domains are also present – the graphitic-like domains are formed by the graphitisation or annealing of the particles at high temperature. The image analysis results allow calculation of parameters such as fringe length, fringe tortuosity and inter-fringe spacing. It was observed that most of the fringes present a low degree of curvature. Nevertheless, the addition of cyclopentene to *n*-heptane flames increases the amount of highly curved fringes. The modelling work developed by Jacob MARTIN (PhD student, CAM) suggested that highly curved fringes are predominantly due to 5-membered ring incorporation into the polycyclic aromatic hydrocarbons contained in the soot nanoparticles. This work is currently being prepared for publication.

In the last few months, Dr Salamanca has also carried out experiments to validate the degradation mechanism of fuel droplets leaking out of the injector nozzle in a direct injection combustion engine. The mechanism has been proposed by Dr Radomir SLAVCHOV, Dr Sebastian MOSBACH (Senior Research Fellow, CAM) and collaborators. The experimental tests allow study of the oxidative degradation of isooctane, as a gasoline surrogate, under conditions that are relevant to the walls of the engine cylinder and the crankcase, namely high temperature and pressure, and the presence of O_2, NO_2 and NO. The results show that no fuel degradation is observed in the absence of NO_x. NO also appears to be able to initiate a radical chain mechanism by producing NO_2. The existence of radical chain reactions was supported by the antioxidative action of a radical scavenger. This work is being prepared for publication.

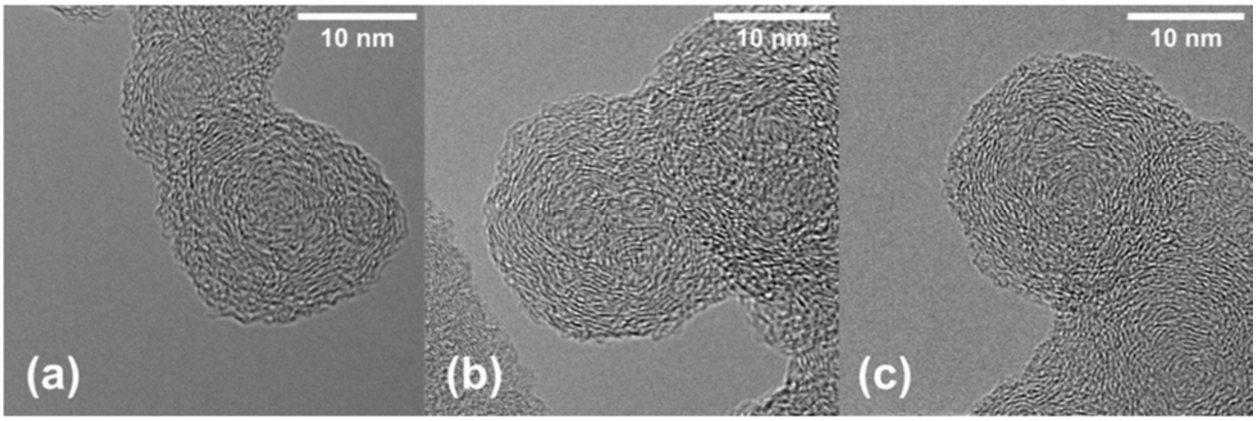


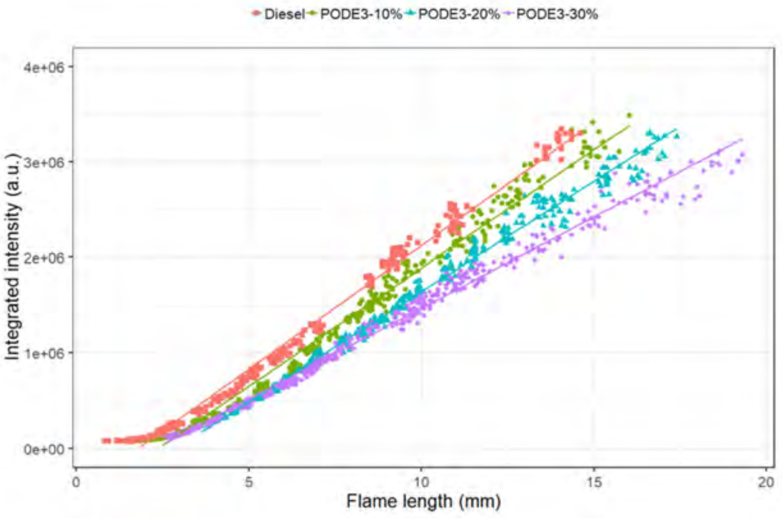
Fig 3.1: High-Resolution Transmission Electron Microscopy (HRTEM) images for samples collected in (a) n-*heptane, (b)* n-*heptane/cyclohexene, (c)* n-*heptane/cyclopentene co-flow diffusion flames at a height above the burner of 32 mm.*

Dr Maurin SALAMANCA

Dr ZONG Yichen (Research Fellow, NUS) has been working on the development and experimental testing of clean diesel mixtures in both flame and engine environments. Jet A-1, PODE3 and PODE4 have proven to be promising alternative fuel additives through the tests, which will significantly reduce the particulate emissions from combustion. With the combined use of the Differential Mobility Sizer particle analyser and laser-based diagnostics techniques, the formation and growth of soot has been systematically studied. The results reveal that the oxygenated fuel additives function at the early stage of the combustion process and nucleation mode particles are mostly affected by the additives. One experimental report is currently under review in the journal *Fuel* and another report is in preparation.

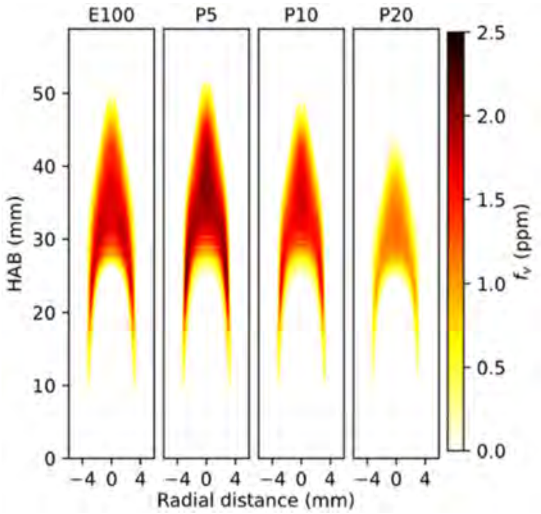
Fig 3.2: Laser-Induced Incandescence (LII) measurements of soot growth in PODE-diesel mixtures.

Dr ZONG Yichen



TAN Yong Ren (PhD student, CAM) is currently studying the effect of PODE (polyoxymethylene dimethyl ethers) biofuel on the soot formation in fuels. PODE is an interesting biofuel to study as it can be synthesised from carbon capture methods, ready to be used in existing diesel engines with minimal modification. It has also been shown to have soot reduction properties. Its molecular structure lacks carbon-carbon bonds, a feature which has been proposed as the key to its soot reduction properties during combustion. Yong Ren is now doping an ethylene flame with PODE at 5% (P5), 10% (P10) and 20% (P20) under a laminar co-flow non-premixed setup to understand how PODE affects the soot formation process in a non-premixed system. Colour ratio pyrometry has been used to determine the soot volume fraction, f-$_\text{v}$ (ppm) through the addition of PODE. From Figure 3.3, it can be seen that in comparison to a pure ethylene flame (E100), with addition of 5% PODE, the soot volume fraction spikes up due to the increase in soot-inducing radicals and insufficient oxidation-favouring radicals to offset it. However, upon increase in PODE further to 20%, the soot volume fraction significantly decreases as the amount of radicals favouring oxidation increases significantly with the addition of more PODE. The next step will be measuring the particle size distribution in the considered flames using a Cambustion DMS500 to understand the soot formation process further for each of the flames.

Fig 3.3: The soot volume fraction (f_v) for the co-flow diffusion PODE/ethylene flames. E100 (Un-doped ethylene flame), P5 (5% PODE-doped ethylene flame), P10 (10% PODE-doped ethylene flame), P20 (20% PODE-doped ethylene flame).



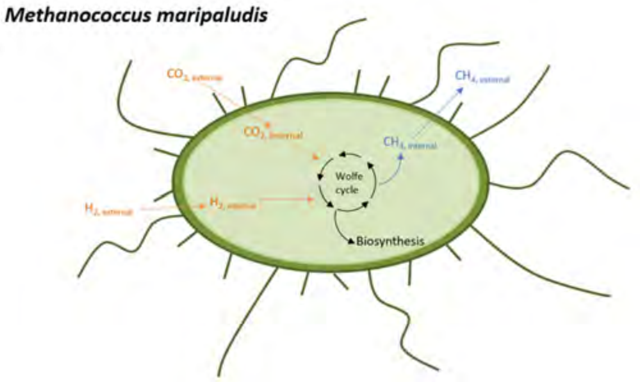


Fig 3.4: Culture of M. maripaludis S2 grows to a high population using CO_2 as the only carbon source.

Clifford VO Chi Hung

Clifford VO Chi Hung (PhD student, NUS) is researching *Methanococcus maripaludis* S2, an archaeon which can convert CO_2 into CH_4 and is therefore an interesting microorganism for application in biological carbon capture and utilisation. His main interest is to examine the metabolic processes behind this microorganism. In the past six months, he has completed a project to unravel the interactions of *M. maripaludis* with N_2, a major component of flue gases. In addition, he analysed the metabolites produced by this microorganism. Two publications are in progress.

Update on work package 3.2

Refinery, fuel and engine of the future — modelling

Chemical mechanisms, PAH chemistry, after-treatment

Jacob MARTIN (PhD student, CAM) has been continuing to explore the formation of the pollutant soot in flames as well as the nanostructure of carbon materials. Experiments have now demonstrated that curvature can be integrated into soot precursor molecules and this increases the rate of nucleation in diffusion flames. Jacob and colleagues are now developing the ability to increase the ionic concentration in flames using a plasma injector and are planning experiments that will be able to determine the influence of ionic species on nucleation. One interesting aspect of the research on the flexoelectric effect in carbon materials is its impact on CO_2 storage. A local secondary school student, Steven Brook, spent a week in the lab under Jacob's supervision. Steven performed calculations of CO_2 bound to carbon bowls and found binding sites arranged near bent carbon structures that could aid in developing new carbon materials for carbon capture.

Working with Dr Laura PASCAZIO in Cambridge, Jacob has published the work on determining the degree of crosslinking in soot particles using cube simulations of crosslinked aromatic molecules' mechanical properties. This work has been extended to nanoparticles that allow direct comparison between experimental nanoindentation data, allowing for the degree of crosslinking to be more accurately computed.

Jacob is assembling a review of soot nanoparticle formation. The review highlights a large number of reactive aromatic molecules that have previously been proposed as a part of soot inception, however, they had not been compared. The recently purchased computer cluster was used to do a systematic comparison of reactive aromatic molecules with many hundreds of calculations performed. Using electronic structure theory Jacob was able to locate reactive sites and classify them into a reactivity series (see Figure 3.5).

Potential crosslinking reactions' bond strengths were then computed and compared with the flame's thermal energy want to fragment the structures. σ-radicals were found to form crosslinks that can withstand thermal breakdown with all aromatic molecules except for high-symmetry polycyclic aromatic hydrocarbons. A partially saturated rim based pentagonal ring was found to form a localised π-radical with significant reactivity. These sites have recently been directly imaged using non-contact atomic force microscopy. Jacob found that these π-radicals could allow for covalent bonding as well as stacked geometries to be formed (see Figure 3.6).

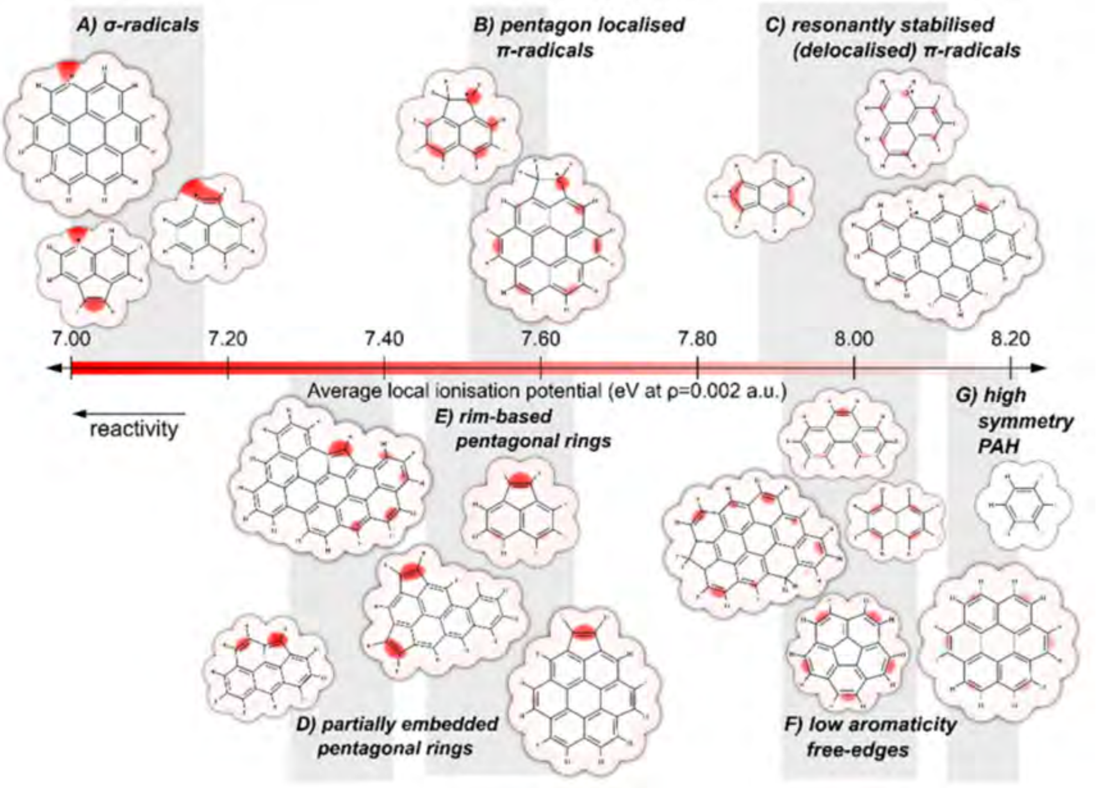


Fig 3.5: Reactive aromatic soot precursors grouped by reactivity using the average local ionisation potential.

Previous mechanisms for soot formation had considered crosslinked and stacked pathways to be mutually exclusive. These complexes show the potential for covalent bonds to stabilise a physical nucleation soot mechanism. Jacob is currently exploring the reaction mechanisms forming these species and the enhancement due to the van der Waals interactions. This will allow consideration of the possibility that these reactive aromatic soot precursors contribute to soot formation. Jacob is also exploring combining flexoelectric species with these reactive radicals to consider synergetic effects.

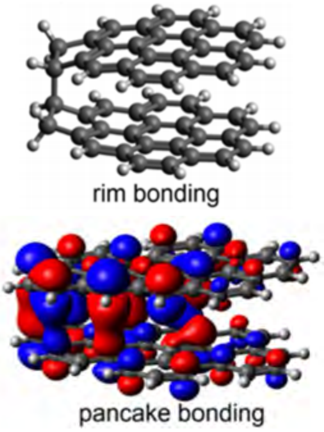


Fig 3.6: Stacked and covalently bonded complexes found to be possible between reactive aromatic soot precursors.

The ongoing work on the topology of disordered 3D graphenes has now been published in *Physical Review Letters*. Jacob had the opportunity to employ 3D printing to explore the nanostructure of the disordered 3D graphenes using a fused deposition modelling 3D printer (see Figure 3.7).

Fig 3.7: 3D printed models of disordered 3D graphenes.

Jacob MARTIN >

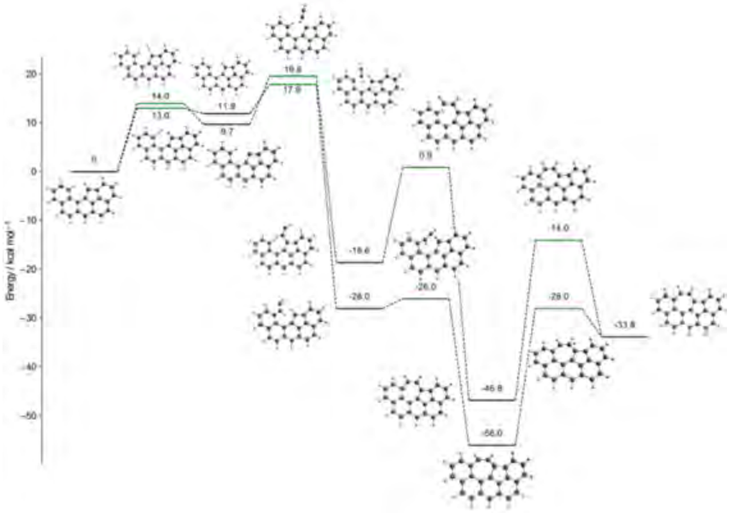


Fig. 3.8: Potential Energy surface computed by ab initio *methods for the formation of a 7-membered ring by the hydrogen-abstraction-acetylene-addition mechanism on a sample polycyclic aromatic hydrocarbon at 0 K.*

Angiras MENON's (PhD student, CAM) work focuses on using state-of-the-art-quantum chemical methods to understand the properties of polycyclic aromatic hydrocarbons (PAHs) and their role in forming soot in flames. Calculations have been completed on the optical band gap of a variety of PAHs, including curved, cross-linked and radical PAHs. From this work, it can be seen that optical measurements typically attributed to moderately sized flat PAHs can also be explained by larger curved PAHs or smaller resonance-stabilised-radical PAHs. Ongoing work has focused on how heptagonal (7-membered) rings can be integrated into graphenic PAH structures and is being completed with Gustavo LEON (PhD student, CAM). This work arose from another project completed by Jacob MARTIN (PhD student, CAM), who showed that three-dimensional contiguous graphenes could only form when they have net negative curvature. This suggests that several heptagons must be able to integrate into a graphenic structure, but current graphene and PAH chemistry lacks kinetic information on how such 7-membered rings could form. This project has shown that existing mechanisms in soot and PAH chemistry, such as hydrogen-abstraction-acetylene-addition may also be able to explain how 7-membered rings could form in flame conditions. Kinetic simulations have suggested that high temperature is likely the key to this formation. Finally, other work with Jacob has focused on the reactivity of resonance-stabilised as well as localised π-radical PAHs. An initial study has shown that localised pentagonal-radicals are particularly radical and may be important for soot formation in flames. Further work is underway on computing the kinetics of reactions involving their π-radicals as well as their equilibrium concentration in flames.

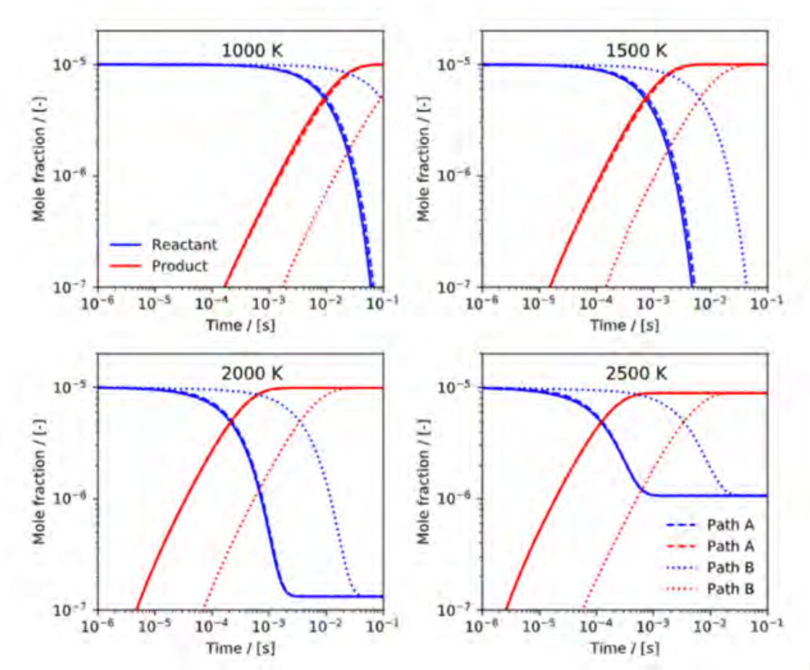


Fig. 3.9: Kinetic simulations of 7-membered ring formation in a batch reactor at different temperatures and conditions relevant to combustion. The reactant and product correspond to the first and last species in Figure 3.8 and the simulations use rates derived from the potential energy surface in Figure 3.8. This figure was produced in tandem with Gustavo LEON.

Angiras MENON

Update on work package 3.3

Better, cheaper, cleaner nanostructures — experimental

Flame synthesis of thin films of mixed metal oxide nanoparticles

Dr SHENG Yuan (Research Fellow, NTU) completed a new premixed stagnation flame burner system with Manoel MANUPUTTY (PhD student, CAM). Dr Sheng built the electronic control box, the gas manifold and the precursor delivery mechanism which he designed during the previous reporting period. He developed a computer program to automate the gas flow and temperature control of the burner system. The in-house system has been tested and is functioning as expected, with higher flame stability and better precursor versatility compared with the existing system acquired in Phase 1. To allow for further expansion of flame synthesis capability, Dr Sheng has also designed a fully digital control system that allows easy integration of future multi-burner set-ups. Major components for these set-ups have been procured.

WU Shuyang's (PhD student, NTU) main research interest lies in the area of flame synthesised metal oxides for energy and environmental applications. His recent research has mainly focused on the visible-light-driven photocatalytic H_2 production and CO_2 reduction using vapour-fed flame-synthesised blue TiO_2. He reports a one -step flame synthesis method for the preparation

Fig. 3.10: The new premixed stagnation flame burner system being tested.

Dr SHENG Yuan

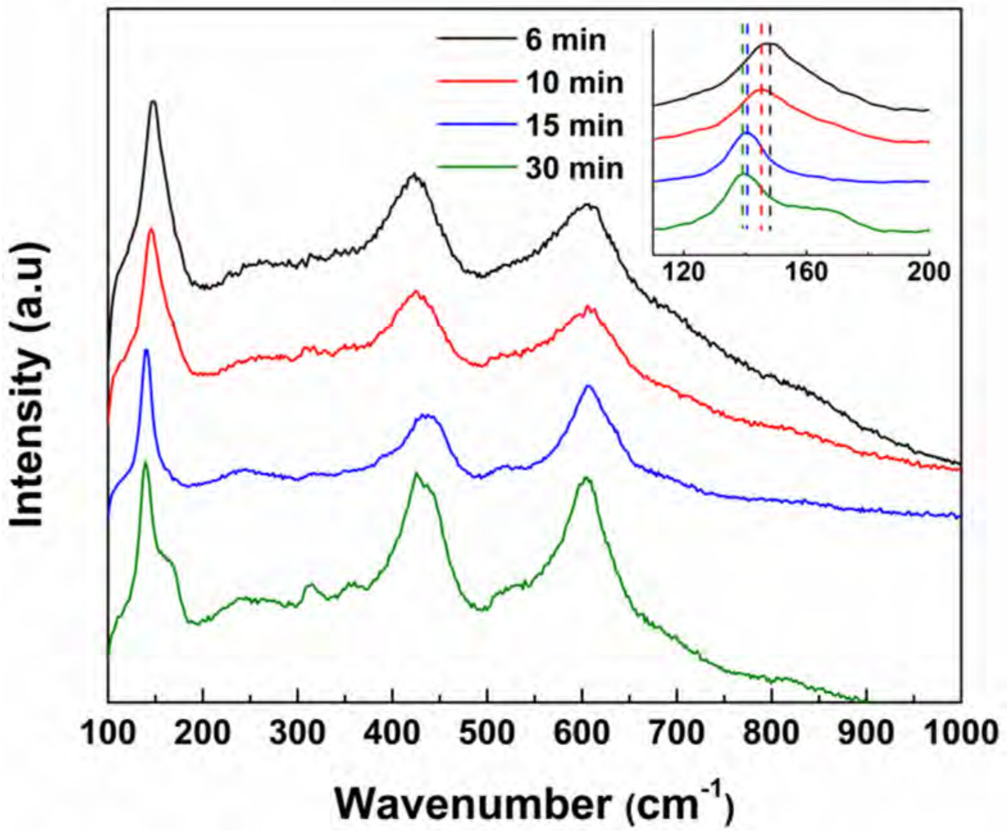


Fig. 3.11: Raman spectra of flame-made TiO_2*.*

WU Shuyang

of defective blue TiO_2 with a crystalline core and amorphous shell structure and tuned the quantity of defects directly by controlling the deposition time. The blue TiO_2 possesses uniform small sizes with an average diameter of ca. 12 nm and relatively high specific surface area of 100-120 m^2g^{-1}. High photocatalytic activity of H_2 generation and CO_2 reduction have been achieved on the blue TiO_2 under visible irradiation. Shuyang found that an appropriate amount of Ti^{3+} and oxygen vacancies (Vo) can greatly improve the charge separation efficiency and thus enhance the photocatalytic activity of H_2 production. He also conducted *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) revealing that the defective surface of blue TiO_2 can effectively stimulate the chemical activation of stable CO_2 molecules through the one-electron photoreduction process, leading to the formation of the key intermediate species which drastically enhances the photocatalytic activity of CO_2 reduction. Shuyang has published a paper in *ACS Sustainable Chemistry & Engineering* studying the photocatalytic effect of flame synthesised TiO_2 with different equivalence ratios.

The disordered structure of flame-made TiO_2 can be further verified by Raman spectra. Upon removal of an O atom the three nearest-neighbour Ti atoms tend to relax away from the vacancy in order to strengthen their bonding with the rest of the lattice. This outward relaxation decreases the overlap between the three Ti dangling bonds, shifting the a1 state to a higher energy. However, if the a1 state is occupied, this upward shift incurs a cost in electronic energy. Therefore, the tendency of the Ti atoms to relax away from the vacancy is counterbalanced by the gain in electronic energy as the Ti atoms are kept closer to their nominal positions in the lattice.

Update on work package 3.4

Better, cheaper, cleaner nanostructures — modelling

Gas- and surface-phase kinetics, molecular modelling and reactor optimisation

Astrid BOJE (PhD student, CAM) is working on modelling synthesis of particulate titanium dioxide (titania) using detailed population balance models. Numerical studies of this process are complicated by the rapid particle formation and growth processes that occur under industrial conditions. Earlier this year, Astrid proposed a hybrid particle-number and detailed particle model to allow more robust and efficient simulations. This new simulation framework provides better resolution of the particle size distributions under high-rate conditions. Astrid recently applied this framework to study industrial synthesis of titanium dioxide, highlighting sensitivity of the process to different design choices such as reactor configuration and dosing strategy. The latest results can be directly compared to plant output using simulated images and SEM images of real product particles. This demonstrates the potential utility of the model to study process operation and inform understanding of how particle properties develop under relevant conditions. The manuscript presenting these results will be submitted for publication soon. Astrid is also currently writing her PhD thesis, which she will submit later this year.

Casper LINDBERG (PhD student, CAM) collaborated with PhD student Manoel MANUPUTTY on his recent work “Understanding the anatase-rutile stability in flame-made TiO_2”. Casper published two papers on a new detailed particle model for titanium dioxide nanoparticles and applied the model to investigate the synthesis of TiO_2 nano-aggregates in a stagnation flame. In collaboration with Manoel, the detailed particle model was extended to describe the formation of the anatase and rutile crystal phases in flame-made titanium dioxide particles. Casper is now writing up his PhD thesis.

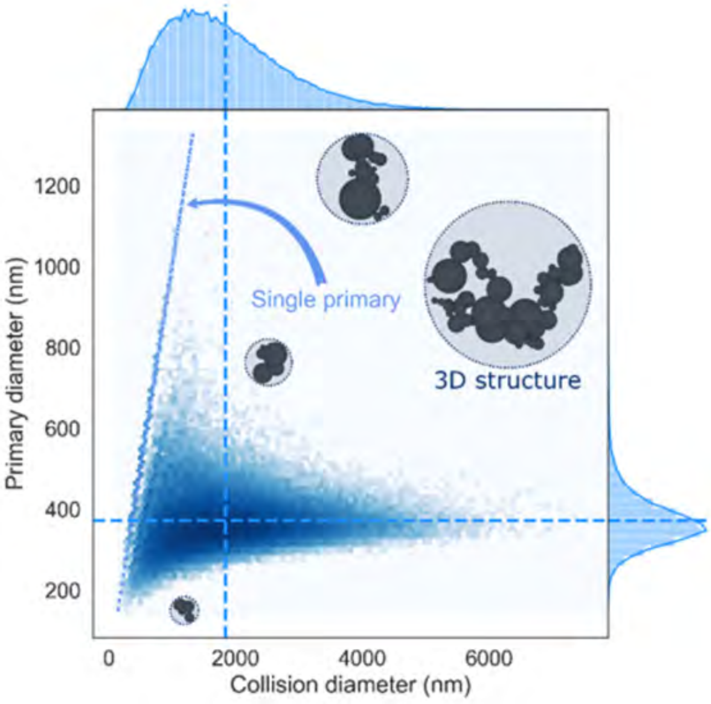


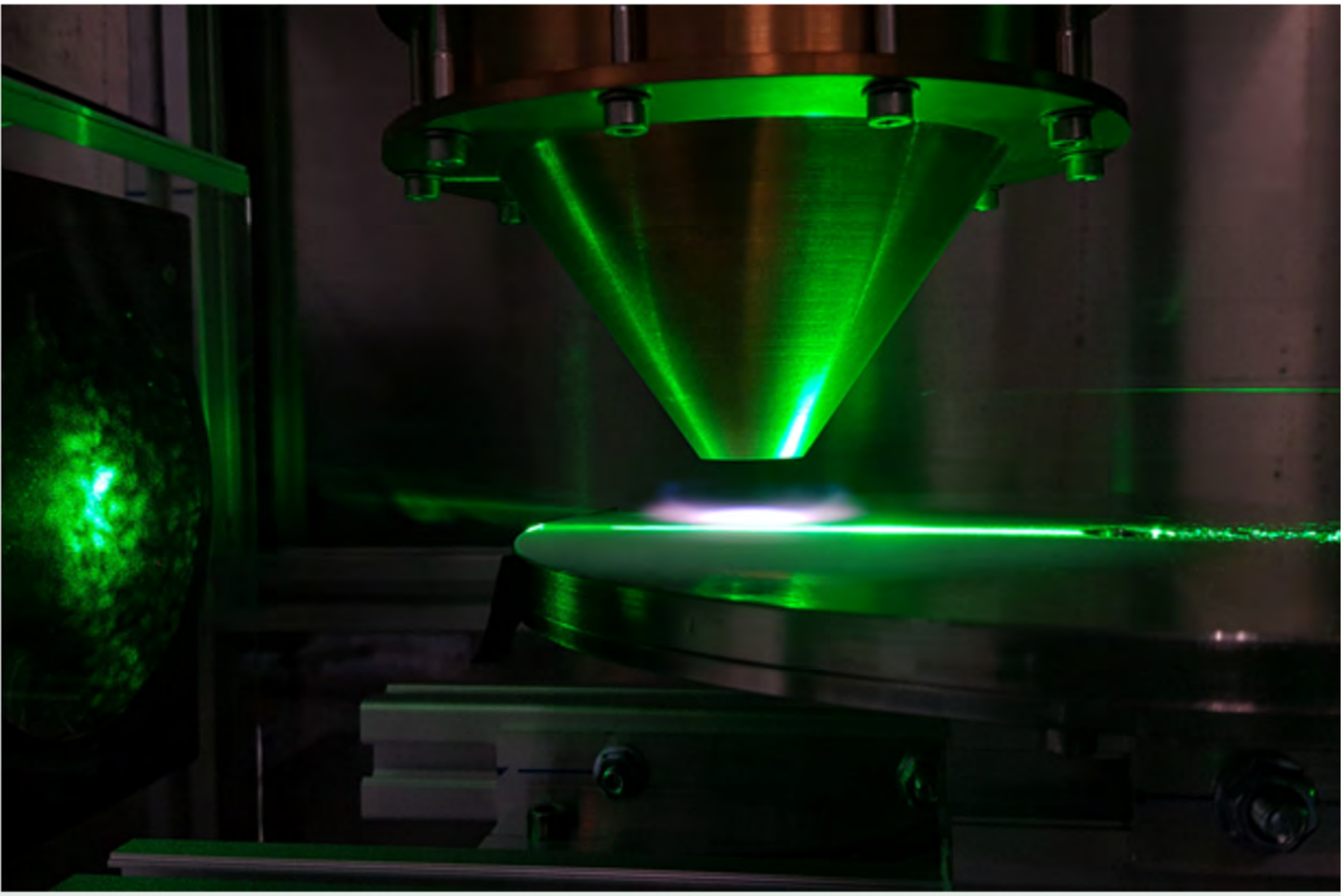
Fig. 3.12: Joint and marginal distributions for primary particle diameter and aggregate collision diameter from a simulation of an industrial titania reactor (Gaussian kernel density estimates for marginal distributions have a bandwidth of 0.01). Inset images show 3D particle structure generated by tracking of primary particle coordinates (using the detailed particle model proposed by Casper Lindberg (2019)).

Astrid BOJE

Manoel MANUPUTTY (PhD student, CAM) has just completed a project aiming at understanding how different crystal structures of TiO_2 nanoparticles are formed in flame synthesis (in collaboration with PhD student Casper LINDBERG). The study was based on new experimental measurements of the crystal phase composition of TiO_2 prepared in premixed stagnation flames with varying flame dilution ratio. The particle formation was modelled with a detailed particle model to test different hypotheses of crystal phase formation. It was found that the conventional hypothesis of crystal phase thermodynamic stability based on surface energies alone does not sufficiently explain the experimental observations. It was proposed that the incipient particle composition is the key factor controlling the crystal phase formation in a flame synthesis condition. A manuscript based on this work has just been submitted for publication in *Journal of Aerosol Science*. Manoel has also finished and submitted his PhD thesis. In the meantime, he is now working on developing laser-based diagnostics for combustion experiments including an *in situ* Raman probe designed to study the initial stages of particle formation (shown in Figure 3.13) together with Dr Yichen ZONG.

Fig. 3.13: A prototype of an in situ *Raman system developed for online diagnostics of particles in combustion experiments. On the left is the Raman optical probe operating with a 532 nm (green) continuous wave laser. In the centre is a premixed stagnation flame (a newly commissioned CARES burner) doped with titanium dioxide (TiO_2) precursor.*

Manoel MANUPUTTY



Scientific output

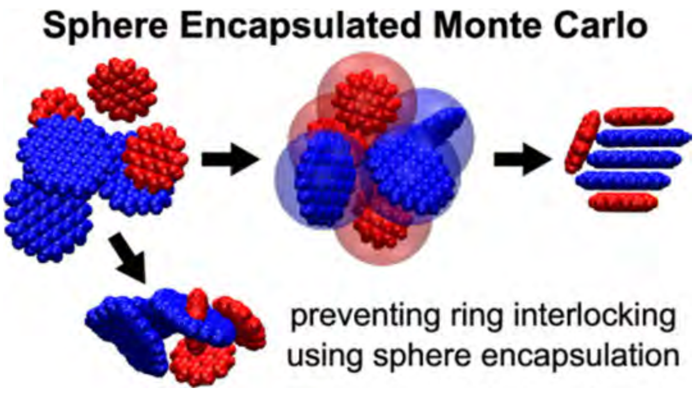
The following are the CREATE-acknowledged publications generated by IRP3 during the reporting period, excluding those already featured in the Scientific Highlights section on page 11.

Sphere encapsulated Monte Carlo: obtaining minimum energy configurations of large aromatic systems

Kimberly Bowal, Peter Grančič, Jacob W. Martin and Markus Kraft, *The Journal of Physical Chemistry A*

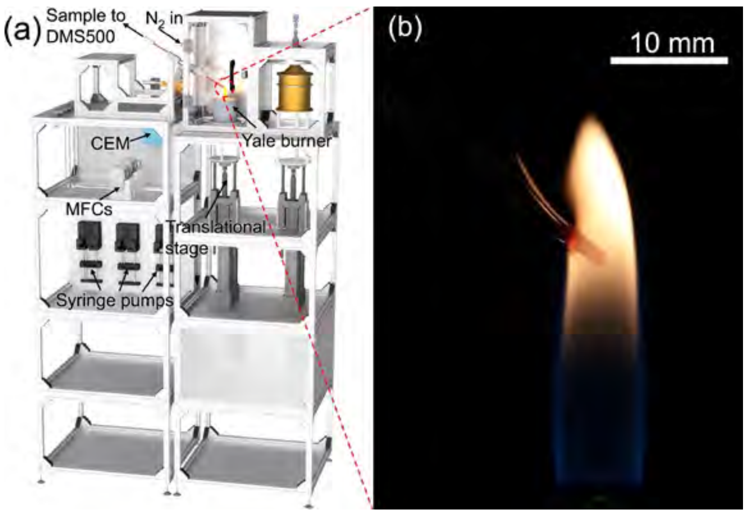
DOI: 10.1021/acs.jpca.9b04821

Abstract: We introduce a simple global optimisation approach that is able to find minimum energy configurations of clusters containing aromatic molecules. The translational and rotational perturbations required in Monte Carlo-based methods often lead to unrealistic configurations within which two or more molecular rings intersect, causing many of the computational steps to be rejected and the optimisation process to be inefficient. Here we develop a modification of the basin-hopping global optimisation procedure tailored to tackle problems with intersecting molecular rings. Termed the Sphere Encapsulated Monte Carlo (SEMC) method, this method introduces sphere-based rearrangement and minimisation steps at each iteration, and its performance is shown through the exploration of potential energy landscapes of polycyclic aromatic hydrocarbon (PAH) clusters, systems of interest in combustion and astrophysics research. The SEMC method provides clusters that are accurate to 5% mean difference of the minimum energy at a 10-fold speed up compared to previous work using advanced molecular dynamics simulations. Importantly, the SEMC method captures key structural characteristics and molecular size partitioning trends as measured by the molecular radial distances and coordination numbers. The advantages of the SEMC method are further highlighted in its application to previously unstudied heterogeneous PAH clusters.



Evolution of the soot particle size distribution along the centreline of an *n*-heptane/toluene co-flow diffusion flame

Jochen Dreyer, Maximilian Poli, Nick Eaves, Maria Botero, Jethro Akroyd, Sebastian Mosbach and Markus Kraft, *Combustion and Flame*



DOI: 10.1016/j.combustflame.2019.08.002

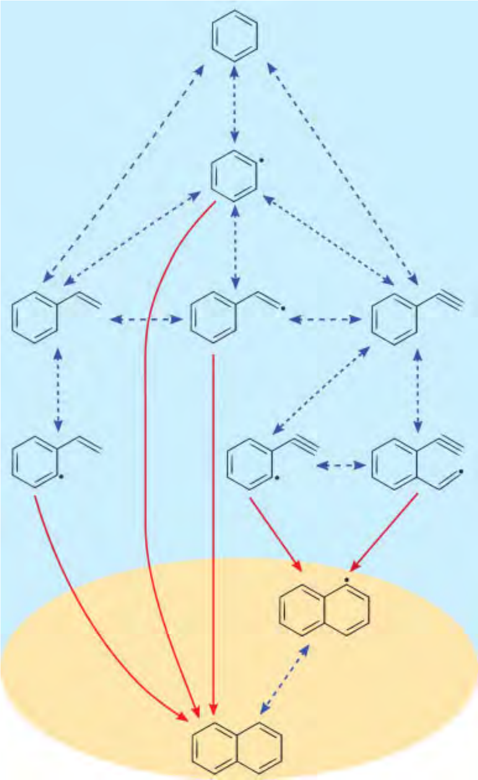
Abstract: A newly developed experimental set-up for studying liquid hydrocarbon combustion in the well-established Yale burner was used to investigate the correlation between fuel composition and its sooting propensity. Soot particle size distributions (PSDs) and flame temperatures along the centreline of an *n*-heptane/toluene co-flow diffusion flame are reported. The results are compared to soot temperature and volume fraction profiles obtained using colour ratio pyrometry. The addition of toluene (0, 5, 10, and 15 mol%) to heptane moved soot inception to lower heights above the burner (HAB). The earlier inception extended the soot growth zone in the toluene-laden flames, leading to larger soot primary and agglomerate particles. Toluene addition had little influence on the maximum soot number density, indicating that the observed increase in soot volume fraction can mainly be attributed to the increase in particle size. The reported PSDs inside a vapour-fed diffusion flame are the first of their kind and provide a comprehensive dataset for future studies of combustion chemistry and soot particle models.

A new methodology to calculate process rates in a kinetic Monte Carlo model of PAH growth

Gustavo Leon, Nick Eaves, Jethro Akroyd, Sebastian Mosbach and Markus Kraft, *Combustion and Flame*

DOI: 10.1016/j.combustflame.2019.07.032

Abstract: This paper develops a new methodology to calculate the process rates in a kinetic Monte Carlo (KMC) model of polycyclic aromatic hydrocarbon (PAH) growth. The methodology uses a combination of the steady-state and partial-equilibrium approximations. It shows good agreement with the results from simulations using a detailed chemical mechanism under conditions relevant to flames (temperatures between 1000 and 2500 K, equivalence ratios between 0.5 and 10). The new methodology is used to calculate the rate of different stochastic processes in KMC simulations of PAH growth of premixed ethylene-oxygen flames. The resulting rates are only a function of temperature and the main gas-phase species present in the flame environment. The results of the KMC model are shown to be consistent with the concentrations of species calculated using a well-established mechanism for the growth of small PAH species.

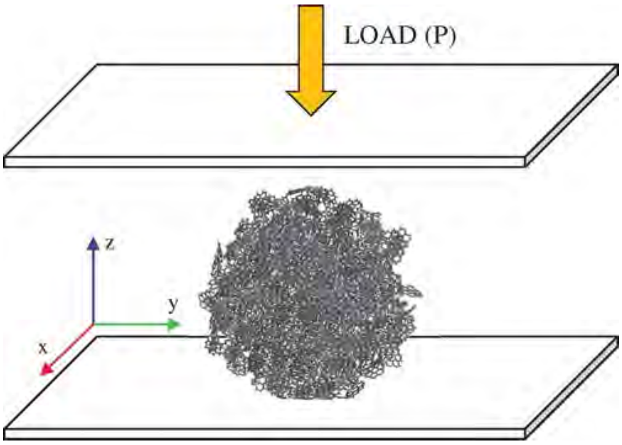


Mechanical properties of soot particles: the impact of crosslinked polycyclic aromatic hydrocarbons

Laura Pascazio, Jacob Martin, Maria Botero, Mariano Sirignano, Andrea D’Anna and Markus Kraft, *Combustion Science and Technology*

DOI: 10.1080/00102202.2019.1668380

Abstract: In this paper, we estimate the degree of crosslinking within soot particles making use of reactive molecular dynamics simulations of mechanical properties of crosslinked polycyclic aromatic hydrocarbons (PAH). Representative systems of PAH (pyrene, coronene, ovalene and circumpyrene) with a density similar to soot and with varying degrees of crosslinking were built. Uniaxial tensile test simulations were carried out on the systems and the yield stress of each sample was calculated. The hardness was estimated from the yield stress using an empirical conversion constant and the obtained values were compared with nanoindentation experiments of soot particles. The results show that mature ethylene and diesel soot particles are expected to present a degree of crosslinking between 2.1–3.0 and 3.0–3.5, respectively, to have a value comparable to the hardness found experimentally. Finally, an MD simulation of nanoindentation of a particle of crosslinked coronene molecules provided an alternative means to compute the empirical constant used to convert the yield stress in hardness. These results reveal the importance of crosslinking reactions during soot maturation that give rise to a structure in which the majority of aromatics are aliphatically linked in a 3D network.



Other activities and achievements

Dr SHENG Yuan gave a talk at the *10th International Conference on Materials for Advanced Technologies* in June, in Singapore. Dr Sheng received the Best Oral Presentation award for the talk, titled ‘One-step flame synthesis of phosphorus-doped Ni-Fe/C nanocomposite films for electrocatalytic oxygen evolution reaction’ (Sheng Yuan, Markus Kraft and Xu Rong).

Astrid BOJE presented work at the *Combustion Aerosol Conference* in Cambridge, UK, in June: ‘Using a hybrid particle-number and particle model to study high-rate aerosol synthesis’ (Astrid Boje, Jethro Akroyd and Markus Kraft).

Jacob MARTIN won the 2019 Mrozowski Award for best oral presentation at the 2019 *Carbon* conference held in Lexington, Kentucky, US in July. The Mrozowski Award is for best oral presentation by a student at international carbon conferences organised and/or sponsored by the American Carbon Society. While at *Carbon*, Jake gave the following presentations:

Understanding the lack of fullerenes in fullerene-like carbons, by J. Martin
Flexoelectricity and the electrical aspects of carbon formation in flames, by J. Martin
Topology of disordered graphene networks, by J. Martin
Degree of crosslinking in combustion carbons, by L. Pascazio
Investigating the self-assembly and structure of nanoparticles containing curved carbons, by K. Bowal

Angiras MENON also attended the *Carbon* conference in Kentucky and gave a presentation on ‘Impact of crosslinks, curvature and radical character on the optical band gap of nanographenes.’

While in the US, Jacob and Angiras also presented their conference talks at MIT, Penn State University, Northeastern University and the materials company Nano-C.

A number of IRP3 and other Cambridge researchers were awarded the Gaydon Prize for the most significant UK contribution to the *37th International Symposium on Combustion* in 2018. The paper is titled ‘Polar curved polycyclic aromatic hydrocarbons in soot formation’, by Jacob Martin, Kimberly Bowal, Angiras Menon, Radomir Slavchov, Jethro Akroyd, Sebastian Mosbach and Markus Kraft.

WU Shuyang gave a presentation at the *8th Asia Pacific Congress on Catalysis* in August, in Bangkok, Thailand. The presentation was titled ‘Premixed stagnation flame synthesised TiO_2 nanoparticles with mixed phases for efficient photocatalytic hydrogen generation.’

Jacob MARTIN participated in the Science, Technology, Prototyping, Policy and Practice workshop (STP^3) organised by the Singapore-ETH Centre and other CREATE entities in June.

IRP4

BETTER, CLEANER HEAT USAGE

Better, Cleaner Heat Usage is a new IRP4 for Phase 2, replacing the former energy/electricity focus in Phase 1. This work is focused on high-performance thermal management and waste heat recovery research for improved, i.e. cleaner and more efficient heat usage in energy conversion technologies. IRP4 addresses two key challenges in power generation systems: a) the efficient management of heat and b) the emission of harmful pollutants, which is particularly problematic in fuel-based technologies such as diesel engine power plants or marine engines. Regulations are increasingly stringent for these systems and a full understanding of the underlying phenomena is necessary to tackle this problem.

IRP4 Principal Investigators:

Professor Epaminondas MASTORAKOS
University of Cambridge

Professor Alessandro ROMAGNOLI
Nanyang Technological University

Professor LEE Poh Seng
National University of Singapore

OVERVIEW

The push for better energy efficiency, lower pollution, and decarbonisation in the marine sector is increasing in pace and importance worldwide. This IRP addresses these issues by a series of work packages, including fundamental studies on particulate emissions from marine engines burning fossil or alternative fuels, waste heat utilisation methods such as the use or Organic Rankine Cycles and the associated turbomachinery, high-efficiency heat exchangers, and estimates of pollutant dispersion from ships and its reception in port and urban areas.

This IRP, which is only one year old, has now started in earnest with all researchers in place. The various contributions outlined below demonstrate the range of activities in this IRP.

Professor Epaminondas Mastorakos, PI
University of Cambridge

Update on work package 4.1

Engine combustion — best fuel, best operating condition

Shrey TRIVEDI (Research Assistant, CAM) joined IRP4 in August 2019. Initial training with the engine CFD code CONVERGE has been completed. A simulation of a marine-engine-like test configuration, with a constant-volume combustion chamber previously studied by Sulzer and ETH Zürich, has been launched. In this configuration, a heavy fuel oil spray injected in a swirl flow, at marine-engine pressures and temperatures, evaporates and then autoignites. The experimental dataset includes pressure vs time signals and spray imaging and will be used for model validation. Figure 4.1 shows the velocity of the air as it enters the combustion chamber at an angle, which will create the needed swirl to promote spray dispersion and efficient fuel mixing. In the future, such simulations will also be performed for reciprocating marine engines for which a well-characterised set of experimental data exists.

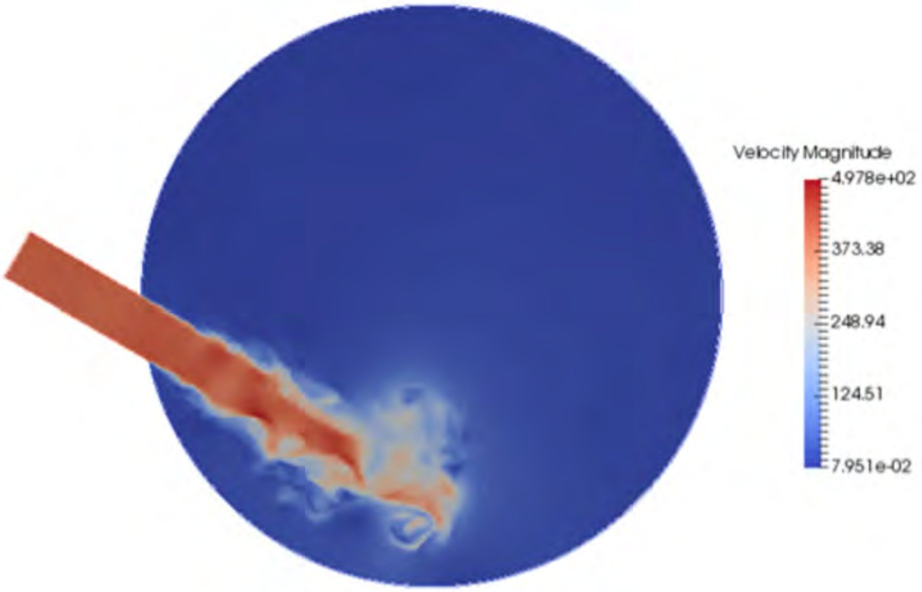


Fig 4.1: Computational fluid dynamics study of the spray evolution in a pancake-shaped marine-engine reference combustion chamber. The velocity of the air entering the chamber during the intake phase is shown.

Shrey TRIVEDI

Update on work package 4.2

Closed power cycles — selection and analysis

Zheng LIU (Research Assistant, NTU) has recently joined the IRP4 team. Along with **Prof. Alessandro ROMAGNOLI (PI, NTU)** he reports that an efficient turbocharger turbines benefits an engine in many aspects, for example lower backpressure and a better transient response. The turbine performance can be further improved by injecting the secondary flow through an injector over the turbine shroud, as shown in Figure 4.2. The secondary flow can effectively reduce the vortex separation on the suction side and reduce associated losses. Without affecting the original impeller design, the injection flow can be achieved by modifying only the turbine housing, which is cost effective. In order to find the injection design that maximises the turbine performance, eleven design parameters have been considered which control the circumferential area distribution, exit flow angles and flow velocities. The mesh sensitivity study has been conducted for the baseline turbine in order to have the best compromise between the numerical accuracy and the computational power. 1.83 million computational nodes of the rotor domain will be used in future analysis.

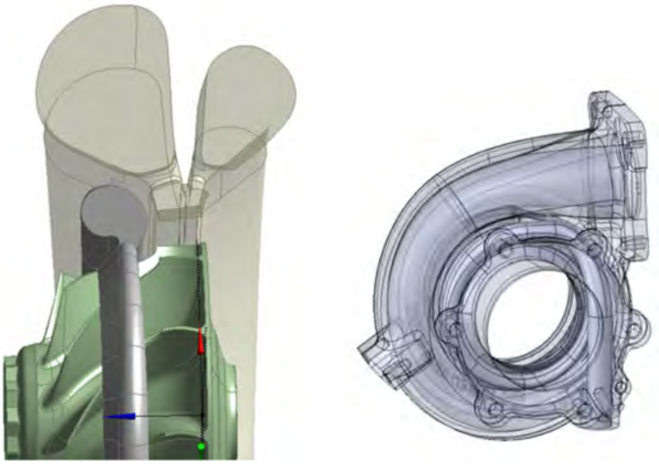


Fig. 4.2: Secondary flow injection to the shroud.

The next step will be a design of experiments (DOE) study with the design parameters varying in the appropriate range. Based on the DOE results, a response surface can be fitted using the Kriging surrogate model. The potential benefit of including the injection flows can be assessed, and the design can be improved further by means of optimisations.

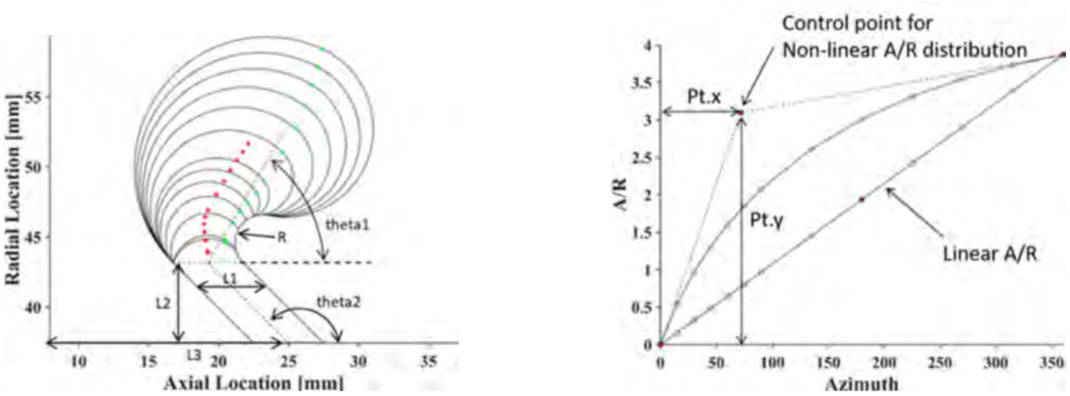


Fig. 4.3: Design parameters of the cross-sections of the injection.

Zheng LIU

Update on work package 4.3

High-efficiency heat exchanger

Dr Matthew LAW (Research Fellow, NUS) has been working on the development of a triple-fluid heat exchanger, focusing on modelling of the air and fin region as porous media. The method of using porous approximation to represent the fin domain, as depicted in Figure 4.4, reduces the fin-tube heat exchanger to a plain-tube model. This brings about a decrease in grid size, which leads to a drop in computational time and resources. However, simplifying the model does not mean that accuracy of the solution has to be greatly compromised. Computational fluid dynamics simulation results show that the air-side pressure drop of the porous model has good agreement with the fin model. As a result, full scale simulations of the entire length of the heat exchanger can be carried out with this porous model without sacrificing accuracy.

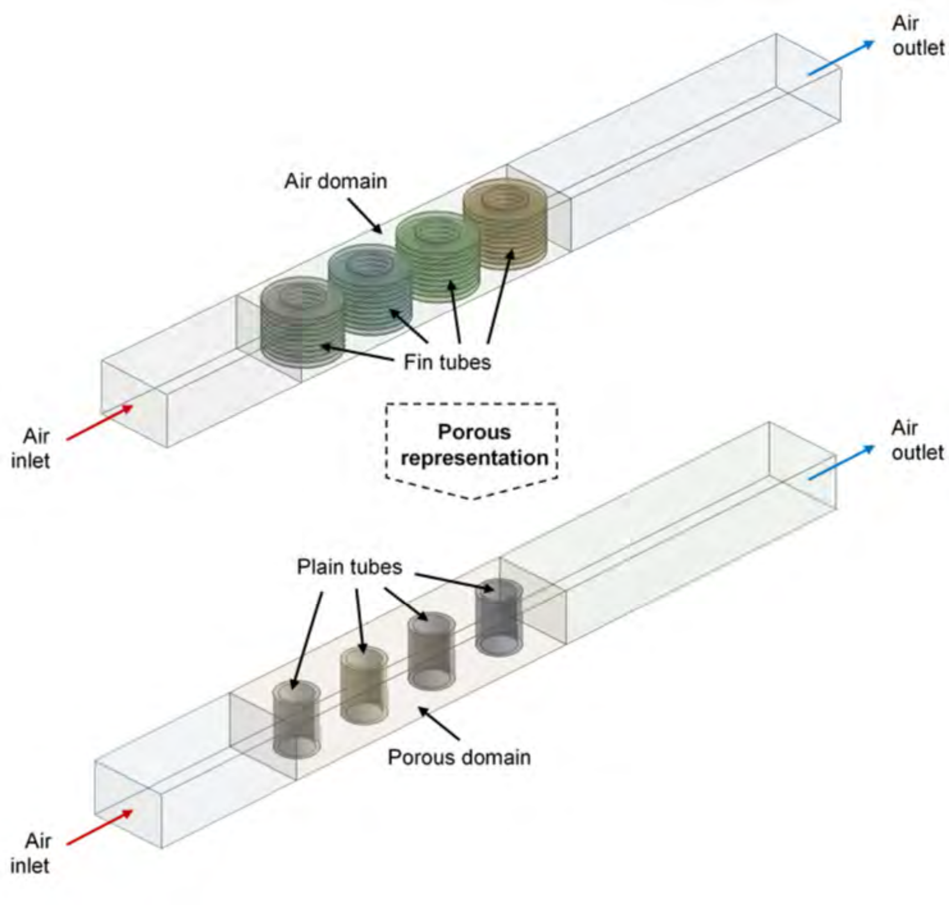


Fig. 4.4: Porous representation of the fin domain in the heat exchanger.

Dr Matthew LAW

Reduction in mesh count

By removing the fins and converting the fin domain to porous region, the mesh count of the porous model (PM) can be reduced by more than half of the fin model's (FM), as listed in Table 4.1. This is because the PM can be meshed with quadrilaterals throughout its domains, whereas the FM can only be meshed with tetrahedrals (Figure 4.5), which greatly increased its grid size. Furthermore, by having a homogenous region in the porous domain, the mesh can be swept from top-down, which provided better mesh control.

Table 4.1: Meshing details for multiple arrays of FM and PM

Array	**Element size**	**Mesh count**		
		FM	**PM**	**% reduction**
1×1	Fluid: 0.25–0.50 mm Solid: 0.5 mm	624,886	367,528	41
1×2		1,206,727	499,408	59
2×1		1,174,853	749,850	36
2×2		2,329,892	1,015,512	56

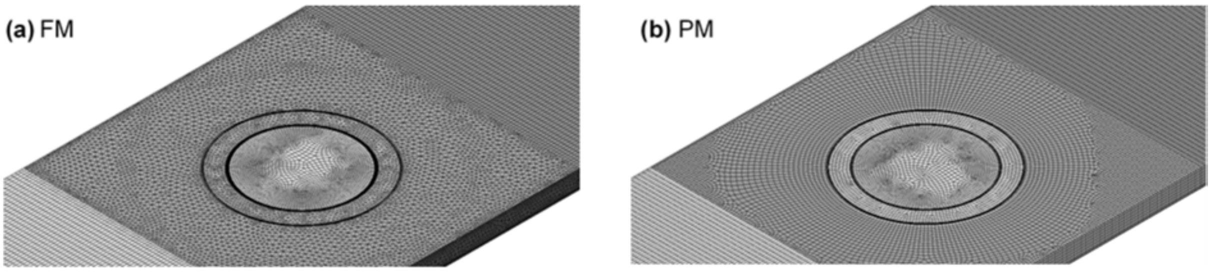


Fig. 4.5: Mesh in FM and PM.

Table 4.2 shows the simulated pressure drop for different arrays and a comparison between the FM and PM pressure drop values. It is found that the pressure drop across the fin region can be closely replicated by the porous domain with very small errors. It is also observed that the 1×1 and 2×1 arrays as well as the 1×2 and 2×2 arrays each have similar Δn. As a result, it can be inferred that Δn is dependent on the streamwise length of the fin area and independent on its spanwise length.

Table 4.2: Pressure drop for different arrays of FM and PM

Array	**ΔP [Pa]**			**Δn [m]**
	FM	**PM**	**% diff.**	
1×1	5.987	6.004	0.3	0.21
1×2	9.948	9.902	0.5	0.26
2×1	5.988	5.970	0.3	0.21
2×2	9.948	9.909	0.4	0.26

Correlations between Δn_{PM} and Δn_{FM}, and between ΔP_{PM} and Δn_{PM}

It has to be noted that the Δn used in these simulations are not the actual thickness of the porous media in the PM model. This is because the porous model is a representation of the fin area in the air domain, and not a representation of an actual porous media. Therefore, the real thickness of the fin area cannot be used in this case.

Further simulations are performed on 1×3 and 1×4 arrays to find a correlation between the thickness of the PM, Δn_{PM} and the actual thickness of the fin area, Δn_{FM}, as well as between ΔP_{PM} and Δn_{PM}. The simulation results are plotted in Figures 4.6 and 4.7.

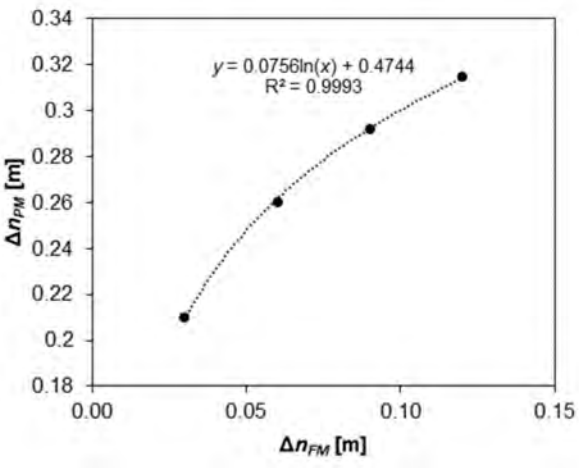


Fig. 4.6: Plot of Δn_{PM} against Δn_{FM} and its corresponding equation.

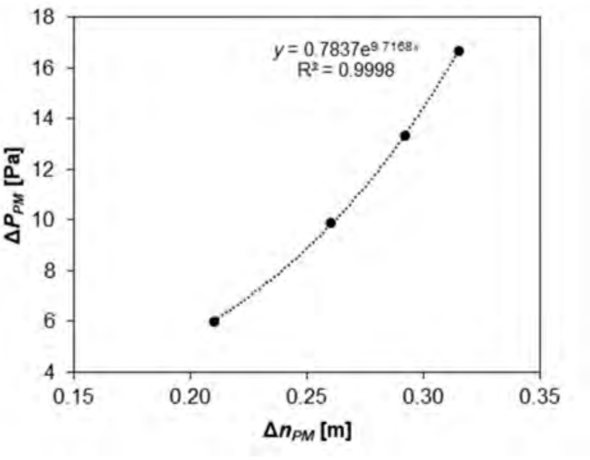


Fig. 4.7: Plot of ΔP_{PM} against Δn_{PM} and its corresponding equation.

Dr Matthew LAW

From the graph in Fig. 4.6, the correlation between the thickness of the PM and the actual thickness of the fin area is given by:

$$\Delta n_{PM} = 0.0756\ln(\Delta n_{FM}) + 0.4744$$

The correlation between the pressure drop across the porous media and the thickness of the PM is given in Figure 4.7 as:

$$\Delta P_{PM} = 0.7837e^{9.7168\Delta n_{PM}}$$

Update on work package 4.4

Process system model for the J-Park Simulator

Shipping emissions are considered major contributors to air pollutants, including NO_x and particulate matter, in coastal cities. Numerical modelling of the shipping emission spread and distribution by using pollutant dispersion models, such as ADMS and CALPUFF, is important for evaluating the impact of maritime activities on human health and air quality in coastal areas. However, a common issue for such modelling is how to accurately estimate the shipping emission rate and specify the shipping emission source models.

Dr PAN Kang (Research Fellow, CARES) reviewed the recent shipping emission dispersion modelling research, and the common assumptions and model setups applied in the emission dispersion simulations are summarised. As shown in Figure 4.8, the marine traffic information (including the ship position, speed, time schedule and name) combined with the ship details (such as gross tonnage and engine type) obtained from online databases or authorities can be integrated into some emission estimation methods, such as Methodology for Estimate Emissions from air pollutants Transport (MEET) and EMEP/EEA methodology. The detailed traffic information determines the operation modes of each ship, and then the shipping emission rates are calculated by estimating the emission factor and fuel/energy consumption under different operation modes, according to the emission estimation methods. In addition, the detailed ship information also determines how to specify the model setups of the shipping emission sources (such as source type and geometry) used in the dispersion modelling. The literature review has shown that the application of these approaches in the emission dispersion modelling can reasonably estimate the shipping emission production and its distribution in the locations of interest.

The summarised scheme from the literature is a good reference for setting up the shipping emission dispersion model integrated in the J-Park Simulator. The simulated results will be suitable to evaluate the environmental impact of shipping emissions to coastal cities such as Singapore and Hong Kong.

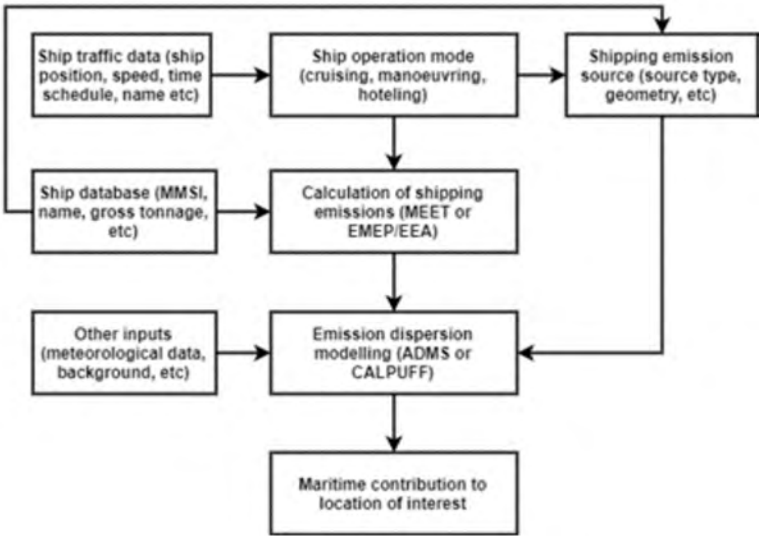


Fig 4.8: Shipping emission dispersion modelling details.

IRP BB

BETTER BUSINESS: PATHWAYS TO INDUSTRIAL DECARBONISATION

The Better Business IRP acts as an incubator for ideas from all other IRPs and will support the acceleration and scaling of the technology outputs from the programme. It will examine different possible business models and compare the situation in Singapore with other important chemical clusters worldwide, engaging with stakeholders to identify the potential benefits and co-benefits of each technology arising from the programme.

IRP BB Principal Investigators:

Professor Steve EVANS
University of Cambridge

Professor S. VISWANATHAN
Nanyang Technological University

Assoc Professor Kenneth HUANG Guang-Lih
National University of Singapore

OVERVIEW

The IRP BB group is now working directly with all IRPs to prioritise their emerging technologies. IRP BB has been working closely with IRP 1 on the first two technologies, analysing them using first-cut IRP BB tools (including value mapping tools). The aim is firstly to identify better business models as well as better IP strategies for these two technologies. This includes preparation for meeting with investors and other funders.

Based on this learning the IRP BB tools will be re-specified and novel development will begin. At the same time, IRP BB will examine other emerging technologies across C4T.

With the exception of one drawn-out and ultimately unsuccessful visa application process, recruitment for IRP BB has increased steadily. There are now four Research Fellows/Assistants on the BB team, with another joining shortly to make up for the vacancy left by the recent visa rejection.

Professor Steve Evans, PI
University of Cambridge

Update on work package BB.1

Business model innovation potentials

As part of WP1, research has commenced using game theory models and choice models to analyse and evaluate alternative business models for adoption of sustainable innovations and technologies. The team's first paper with application to the solar energy market focuses on the interaction of consumer's choice, firms' business model adoption and pricing decision in light of government's policies related to subsidies for installation of solar panels and carbon tax. The study is partly motivated by the fact that Singapore is trying increase adoption of solar energy and recently introduced carbon tax. From this research, insights are expected on how the government's policies impact consumption behaviour and incentivise business model innovation for sustainability. The developed model and approach can also be extended to conduct pre-analysis on the performance of potential business models for the emerging chemical technologies of C4T that are going to be launched on the market. The team has also started to look further at the effects of business model innovation for sustainability, applying life-cycle thinking to evaluate economic and environmental performance of selling versus leasing in the context of remanufacturing. These research works support the development of business model to increase adoption of sustainable innovations.

Update on work package BB.2

Policy formulation, customer and industry perceptions

IRP BB has completed the curation of a document that provides information and guidelines on writing business plans, and lists the supporting resources available in NTU, NUS and the Singapore ecosystem for researchers embarking on their start-up journey. This document is under final processing and will be ready to circulate to all IRPs soon. A preliminary survey form to study the willingness of procurement managers to adopt clean technologies or purchase green materials has been completed. This will be refined and pilot-tested in the following months.

As part of work package 2, the aim is to generate key insights into the innovation landscape and analysis of Singapore's chemical industry. To achieve this goal, the study was designed and is moving forward in two interrelated directions.

First, Singapore's chemical company list was compiled, which contains more than 2,000 companies (industry coverage: pharmaceuticals, biotechnology, oil and gas, utilities and chemicals). These were differentiated by screening out the public companies through a web search. For the public or listed companies (or companies that had ever been publicly listed), their detailed financial data were collected. Financial data include the following fields: cash and equivalents, total cash and short-term investments, accounts and notes receivable, total receivables, inventories, total current assets, net property, plant and equipment, long-term investments, deferred charges, total assets, total current liabilities, long-term debt, total liabilities, total equity, revenue, profit, operating expense, operating income, EBITA, EBIT, cash from investing, total debt issued/repaid, dividends paid, cash from financing, etc. During the process of gathering and compiling data, the name variants were manually and carefully checked for each company. Besides this, the team collected (through various sources including annual reports and official company websites) the founding year for each company to further ascertain the relationship between a company's level of maturity and innovation.

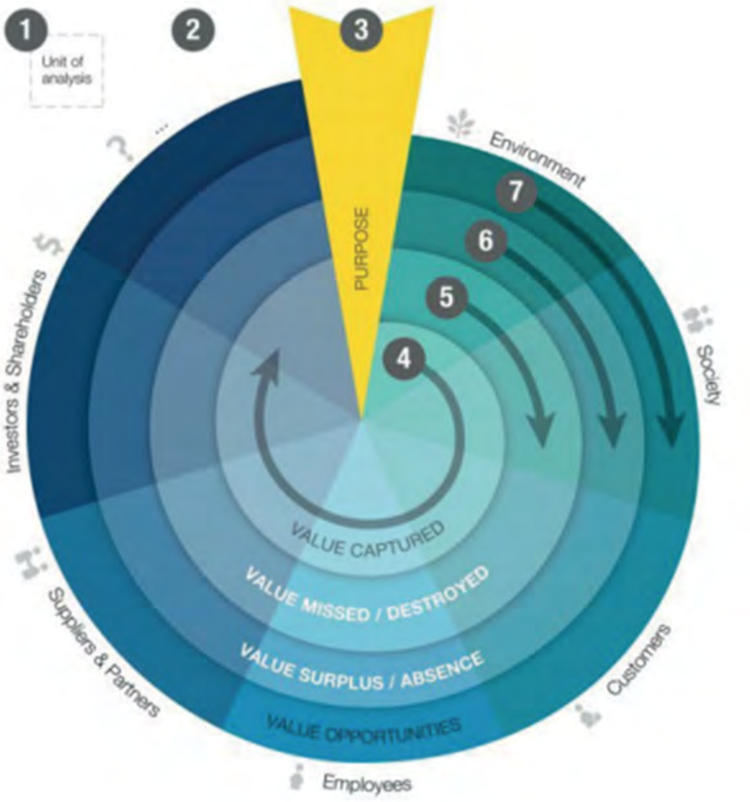


Fig. 5.1: The Cambridge value mapping tool. The IRP BB team has started applying this to explore the ecosystem and find new business opportunities for the emerging cutting-edge chemical technology of C4T.

Image credit: Prof. Steve EVANS and IfM's Centre for Industrial Sustainability.

Second, a patent database was built for these companies. The database contains all 6,818,522 patents granted by the United States Patent and Trademark Office (USPTO) from 1985 to 2017. The USPTO patent data was chosen because the US is the largest economy in the world, the most technologically sophisticated and usually the most important market in which to file a patent for these industries. The original data was parsed into several related tables, including basic information on patent numbers, their application and grant dates, assignees, inventors, IPCs, locations and citations. The process of merging and cleaning the company/financial database and patent database to build a comprehensive database of firm-level financial and innovation activities of Singapore's chemical companies is ongoing. Since this important database is being built from scratch, this ongoing work has taken a substantial amount of time and effort but we are making good progress. It is expected that the outcome will yield important and useful insights into the innovation and financial performance of companies in these key industries most pertinent for the C4T research project.

Update on work package BB.3

Future roadmap for industrial decarbonisation, including international comparisons

The research being done in work packages 1 and 2 continues to inform the development of the future roadmap. Particular attention is being paid to the barriers faced by industry when considering the adoption of carbon reduction technologies. When complete, the roadmap will be based on the research outcomes of IRP BB's current and upcoming studies.

Other activities and achievements

PI Prof. Steve EVANS (PI, CAM) was elected to membership of Academia Europaea.

PI Assoc. Prof. Kenneth HUANG Guang-Lih was appointed as the Editorial Board Member/Associate Editor of *Organization Science*, a top-tier management journal. In addition, Prof. Huang continues to serve a subsequent term as the Editorial Board Member of the *Academy of Management Journal* and *Strategic Management Journal*, which are also top-tier management journals.

IRP JPS

THE J-PARK SIMULATOR

IRP JPS is an overarching research activity, with the ultimate purpose to show how research coming from each IRP affects the CO_2 output in Singapore and in particular the operations on Jurong Island. The research utilises the latest ideas from semantic web technologies and Industry 4.0 to integrate real-time data, knowledge, models and tools to fulfil objectives such as simulation and optimisation in cross-domain and multi-level scenarios. A main focus is to create superstructures of models contained within the developed ontologies for industrial parks to provide an accurate and fast-to-evaluate approximation of computationally expensive mathematical models for process industry plants in high dimensions.

IRP JPS Principal Investigators:

Professor Markus KRAFT
University of Cambridge

Assoc Professor Raymond LAU Wai Man
Nanyang Technological University

Professor Iftekhar KARIMI
National University of Singapore

OVERVIEW

Over the past six months, the J-Park Simulator (JPS) has progressed on several fronts with regard to connecting and integrating previously unrelated entities and demonstrating their interoperability by means of Semantic Web technologies. This includes implementing new features for the ADMS-Ship project i.e. integration of real-time marine traffic data. With this inclusion, the JPS is now capable of utilising Automatic Identification System (AIS) based information to model ship emissions and simulate its atmospheric dispersion (using Atmospheric Dispersion Modelling System (ADMS)) with the help of the knowledge graph. In addition, we have provided a solution to annotate resources i.e. entities in the knowledge graph, e.g. dispersion data, with metadata such as time and location in order to allow "soft sensor" to estimate the pollutants' concentration for a specified location and time.

We have also implemented the first use case (in the context of a carbon tax scenario) to exemplify the main ideas of the "parallel world" framework. The use case aims to address the following questions: 1) For a set of conditions, what is the minimum value of carbon tax required to motivate the replacement of existing power plant(s) with small modular nuclear power plants, 2) which existing power plant(s) / generator(s) need to be replaced, 3) what are the required number and optimal locations for the new small modular nuclear power plants and 4) how to connect the small modular nuclear power plants to an existing electrical grid. The developed framework keeps agents involved in the same what-if scenario together and delegates their access, queries and updates on the knowledge graph to a scenario-specific "sandbox". This architecture allows agents involved in the carbon tax scenario to have the same view on data as other agents operating on the knowledge graph and at the same time, operate in a "secured portion" of the knowledge graph without interfering with other agents or impacting the "real" world.

In addition, we have developed a single knowledge graph using a linked-data approach that connects species in chemical kinetic reaction mechanisms to computational chemistry data. This work is motivated by the fact that currently, a major barrier to using chemical models in an Industry 4.0 environment is that there is significant inconsistency between chemical kinetic reaction mechanisms, both in terms of naming of chemical species and in terms of thermodynamic, kinetic and transport data. The inherent complexity of chemical kinetic reaction mechanisms and the above-mentioned inconsistency challenges render it infeasible to solve these problems manually. Instead, a systematic and automated approach is required. For addressing the data inconsistency issues, computational chemistry data was used to calculate thermodynamic properties for each species, and subsequently link the thermodynamic property data such that it can be used in the context of the chemical kinetic reaction mechanisms. In order to link chemical kinetic reaction mechanisms with quantum chemistry calculations in the described approach, both the existing OntoKin and OntoCompChem ontologies were extended accordingly. Furthermore, a new ontology called "OntoSpecies" was developed for uniquely representing chemical species by having a set of unique entries, each of which corresponds to a unique real-world species. OntoSpecies also provides an infrastructure to link data about species derived from different sources with different levels of granularity; in this case, chemical kinetic reaction mechanisms and computational chemistry calculations. A framework for hosting and visualising linked data was also developed and deployed so that it can be used by other agents to navigate across semantically related data populated in the knowledge graph to solve species naming and data inconsistency issues.

Furthermore, we have demonstrated the application of OntoPowSys, a domain ontology for power systems in a use case involving both chemical and electrical domains of a debutaniser section of a typical natural gas processing plant. In this use case, we investigate the effect of different feed flow ramp up rates on the power quality at the Point of Common Coupling (PCC). PCC is the point in the transmission and distribution network where multiple customers or electrical loads may be connected. The preliminary results reveal that a surge in the feed pump's power requirement due to rapid feed flow ramp up rates can cause frequency and voltage fluctuations that are exceeding the allowable limit.

Professor Markus Kraft, PI
University of Cambridge

Update on work package JPS.1

Big data — sensors and data modelling

In this reporting period, new features have been implemented for the ADMS-Ship project—integration of real-time marine traffic data and its application to Hong Kong. The current ADMS-Ship project utilises Automatic Identification System (AIS) based information to model ship emissions and simulate their atmospheric dispersion (using the Atmospheric Dispersion Modelling System (ADMS)) with the help of the knowledge graph shown in Figure 6.1. **Dr Andreas EIBECK (Computer Scientist, CARES)** and **Arkadiusz CHADZYNSKI (Senior Software Developer, CARES)** are responsible for driving forward the overall architecture. Arkadiusz and **Leonardus Kevin ADITYA (Project Officer, NTU)** are heavily involved in the implementation of the new features while **Dr PAN Kang (Research Fellow, CARES)** in collaboration with Kevin, is responsible for developing the underlying atmospheric dispersion models using ADMS. Dr Eibeck provided the preliminary design to integrate data into the knowledge graph, periodically trigger the agents that estimate ship emissions based on the AIS data and simulation of its atmospheric dispersion, and to estimate the pollutants' concentration for a specified location and time via a "soft sensor." In order to accomplish this, Dr Eibeck produced a solution to annotate resources (entities) in the knowledge graph, e.g. dispersion data, with metadata such as time, location and creating agent. Dr Eibeck also implemented components within the solution to facilitate updating, annotating and querying of the knowledge graph. Furthermore, Dr Eibeck is involved in the analysis of the correlations between air quality measurements, weather and AIS data.

While building upon the baseline JPS designs and codebase, Arkadiusz redesigned and enhanced existing components for the ADMS-Ship project. This work was preceded by conducting thorough testing, profiling, gap and impact analyses. Elicitation of live AIS data acquisition requirements was followed by a process of design and implementation of a data acquisition agent. This was built around an idea of "web scraping" and integrated Open Source components. The overall design for the data acquisition agent is presented in Figure 6.2, a component diagram. The above-mentioned non-functional requirements are satisfied by integrating Open Source relational database, Object Relational Mapper (ORM) engine and web scraping framework. Currently, information about over 17,000 ships and over 6,000,000 of their dynamic statuses has been incorporated. The JPS Ship Entity Relationship (ER) model, covering the relationships between static

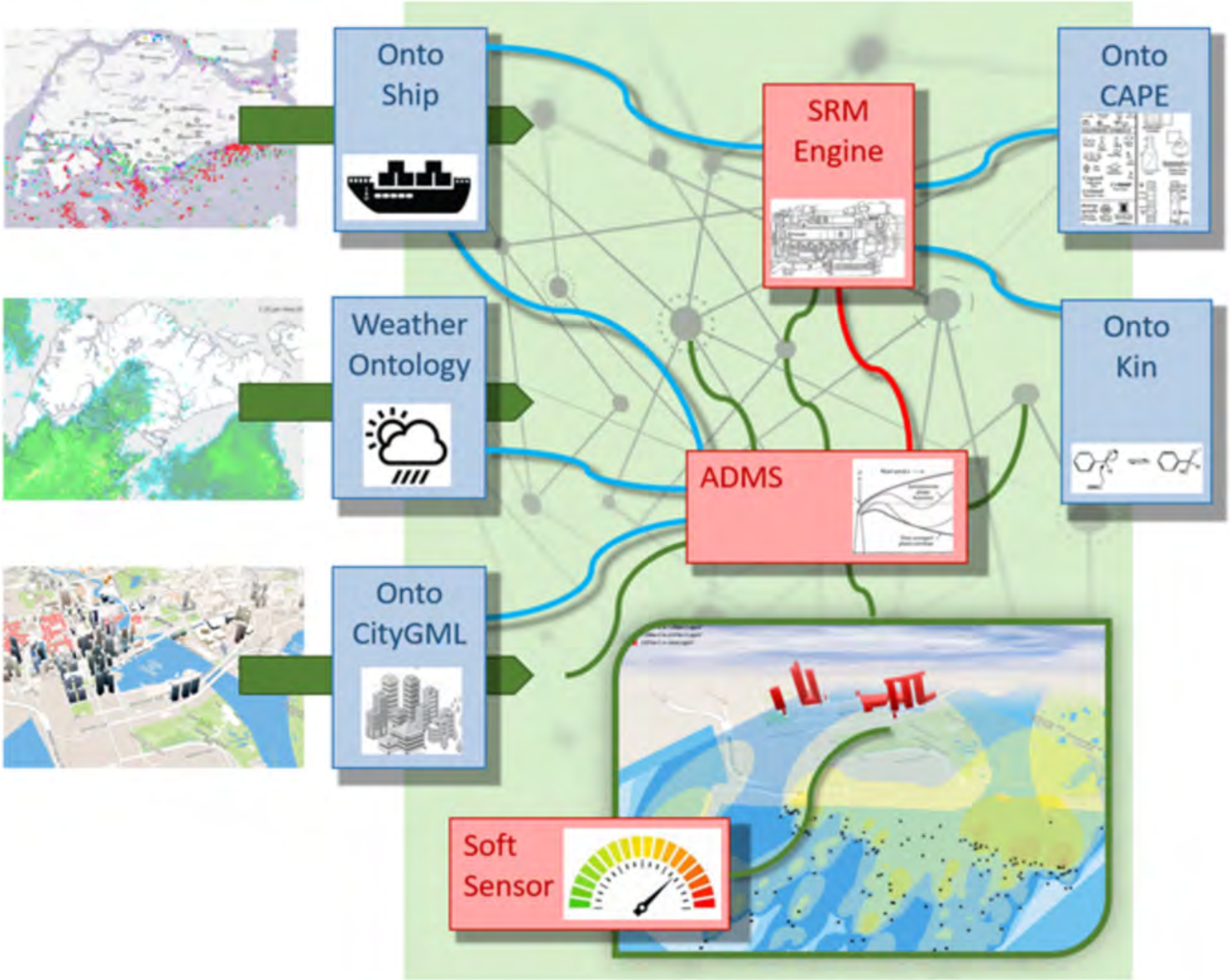


Fig. 6.1: The JPS knowledge graph (green) integrates and links cross-domain data (e.g. real-time ship and weather data, and static building data (shown on the left-hand side)) and models (e.g. for engines, chemical reactions etc.). The data and models are described semantically using domain ontologies (blue boxes). Agents (red boxes) use the domain ontologies (blue lines) to collaborate with each other (red line) and to operate on the knowledge graph (green lines).

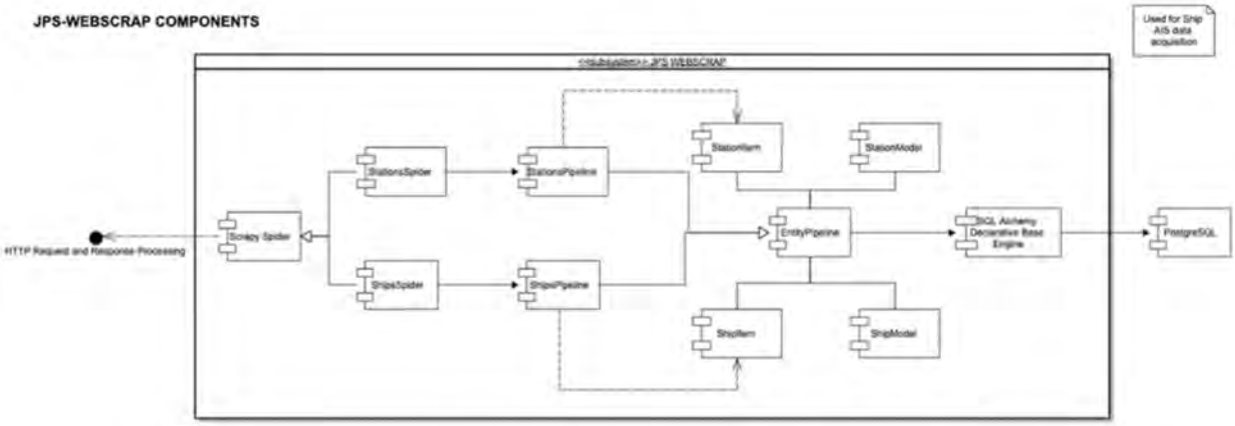


Fig. 6.2: Component diagram for AIS data acquisition agent.

and dynamic ship data, as well as non-reusable waste stream ontology model, is illustrated in Fig. 6.3. As increased amount of data processing necessitated rethinking of the structure of the JPS components involved in building the ADMS model, Arkadiusz also made improvements to the components which were preceded by redesign and re-implementation using Strategy and Builder Object Orientated design patterns. Modelling up to 300 ships as pollution sources also required implementation of asynchronicity to the JPS agents. Arkadiusz implemented this feature to allow concurrent model building and reduce computational time by parallelising workload across multiple CPUs. In addition, Arkadiusz also implemented adaptable legend thresholds calculations as well as image resolution selection based on the size of the selected region to handle visualisation of an increased amount of simulation results.

In order to extend the ADMS-Ship project to Hong Kong, Kevin created agents based on Dr Eibeck's design to query for Hong Kong's air quality ("HKU air" agent) and weather data ("HKU weather" agent) from the repository hosted in the University of Hong Kong. However, due to the lack of precipitation information in the weather data and the impending work on model calibrations, the two agents are currently unused. Kevin also created a new "coordination" agent, in conjunction with previous ADMS-Ship work, that utilises Hong Kong's weather data from accuweather.com, ships' data from a database which periodically acquires data from aishub.net, 25 buildings within the selected region and estimated exhaust gas emissions from each ship to simulate the atmospheric dispersion using the ADMS software. The simulation results are annotated with metadata to facilitate their querying. In

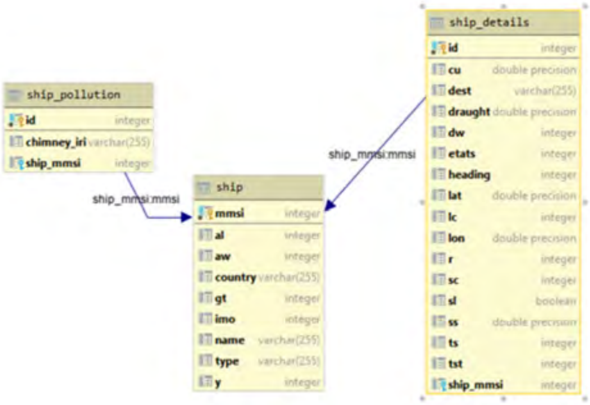


Fig. 6.3: Ship entity relationship diagram.

the next phase, the Hong Kong's air quality measurement data provided by the HKU air agent will be used to calibrate the models. In addition, Kevin created the "soft sensor" agent based on Dr Eibeck's design, to query for the relevant ADMS simulation results and perform approximation to derive estimation for the pollutants' concentration for a specified location and time.

Kevin has also extended the ADMS model with chemical reaction features. This allows the ADMS model to consider the effects of chemical reactions between NO_2, NO_x and ozone on the pollutants' dispersion profile. Kevin is in the process of evaluating the current definition of relevant pollutants' background concentration (measurement data from one of the air quality monitoring stations) for the atmospheric chemistry. Kevin also performed sensitivity analysis for selected ADMS' modules and parameters to investigate their effects on the simulation results. In addition, as information about specific ships is scarce, Kevin concluded from his literature review that it might be possible to estimate individual ships' emissions based on properties such as fuel type, engine capacity, ship status (cruising/manoeuvring/hoteling) and emission factors etc.

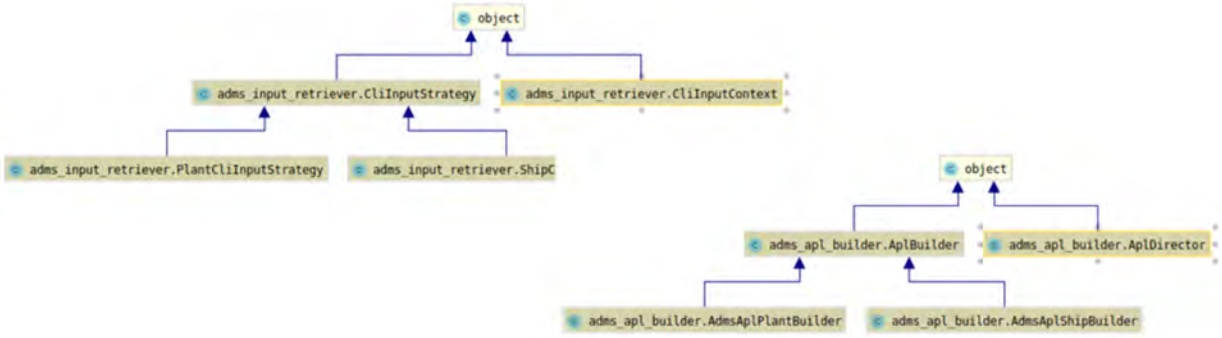


Fig. 6.4: Input retriever strategy and model builder using APL for ADMS.

Update on work package JPS.2

Surrogate models and superstructure

Dr Andreas EIBECK (Computer Scientist, CARES) is investigating a framework to enable agents to execute several parallel optimisation strategies or to simulate cross-domain scenarios with varying initial assumptions, i.e. what-if scenarios analysis. Agents are applications and services that utilise semantic technologies and are accessible on the World Wide Web. In addition, Dr Eibeck is also responsible for coordinating the individual work activities within the project. The first use case implemented to exemplify the main ideas of this framework is the carbon tax scenario. The use case aims to address the following questions: 1) For a set of conditions e.g. generator's characteristics (design capacity, carbon emission factor, capital cost, fuel cost etc.), project life span, depreciation rate and load profile, what is the minimum value of carbon tax required to motivate (i.e. becomes profitable) the replacement of existing power plant(s) with small modular nuclear power plants, 2) which existing power plant(s)/generator(s) need to be replaced, 3) what are the required number and optimal locations for the new small modular nuclear power plants and 4) how to connect these small modular nuclear power plants to an existing electrical grid.

This use case leverages research results from the previous work of **Aravind DEVANAND (PhD student, NUS)** i.e. a mathematical optimisation model capable of identifying the optimal location for small modular nuclear power plants in a region. In this extended work, Aravind developed two optimisation models (agents) to address the above-mentioned questions 1, 2 and 3. The first optimisation agent determines the minimum value of carbon tax, the existing power plant(s)/generator(s) to be replaced and the number of new small modular nuclear power plants by modelling the optimisation problem as a Mixed Integer Non-Linear Programming (MINLP) in GAMS and solving it with the BARON solver. The results from the first optimisation agent is fed into the second optimisation agent to determine the optimal locations for the new small modular nuclear power plants.

Gourab KARMAKAR (Research Engineer, CARES) has developed recommendations and heuristics on how to connect these small modular nuclear power plants to an existing electrical grid. Figure 6.5 illustrates how the use case is implemented in the context of JPS, i.e. the "parallel world" concept. JPS represents and links entities semantically in the knowledge graph while agents collaborate and operate on the knowledge graph to read/write, estimate, simulate and/or query etc. to fulfil objectives in scenarios. In Figure 6.5, the blue and red boxes represent the semantic descriptions of the electrical grid and the three natural gas power plants respectively. The developed framework keeps agents involved in the same what-if scenario together and delegates their access, queries and updates on the knowledge graph to a scenario-specific "sandbox". In Figure 6.5, this is exemplified by the "what-if scenario" layer on which the yellow box, representing a new instance of a small modular nuclear power plant, is connected to the adapted electrical grid (blue box). The "sandbox" only overshadows the portion of the knowledge graph where modifications are necessary. Entities that are unchanged, e.g. the two natural gas power plants, transmission lines and buses (not shown in the figure), remain connected to the "base scenario." This architecture allows agents involved in the carbon tax scenario to have the same view on data as other agents operating on the knowledge graph and at the same time, operate in a "secured portion" of the knowledge graph without interfering with other agents or impacting the "real" world. This is represented by the "parallel world" layer in Figure 6.5.

Leonardus Kevin ADITYA (Project Officer, NTU) is involved in the implementation and unit testing of the individual agents for this use case. This includes describing the two optimisation agents developed by Aravind semantically, modifying the existing electrical grid and agents to be compatible with the "parallel world" framework, creating CSV inputs by reading data from the knowledge graph, developing codes to execute the agents and writing the simulation results back into the scenario-specific "sandbox" of the knowledge graph. Kevin is also responsible for the overall integration of the project.

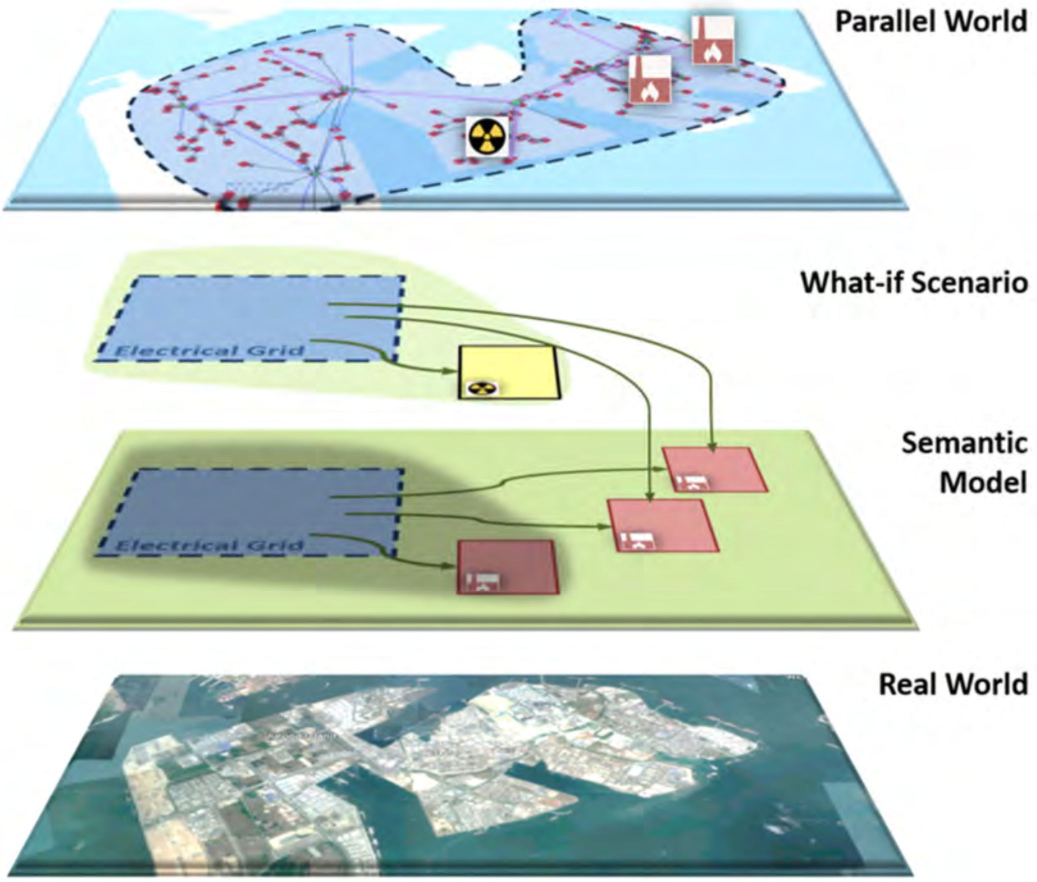


Fig. 6.5: "Parallel world" framework for what-if scenarios analysis of the carbon tax scenario. Entities are represented and linked semantically in the knowledge graph. Agents involved in the same what-if scenario operate in a scenario-specific "sandbox" of the knowledge graph. Agents involved in the carbon tax scenario have the same view on data as other agents operating on the knowledge graph and at the same time, operate in a "secured portion" of the knowledge graph without interfering with other agents or impacting the "real" world.

Update on work package JPS.3

Implementation

Dr Andreas EIBECK (Computer Scientist, CARES) is responsible for the overall architecture of the JPS and has been working on several steps to drive the JPS forward. He is heavily involved with supporting the JPS team concerning questions of software design and non-functional requirements such as performance and scalability.

Dr Jethro AKROYD (Senior Research Fellow, CAM), **Dr Sebastian MOSBACH (Senior Research Fellow, CAM)**, **Dr Feroz FARAZI (Research Associate, University of Cambridge)**, **Dr Nenad KRDZAVAC (Senior Software Developer, CARES)** and **Angiras MENON (PhD student, CAM)** have developed a single knowledge graph using a linked-data approach that connects species in chemical kinetic reaction mechanisms to computational chemistry data. This work is motivated by the fact that currently, a major barrier to using chemical models in an Industry 4.0 environment is the significant inconsistency between chemical kinetic reaction mechanisms, both in terms of the naming of chemical species and in terms of thermodynamic, kinetic and transport data. The inherent complexity of chemical kinetic reaction mechanisms and the above-mentioned inconsistency challenges render it infeasible to solve these problems manually. Instead, a systematic and automated approach is required.

For addressing the data inconsistency issues, computational chemistry data was used to calculate thermodynamic properties for each species and subsequently link the thermodynamic property data such that it can be used in the context of the chemical kinetic reaction mechanisms. This was accomplished using a number of knowledge and data-representational and computational agents. In order to link chemical kinetic reaction mechanisms with quantum chemistry calculations in the described approach, both the existing OntoKin and OntoCompChem ontologies had to be extended accordingly. In addition, a new ontology called "OntoSpecies" has been developed for uniquely representing chemical species. A species belonging to a chemical kinetic reaction mechanism can be linked to multiple computational chemistry calculations, each generated at a different level of theory and the same species belonging to multiple chemical kinetic reaction mechanisms can be linked to the same computational chemistry calculation. OntoSpecies helps to resolve these issues by having a set of unique entries, each of which corresponds to a unique real-world species. It also provides an infrastructure to link data about species derived from different sources with different levels of granularity;

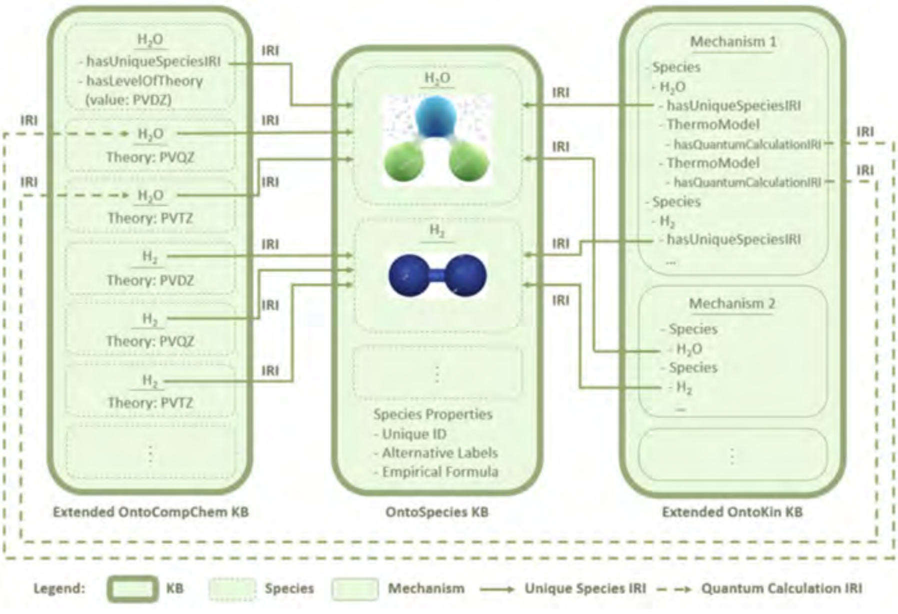


Fig. 6.6: Links between individuals in the OntoSpecies, extended OntoKin, and extended OntoCompChem knowledge bases. Instances of quantum chemistry calculations at various levels of theory as well as instances of species within mechanisms are connected to unique species by means of IRIs. Similarly, thermodynamic data associated with species in mechanisms can be connected to quantum calculations through IRIs.

in this case, chemical kinetic reaction mechanisms and computational chemistry calculations. The reason for the use of these ontologies in this work is their logical and infrastructural capabilities to manage different types of properties of chemical species. OntoSpecies has been designed to capture generic information about species, such as empirical formula and molecular weight. OntoKin, on the other hand, supports the encoding of properties that are relevant to chemical kinetic reaction mechanisms, such as thermodynamic data and transport data. OntoCompChem describes features related to computational chemistry calculations of various properties of species, such as functional and basis set. A framework for hosting and visualising linked data was also developed and deployed so that it can be used by other agents to navigate across semantically related data populated in the knowledge graph to solve species naming and data inconsistency issues.

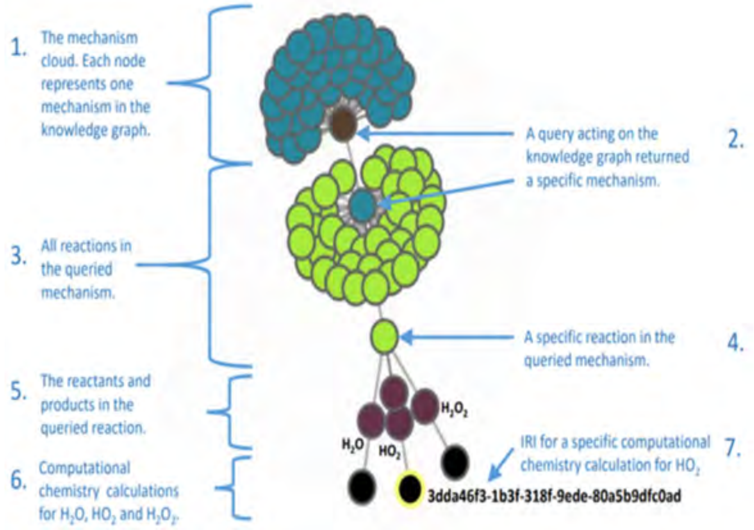


Fig. 6.7: Annotated screenshot demonstrating how chemical species in reaction mechanisms are connected to computational chemistry calculations via the linked data approach.

Furthermore, three knowledge-representational agents were designed and deployed to populate the corresponding parts of the knowledge graph built using the aforementioned ontologies and linked infrastructure. An agent was developed for representing NASA polynomials of species calculated via the hydrogen mechanism web service using OWL and to populate the OntoKin knowledge base with thermochemical data generated by the "Thermodynamic Property" agent at a specific level of theory selected by the user.

In order to illustrate the representation, linking and agent navigation capabilities of the developed framework, a use case was developed using a hydrogen combustion mechanism. Hydrogen combustion was selected mainly for two reasons: 1) it forms the basis of all hydrocarbon combustion mechanisms and 2) it is the most well-established mechanism in terms of species, reactions, thermodynamic data and kinetic data. The hydrogen mechanism used in this work consists of 10 species and 40 chemical kinetic reactions. To obtain consistent thermodynamic and kinetic data for the mechanism, Density Functional Theory (DFT) calculations were performed on all species in the mechanism using Gaussian 16. The widely applicable DFT functional B3LYP was used for all of the calculations. Geometry optimisations were performed using the tight convergence criteria. Frequencies were calculated for molecules to ensure that a minimum on the potential energy surface was located. To evaluate the effect of basis set, three different Dunning-type basis sets were used: cc-PVDZ, cc-PVTZ, and cc-PVQZ. All log files for the calculation were set to the "verbose" print standard to allow as much information to be included in the log file as possible. The resulting Gaussian 16 log files were parsed by the "Thermodynamic Property" agent, enabling the calculation of thermodynamic properties and NASA polynomial fittings for thermochemical data of the mechanism. The "Thermodynamic Property" agent calculates heat capacities, enthalpies and entropies from the species molecular partition functions using the rigid-rotor harmonic -oscillator (RRHO) treatment, which includes translational, vibrational, rotational and electronic energy contributions. Standard enthalpies of formation, together with their reference temperature, are also provided as inputs to the agent for each species.

Moreover, an API was created for extracting different types of structural and thermochemical properties of species, e.g. geometry and enthalpy of formation, from published data originating in journals or conferences to build a species knowledge base with experimental data. This knowledge base supplies the required background knowledge and inputs for quantum chemistry calculation and cross-validation tasks.

Dr Farazi is in the process of developing a web-based user interface (UI) to enhance the existing SPARQL Endpoint-based query facility of the OntoKin knowledge base. The UI will fulfil the needs to query, and compare species and reaction data across different mechanisms with minimum effort.

Dr Krdzavac is in the process of testing the Java code that performs cross-validation of a reference species set, the modification of the cross-validation algorithm and validation of model results with Angiras.

Gourab KARMAKAR (Research Engineer, CARES) and **Aravind DEVANAND (PhD student, NUS)** have demonstrated the application of OntoPowSys, a domain ontology for power systems which is expressed using a Description Logics (DL) syntax and OWL2 language, in a use case involving both chemical and electrical domains of a chemical plant. Although chemical processes and electrical power system operations are usually analysed separately, in reality, any change in the chemical processes will be reflected in the corresponding electrical load demand profile and might affect the transient stability and power quality of the electrical system. Therefore, Gourab and Aravind propose to investigate the effect of different feed flow ramp up rates on the power quality at the Point of Common Coupling (PCC). PCC is the point in the transmission and distribution network where multiple customers or electrical loads may be connected. In this use case, the debutanizer section of a typical natural gas processing plant (as shown in Figure 6.8) is considered. The debutanizer section consists of a feed pump that receives feed from upstream processes. The feed pump increases the pressure of the feed stream to the required level before sending it to the feed heater for heating. The heated feed stream is then fed into the distillation column where propane is being separated as the distillate and isobutane as the bottom product. The pressure and temperature profiles in the distillation column are maintained by the duty of the column's condenser and reboiler respectively. The corresponding electrical model of the debutanizer section (as shown in Figure 6.9) comprises a three-phase voltage source (6.6 kV Line to Line) which is used to supply electrical power to the loads connected to the transformer. The incoming voltage of 6.6 kV is lowered to 400 V using a three phase two winding step down transformer (both the windings are star connected). A constant resistive load of 5 kW and an electric motor of 200 kW (representing the feed pump) are connected to the transformer. The electric motor of the feed pump has been modelled as a dynamic load. The chemical and electrical aspects of the debutanizer section have been modelled using gPROMS and MATLAB respectively. The real power consumed by the feed pump is used to couple the chemical and electrical systems. The system is subsequently exposed to different feed flow ramp up rates. In the first case, the feed flow rate is increased from 52 kg/s to 62kg/s as a single step input. This resulted in a surge in the feed pump's power requirement that caused a fre-

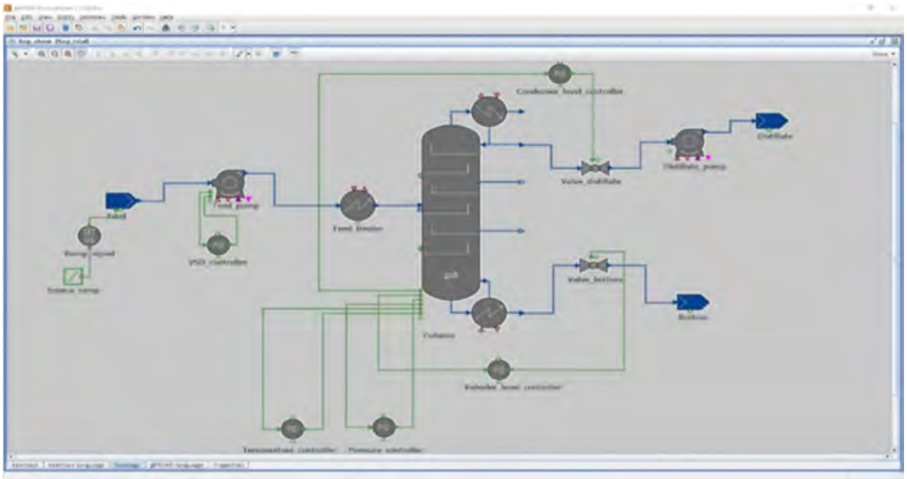


Fig. 6.8: Dynamic simulation of the debutanizer section in gPROMS.

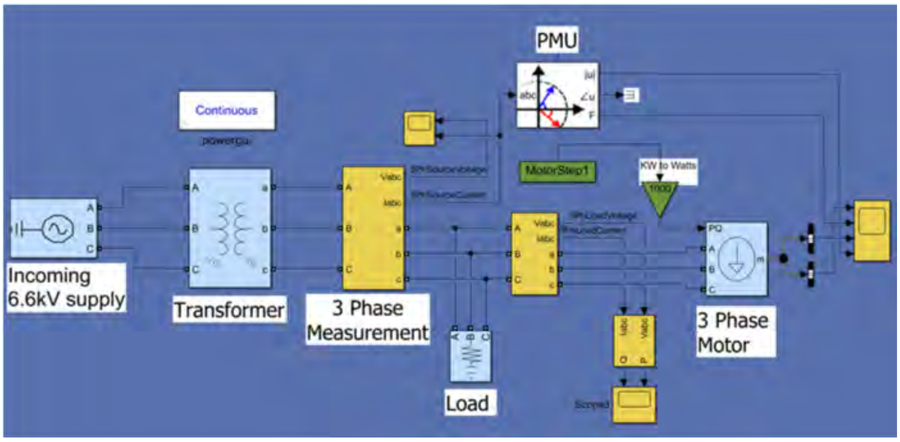


Fig. 6.9: Simulation of the electrical network of the debutanizer section in MATLAB.

quency dip of 0.4 Hz, exceeding the maximum allowable limit of 0.2 Hz set by the Singapore Energy Market Authority. The power surge also produced voltage fluctuation which exceeded the allowable limit of 3%. In the second case, the feed flow rate is increased from 52 kg/s to 62kg/s as a series of five step changes, each with a magnitude of 2.5 kg/s over a time interval of 100 s each. In this case, the frequency and voltage fluctuations are within the stipulated limits. Gourab and Aravind are in the process of extending the electrical engine model to generate a reactive power (Q) profile based on the active power (P) profile of the feed pump and translating both the chemical and power quality profiles into metrics for further analysis.

Gourab is also involved in supervising **Joel FOO (Intern, NTU)** who is developing an optimal power flow model for the Singapore's power grid by utilising OntoPowSys. In this work, OntoPowSys is used to describe the grid which currently consists of 15 buses and 25 branches. In addition, Gourab has successfully established a remote connection to the OPAL-RT, a real-time digital simulator located in NTU. This connection will allow JPS to perform real-time simulation studies for the electrical network. Furthermore, Gourab has been working on an Intra-CREATE project which involves integration of an energy demand side management framework based on advanced blockchain technologies and an energy storage technology decision-making tool with the JPS. To accomplish this, Gourab has extended OntoPowSys to describe the relevant technologies, prosumers, electrical and energy components, etc. Gourab is in the process of developing an algorithm to determine the optimal placement of energy storage element for a given grid topology.

Fig. 6.10: Remote connection of OPAL-RT in NTU to CARES office.

ZHOU Xiaochi (Software Developer, CARES) has extended his previous work on semantic web service composition framework by developing and implementing a new integrated graphical user interface (GUI), as shown in Figure 6.11, and an additional module to allow the user to further specify the internal dataflow of a composite agent. This new feature enables composite agents with identical input/output (I/O) signatures with different functional details to be created. For instance, since the classes "power plant" and "ship" are subclasses of the class "pollutant source", the two distinct agents that simulate the exhaust gas emissions from ship and power plant will be discovered and made available to the composite agent that involves the class "pollutant source" in its dataflow. With the new feature, the user can specify their interested class, e.g. ship, and create a composite agent using the composition framework to simulate the atmospheric dispersion of its exhaust gas emissions.

Xiaochi has also extended “OntoAgent”, an ontology for JPS agents, with a new property “OntoAgent:hasBlockchainAddr” to introduce compatibility with blockchain infrastructures. The new property describes and stores a hexadecimal address of the blockchain account that is assigned to the agents. This feature facilitates the agents to generate and receive transactions via blockchains and provides a decentralised yet secure way to store and manage any sensitive information of the agents, e.g. performance score.

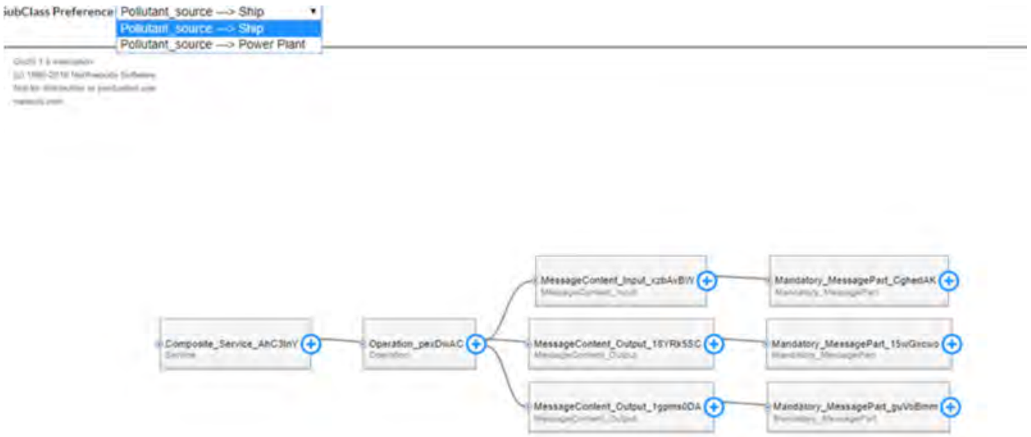


Fig. 6.11: New integrated graphical user interface (GUI) to allow the user to further specify the internal dataflow of a composite agent.

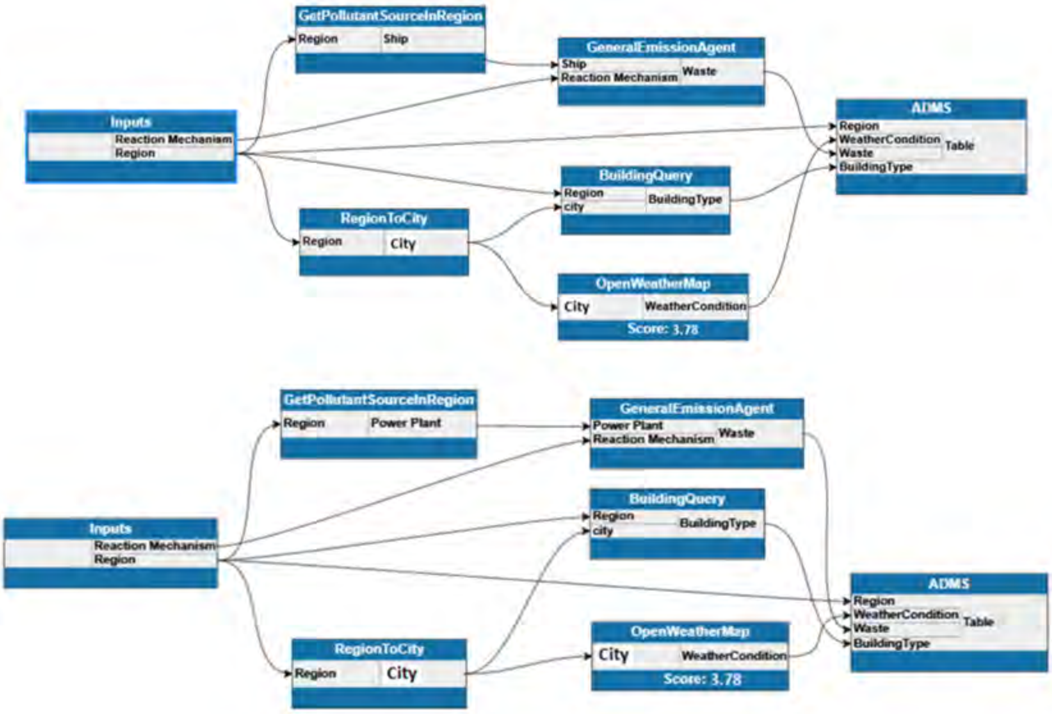


Fig. 6.12: Dataflow of composite agents that simulate the atmospheric dispersion of ship’s (top) and power plant’s (bottom) exhaust gas emissions.

Update on work package JPS.4

Model analysis and visualisation

ZHANG Shaocong (Software Developer, CARES) has investigated the use of ontology matching to integrate semantic data for power plants domain from DBpedia with the relevant data available in JPS. Ontology matching is a general technique in the semantic web technology stack that plays a pivotal role in various applications such as ontology editing, data consolidation, web service composition and multi-agent communication. Shaocong concluded from her literature review that most of the current ontology matching methodology assumes that matching is performed within similar domains. However, many platforms (such as JPS and DBpedia) are highly cross-domain in nature. In cross-domain scenarios, language ambiguity arises, e.g. the term "vessel" in the chemical engineering domain usually means a pressurised container, yet refers to a large boat in the transportation domain.

Consequently, Shaocong proposed to resolve this challenge by introducing domain information as an additional metric for ontology matching. After evaluating various frameworks, Shaocong extracted and built a minimal ontology matching framework based on “AgreementMakerLight.” In addition, Shaocong created an elemental level matcher that considers the ontology graph as a probabilistic mixture of topics and subsequently assigns topics to its entities. This enables entities to be compared on the topical metric level. Comparing the performance of the minimal framework with the novel matcher, i.e. minimal framework with elemental level matcher, the novel matcher is able to improve the F-measurement of the ontology matching by 70% in our use case. Since ontology matching is not error-free, and is meant to facilitate the matching process, i.e. a semi-automated solution, Shaocong has developed a graphical user interface (GUI) to assist human verification by displaying the scores for automatically discovered alignments. The GUI, built with HTML5, enforces cardinality constraints and visually reminds these constraints by graying out the alignments that are no longer available under the current selected set. Shaocong is in the process of extending her work from concept to instance level, i.e. data consolidation.

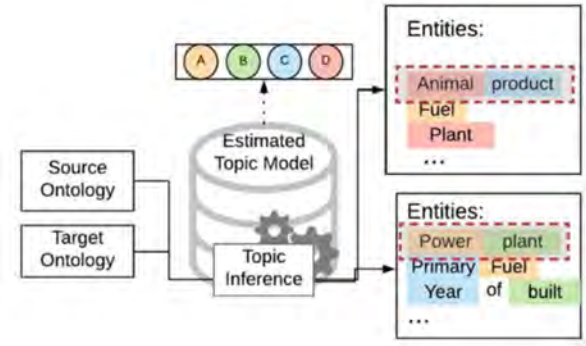


Fig. 6.13: The universal topic model generated in the installation step is used to infer the processed source / target ontology pseudo documents. In the inference step, each word in the pseudo document is assigned a topic index. Each entity, consisting of several words, is represented as a vector of K dimensions, where K is the number of overall topics in the universal topic model. The elemental comparison is realised by comparing the vectors.

Scientific output

The following are the CREATE-acknowledged publications generated by IRP JPS during the reporting period, excluding those already featured in the Scientific Highlights section on page 11.

From database to knowledge graph — using data in chemistry

Angiras Menon, Nenad Krdzavac and Markus Kraft, *Current Opinion in Chemical Engineering*

DOI: 10.1016/j.coche.2019.08.004

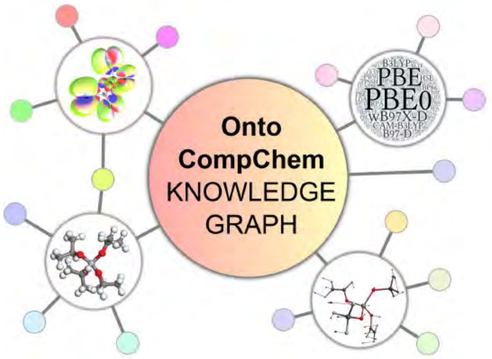
Abstract: Over the last couple of decades, the scientific community has made large efforts to process and store experimental and computational chemical data and information on the world wide web. This review summarizes several databases and ontologies available on the web for researchers to use. We also discuss briefly the categories of chemistry data that are stored, its main usage and how it can be accessed and understood in the framework of the Semantic Web.

An ontology and semantic web service for quantum chemistry calculations

Nenad Krdzavac, Sebastian Mosbach, Daniel Nurkowski, Philipp Buerger, Jethro Akroyd, Jacob Martin, Angiras Menon and Markus Kraft, *Journal of Chemical Information and Modeling*

DOI: 10.1021/acs.jcim.9b00227

Abstract: The purpose of this article is to present an ontology, termed OntoCompChem, for quantum chemistry calculations as performed by the Gaussian quantum chemistry software, as well as a semantic web service named MolHub. The OntoCompChem ontology has been developed based on the semantics of concepts specified in the CompChem convention of Chemical Markup Language (CML) and by extending the Gainesville Core (GNVC) ontology. MolHub is developed in order to establish semantic interoperability between different tools used in quantum chemistry and thermochemistry calculations, and as such is integrated into the J-Park Simulator (JPS)—a multidomain interactive simulation platform and expert system. It uses the OntoCompChem ontology and implements a formal language based on propositional logic as a part of its query engine, which verifies satisfiability through reasoning. This paper also presents a NASA polynomial use-case scenario to demonstrate semantic interoperability between Gaussian and a tool for thermodynamic data calculations within MolHub.



Other activities and achievements

Prof. Markus KRAFT (PI, CAM) visited Germany in June and was awarded one of Germany's top research prizes, the Friedrich Wilhelm Bessel Research Award. The award is given in recognition of an outstanding record of scientific achievement for internationally renowned scientists, particularly those whose work is expected to have a formative influence on their discipline.

Prof. Kraft also gave a presentation on 'Carbon capture/offset for transportation fuels' at the NUS Green Energy *Sunshine into New Energy (SHINE)* conference in August.

Prof. Kraft and **Mei Qi LIM** presented the J-Park Simulator to several visitors from A*STAR in September and discussed possible collaborations for carbon capture and utilisation projects.

Prof. Kraft receives the Friedrich Wilhelm Bessel Research Award.

Prof. Kraft gives his presentation at the NUS Green Energy SHINE *Conference.*

eCO$_2$EP

CARBON CAPTURE AND UTILISATION USING A TABLE-TOP CHEMICAL FACTORY

This is CARES’ first Intra-CREATE project, which aims to develop a “table-top chemical factory” that uses electrochemical processes to convert CO_2 into ethylene or to 1-propanol – two molecular products widely used in the chemical industry. Earlier research carried out at CREATE has demonstrated that CO_2 molecules can be transformed into hydrocarbons through the application of electro-catalysis. eCO$_2$EP’s research studies the viability of scaling CO_2 reduction processes, including techno-economic evaluation of the use of off-peak renewable electricity in areas with excess capacity. The project will allow the exploration of a new energy-chemistry solution for a more sustainable future.

eCO$_2$EP Principal Investigators:

Professor Alexei LAPKIN
University of Cambridge

Professor Joel AGER
University of California, Berkeley

OVERVIEW

The eCO_2EP project is currently in its months 18-24. The new mass-spectroscopy system (PTR-MS) has been shown to provide dynamic data on the evolution of multiple chemical species in the reaction. This information will be crucial for the elucidation of the operating regime and the reaction pathway. Also the team is expanding the range of catalysts under development and has made parallel progress in development of gas diffusion electrode system and in identifying the more selective catalysts. The latest team member to join the project is Dr Magda Barecka, who will be working on the overall technoeconomic evaluation of the proposed process.

Professor Alexei Lapkin, PI
University of Cambridge

Professor Joel Ager, PI
University of California, Berkeley

Update on work package 1

New catalyst discovery and characterisation

Dr CHEN Yubo (Research Fellow, NTU) has been looking deconvoluting the evolution of surface reconstruction in perovskites for water oxidation. He is attempting to kinetically control the perovskite's surface reconstruction, identifying its role in perovskites for the oxygen evolution reaction (OER).

Dr Chen synthesised two model OER perovskite catalysts of $Sr(Co_{0.5}Ir_{0.5})O_3$ and $Sr(Sc_{0.5}Ir_{0.5})O_3$, in which Ir is the OER active site and has a high thermodynamic stability in all PH values. The Co and Sc, with adjustable thermodynamic stability, can tune the B-site stability. Specifically, the Co is thermodynamically unstable at both high and low pH values and the Sc is thermodynamically stable at high pH values but unstable at low pH values. After analysing the surface structures of these two model perovskites before and after electrochemical tests, it was confirmed that the surface reconstruction in perovskite can be kinetically controlled. The surface reconstruction can induce an apparent activity improvement (normalised to catalysts' BET surface area) of approximately 1,000 times. This apparent activity improvement is contributed by two factors: the formation of highly amorphous surface phase(s), which has an intrinsic activity (normalised to catalysts' electrochemical surface area) of one to two orders of magnitude higher than the activity of initial crystal surface. However, the perovskite surface amorphous itself contributes little to the improvement of intrinsic activity. It is the leaching of thermodynamically unstable cations (both A-site and B-site cations), from the amorphous surface, which produces the highly active site for OER.

Dr LIU Guanyu (Research Fellow, NTU) developed a Cu-based catalyst with another metal as a dopant. It was discovered that the doped catalyst demonstrated improved activity for C-C coupling compared with the non-doped counterpart. Faradaic efficiency for C_{2+} products reached around 65%. Higher current density of C_{2+} products was also achieved. Various characterisations, such as X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy, were conducted to understand its working mechanism. In addition, a nanostructured photocathode was integrated with different electrocatalysts for photoelectrochemical carbon dioxide reduction. The products can be tuned by adjusting the parameters of the co-catalysts. A planar Si-based photocathode was also fabricated with TiO_2 passivation layer.

Dr Liu is currently working on deposition of highly selective co-catalysts to further improve their selectivity and activity for photoelectrochemical CO_2 reduction. More recently, his review article entitled "Research advances towards large-scale solar hydrogen production from water" has been published in the journal *EnergyChem* (co-authored by Yuan Sheng, Joel Ager, Markus Kraft and Rong Xu).

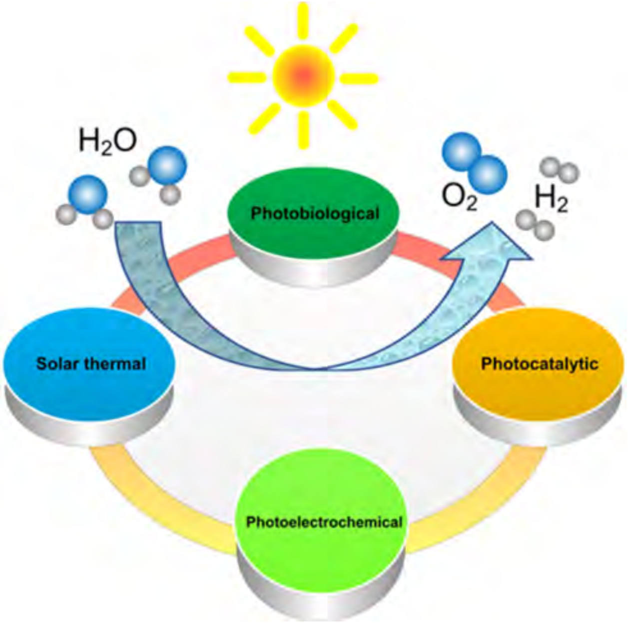


Fig. 7.1: Four pathways for large-scale solar hydrogen production from water, which are also applicable for carbon dioxide reduction.

Dr LIU Guanyu

There is a large gap in the understanding of the mechanistic chemistry occurring in the electrochemical cell to achieve its faradaic efficiencies. To better understand this, real-time analysis of the electrochemical CO_2 reduction products using proton transfer reaction time-of-flight mass spectrometry (PTRTOF MS) is the best analytical technique to provide the time dynamics of the products being studied in the eCO_2EP project. There is great potential to make use of the real time profiles to build the mechanistic models. These real-time measurements can further complement the chemical kinetics measurements and computational modelling.

With the focus above mentioned, **Dr Divya NAGARAJU (Research Fellow, NUS)** is now capable of demonstrating the eCO_2EP reduction products using PTRTOF MS in real time. Initially, an external calibration was performed to determine the instrument response to standard known analyte concentrations. In the process she has identified the unique product ion signals obtained during the ionisation of analyte molecules using reagent ions like H_3O^+, NO^+ and O_2^+. Furthermore, the work is channelled in the direction of developing automation methods for the product ion signals with greater resolution factors. The time profile data thus obtained are further used to corroborate chemical kinetics measurements.

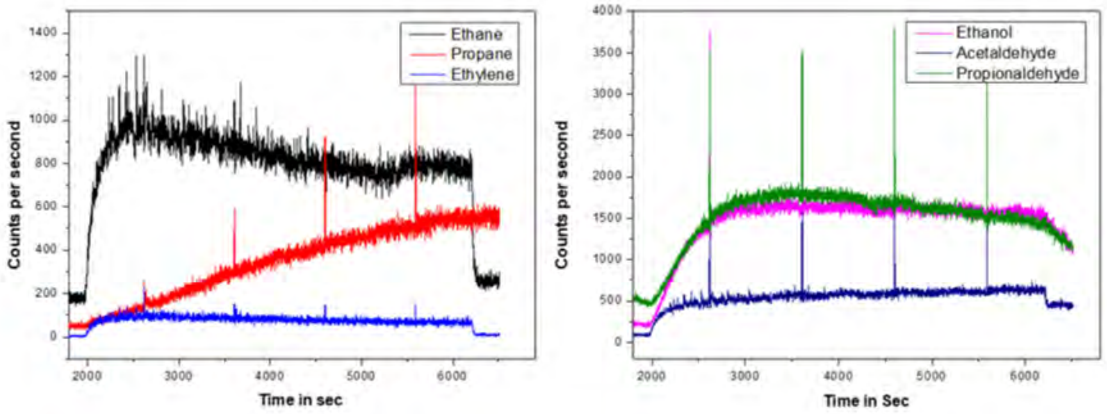


Fig. 7.2: Real-time analysis of electrochemical CO_2 reduction products. Left: gaseous products profile. Right: liquid products profile.

Dr Divya NAGARAJU

Update on work package 2

Modelling and data informatics

Dr Kuppa Ashoke RAMAN (Research Fellow, NUS), reports that with data generated from Monte Carlo simulations performed on the electrochemical reactor, along with the sensitivity ranks, he developed reduced order models using machine learning techniques. Regression models were derived to estimate the overall cell performance given by the total current density. The verification of both REG and GPR models by comparing the true values with the model predictions is shown in Figure 7.3. We observe more deviations from the true values for REG model predictions which is indicated by a smaller R^2 value when compared to the GPR model predictions.

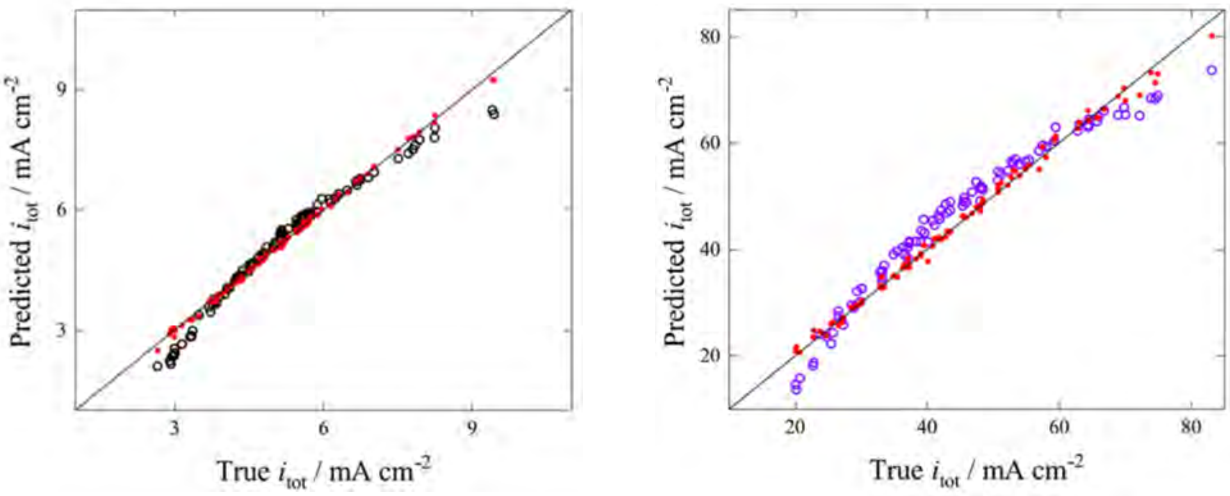


Fig. 7.3: Comparison between the REG model (circles) and GPR model (dots) for SIM scenario at E_{cell} = (a) −2.7 V and (b) -3.1V.

It is observed that with an increase in applied voltage, the deviation from linear to non-linear behaviour of the cell performance is noted due to the inherent non-linear nature of the electrochemical reaction kinetics at higher applied potential. Depending on the operating conditions, these reduced models can be used directly to perform process optimisation of the entire system.

One of the common modes of system shutdown for electrochemical reactors is through water flooding. Understanding of the interplay between the reactant transport in the gas flow channel and the liquid products is essential to mitigate this problem. In addition, catalyst degradation and pinholes in the membrane would lead to system shutdown. Under such circumstances, these is a sudden drop in the applied potential, which in turn, tunes the wettability of the gas diffusion electrode. A study to investigate the flow physics inside the gas flow channel under such conditions has been conducted. A high-density ratio based lattice Boltzmann method is employed to model the ejection dynamics and a geometry based contact angle formulation is used to cap-

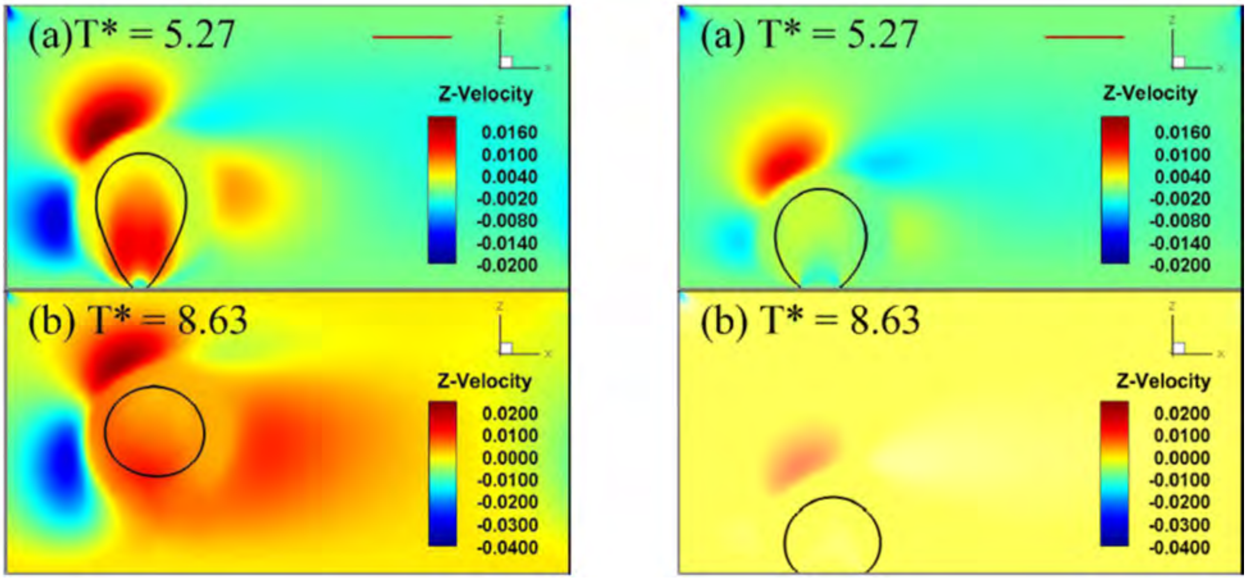


Fig. 7.4: Time sequence of droplet morphology during electrowetting induced ejection for different applied voltage: left: θ_{LY} = 40° and right: θ_{LY} = 110°.

Dr Kuppa Ashoke RAMAN

ture the three-phase contact line. We observe a characteristic head vortex at the leading end of the droplet, the strength of which increases with an increase in the shear rate. The droplet trajectory, deformation parameter, and surface energy is found to increase with an increase in the applied voltage. Variations in pulse width induce a phase shift in the temporal evolution of trajectory and deformation parameter. Due to an increase in drag forces, the droplet traverses larger streamwise distance at higher gas densities.

Dr Quang Thang TRINH (Victor) (Senior Research Fellow, NTU) reported the benchmarking study on how to choose the appropriate theory level for density functional theory (DFT) calculations of CO_2 adsorption and reactivity on transition metal surfaces. Using Ni (110) as a model catalyst surface, the binding energies of CO_2 and CO (being an essential intermediate in CO_2 conversion reactions) on the Ni surface were calculated using different DFT functionals and were compared with experimental binding energies from the literature. It was found that none of the DFT functionals could predict both CO_2 and CO binding energies on the Ni surface correctly. CO_2 binding energy on the Ni surface was correctly predicted by optPBE-vdW functional (~ -62 kJ/mol). rPBE-vdW functional underpredicted CO_2 binding energy by 33 kJ/mol while it correctly predicted CO binding energy on Ni (~ -138 kJ/mol). The DOS analysis showed that the Ni-CO_2 interaction was captured similarly by both the functionals. Three alternate reaction systems were used based on methane (no carbon-oxygen bond), methanol (no carbon-oxygen double bond) and formic acid (one carbon-oxygen double bond) in the place of gas-phase CO_2 (two carbon-oxygen double bonds) to reveal that the error in the prediction increased proportionally with the number of C=O bonds presented in the gas phase molecule. Hence, the error in prediction of CO_2 binding energy by rPBE-vdW functional was due to the treatment of carbon-oxygen double bonds in gas phase CO_2. This was further confirmed by calculating the CO_2 activation barrier and XPS shifts, as these calculations involved chemisorbed CO_2 as the reference state. The C═O activation barrier (~40 kJ/mol) and C 1s chemical shifts for probe species (~ -2.6 eV for CCH_3 and ~ +1.5 eV CO_3^-) with respect to the adsorbed CO_2 were predicted similarly by both the functionals. Therefore, it was concluded that the rPBE-vdW functional with a correction of 28 kJ/mol for gas phase CO_2 should be employed to study CO_2 conversion reaction pathways. This study and the proposed correction factor was applicable to other metals since the source of error lies in predicting the energy of gas-phase CO_2 and not in the metal-adsorbate interaction. The paper based on those results has been published on the special issue 'Recent advances in molecular simulation' of the journal *Molecular Simulation*.

Besides this, Dr Trinh also developed micro-kinetic modelling using the results from DFT simulations as input data, which could be very useful to evaluate the performance of the catalysts in the eCO_2EP project. The case study chosen was the selective oxidation of glucose to glucuronic acid on CuO catalyst under high frequency ultrasound conditions. In that study, Dr Trinh, under the supervision of Dr Matthew SHERBURNE (PI, BEARS) and collaborators from the University of Poitiers, France (under Prof. François Jérôme), provided theoretical and experimental evidence for an alternative reaction pathway provided by synergistic cavitation-copper oxide catalyst interactions. That was, H• and •OH radicals generated during cavitation bubble implosions in water were diffused onto the surface of the CuO catalyst, and selectively promoted the oxidation of glucose to glucuronic acid under argon, in contrast to the gluconic acid formation in homogeneous bulk liquid solution. Through a combined experimental-theoretical approach, it was showed that the H• radicals formed *in situ* by sonolysis of water were trapped by the surface lattice oxygen of CuO, making the ring opening of glucose energetically non-favourable. Instead, the reaction took an alternative pathway oriented to the selective oxidation of glucose to glucuronic acid, a valuable chemical whose synthesis remains a formidable scientific challenge in the field of catalysis. These results, providing first-hand insight into the participatory role of H• in the overall oxidation mechanism, also opened a scientific line of thought on the unexplained role of the atmosphere (O_2 vs Ar) observed on the catalyst-free oxidation of glucose assisted by ultrasound. From a more general point of view, this work demonstrates the general concept that the insertion of a solid catalyst during ultrasonic irradiation of organic solutes at a high frequency allows *in situ* radical reactions to be finely controlled. It also points towards a path to optimise the size of the catalyst for an ultrasonic frequency which minimises the damage to the catalyst, resulting in reusable catalyst. The paper based on those results has been published in the prestigious *Journal of the American Chemical Society*.

Furthermore, Dr Trinh also performed DFT simulations to understand the inhibitive behaviour of water extract of Aganonerion polymorphum leaf (APLWE) on a steel surface in holding back the electrochemical corrosion reactions by the establishment of a highly resistive layer, resulting in a reduction of the corrosion penetration rate. In this study with collaborators from Vietnam, it is recognised that the new green water extract of Aganonerion polymorphum leaf proves to be highly active under naturally-aerated acidic conditions of 0.1 M HCl. Moreover, this new natural compound still showed a comparatively great inhibition efficiency and a relatively low corrosion rate even at a low concentra-

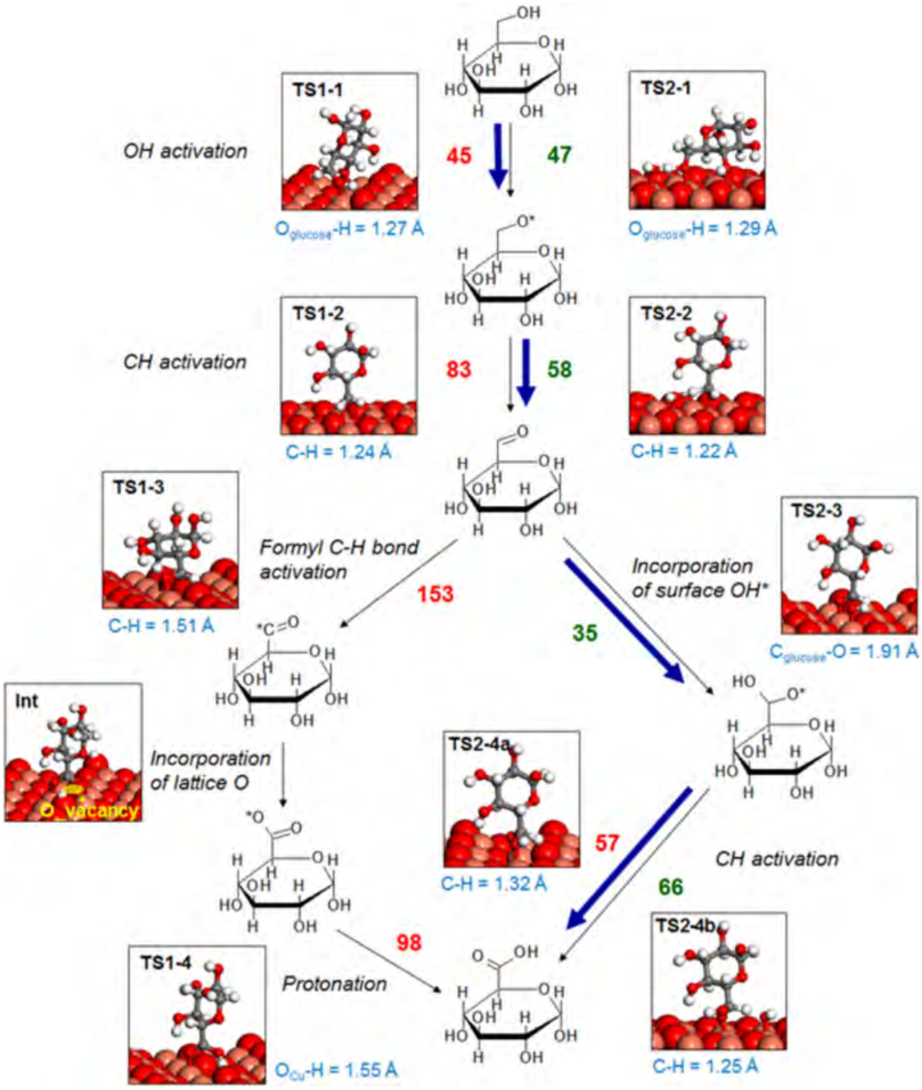
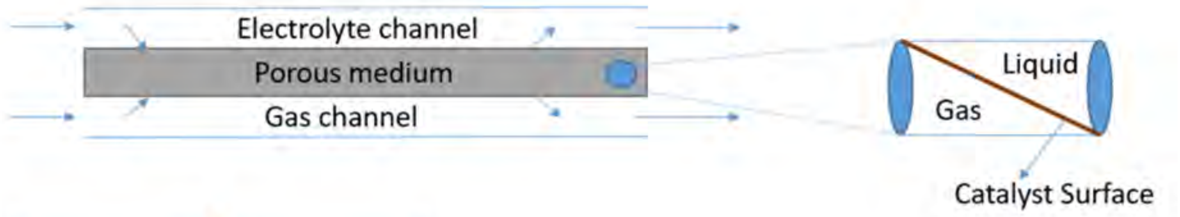


Fig. 7.5: Overall reaction network for the glucose selective oxidation to glucuronic acid on CuO surface under HFUS conditions.

Dr Quang Thang TRINH (Victor)

tion, indicating inhibitive potential of this compound under acidic conditions. Surface analysis results of steel specimens immersed in various conditions combined with electrochemical measurements showed more severe corrosion in solution without inhibitor addition, resulting in a higher corrosion rate. The theoretical methods of molecular dynamics simulations and quantum mechanics techniques suggest the contributions of active compounds as effective partial corrosion inhibitors responsible for the corrosion protection performance of APLWE. Across the range of the investigated concentrations, the incorporation of APLWE components and metal ions resulted in better preservation of the steel surface, leading to smarter inhibitor choices to provide better inhibition characterisation of these new natural compounds. The results also indicated that an increase in the APLWE concentration fully met the expected corrosion resistance for steel in naturally aerated hydrochloride solution via protective film formation that gave high inertness, good electron donation and good adhesion to the steel substrate. It resulted in a strong reduction in corrosion rates and grew the surface resistance value of steel after 24 h immersion in naturally-aerated hydrochloric solution. Therefore, it could create an expansion of the next generation for corrosion protection systems of steel used in hydrochloric acid systems. The paper based on those results has been accepted for publication in the journal *New Journal of Chemistry*.

Martin MARTIN (Research Scientist, CARES) is working on the mathematical modelling of the electrochemistry macro-kinetic system. After half a year of mathematical investigation and discussion of the Marcus Theorem for electrochemistry, he managed to implement the full model into the *k*inetics software owned by CMCL Innovations UK in August. This first implementation will be further evaluated by developers at CMCL Innovations for permanent software architecture implementation. At the moment, the standard hydrogen electrode (SHE) is used as a test case as this is a valid example from Sandia National Laboratories (USA).



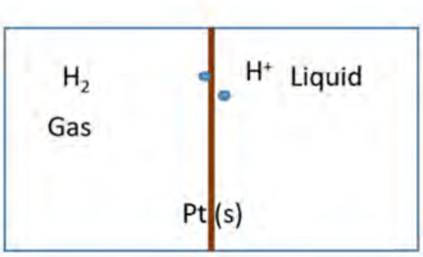


Fig. 7.6: A simplified diagram of an electrochemical reactor system. An example of the standard hydrogen electrode is illustrated.

Martin MARTIN

In reality the electrochemistry reactions only occur at the three-point boundary between the gas, surface and liquid phases as shown in Figure 7.6. Electrochemical reactions happen inside the porous catalyst. The catalyst carries the current (electron) which will interact with the ions from the liquid. In the context of standard hydrogen electrodes, the system consists of hydrogen gas, hydronium ion and hydrogen surface species where platinum acts as the available surface site (empty site).

The first reaction is a Volmer reaction,

$H^+(aq) + e^- + Pt(s) \leftrightarrow H(s)$

where, A_i, β_i and C_i are set to 1.118×10^5, 0.0 and 40000.0 respectively. In this reaction, a proton is transferred across the electric double layer to an adsorbed hydrogen on the surface where an electron combines. On platinum-like surface, it is the rate limiting elementary reaction. The parameter β^e is set to 0.5.

The second reaction is

$2\ Pt(s) + H_2(g) \leftrightarrow 2\ H(s)$

Where A_i, β_i and E_i are set to 1.90×10^{13}, 0.0 and 10000.0 respectively. This is a normal surface reaction, which is also a Tafel reaction where adsorbed hydrogen forming gas phase hydrogen in the reverse.

An additional electrochemical reaction is the Heyrovsky reaction

$Pt(s) + H_2(g) \leftrightarrow H^+(aq) + e^- + H(s)$

where A_i, β_i and E_i are set to 6.0×10^{-5}, 0.0 and 30000.0 respectively. In this reaction, the direct transfer of a proton across the electric double layer occurs. The proton then reacts with an adsorbed hydrogen atom and an electron forming a hydrogen gas. It is a rate limiting step of the hydrogen evolution reaction on some other metals, e.g. Hg. In addition, the parameter β^e is set to 0.5.

For all three reactions above, the units of the pre -exponential factor are provided in cm, mol and second and the units of the activation energy is provided in Joule and mol.

Initial and boundary conditions must be given before the simulation. The mol fraction for gas species $H_2(g)$ is set to 1.0. The site fraction for surface species is Pt(s) = 1.0 and H(s) = 0.0. Additionally, the mol fraction for H^+ ion is set to 1.0 and accordingly, its concentration is 40.62 mol/m^3. The reactor is isothermal. Reactor gas volume and liquid volume can be worked out using the ideal gas law.

Reactor gas temperature is initialised to 300.0 K, and similarly, with the surface or wall temperature. Gas pressure is set to atmospheric pressure of 1.0 atm. The site density of the catalyst which is constant is 3.0×10^{-9} mol/cm^2, specific area (ratio of surface area to volume) in electrochemical system is always 1.0.

The CANTERA software by default uses 1,000 moles instead of 1 mole, consisting of hydrogen gas (H_2). Thus, the volume of the reactor becomes 24.617 m^3. The simulation is run for 100.0 seconds and it starts at t = 0.0 seconds. Other constants such as universal gas constant and molecular weights of gas species, are also set, e.g. molecular weight of H_2 is 2.016 g/mol and of H^+ is 1.007 g/mol.

The results from SHE reaction simulation using Marcus theory are provided below. A comparison with CANTERA C++ is performed to ensure that the implementation of Marcus formalism into *k*inetics is as accurate as expected.

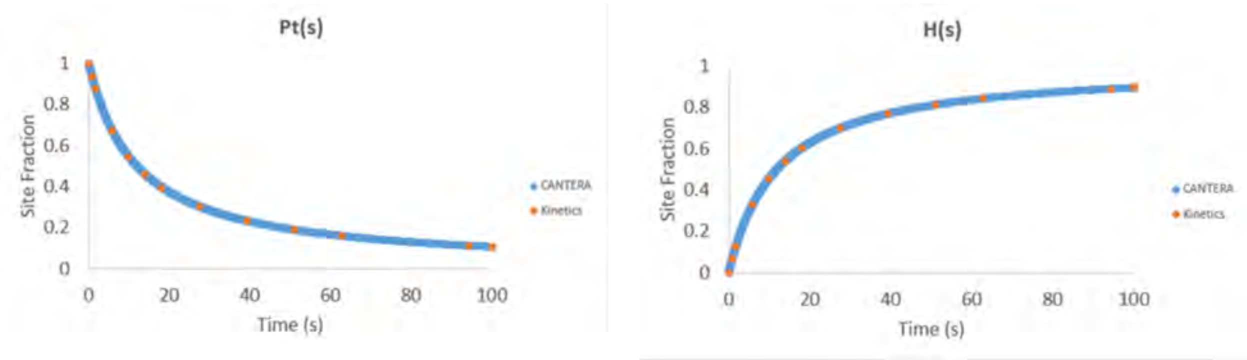


Fig. 7.7: Surface fraction of the catalyst Pt(s) and of species H(s).

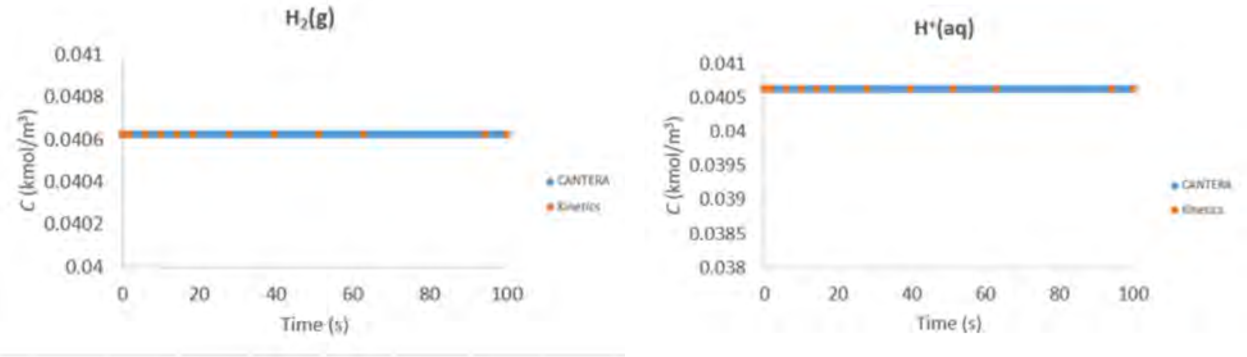


Fig. 7.8: Gas and liquid concentration of $H_2(g)$ *and of* $H^+(aq)$*.*

Martin MARTIN

The results, shown in Figures 7.7 and 7.8, show very good agreement between CANTERA C++ and *k*inetics. In the near future, *k*inetics will be used to do a sensitivity study of parameters that maximise the products, which are ethylene and 1-propanol.

Update on work package 3

Chemical factory on a table

Dr Alexandr KHUDOROZHKOV (Research Fellow, CARES) reports that development of an effective process of separation of products of CO_2 electrocatalytic reduction is mainly focused now on separation of ethylene as one of the main key components. Via the utilisation of computational chemistry (Grand Canonical Monte Carlo - GCMC) techniques several metal-organic framework (MOFs) structures were chosen and synthesised as potentially the most effective for the above mentioned separation process. Along with MOFs, some zeolite structures which demonstrate necessary pore diameter and capacity were chosen and synthesised. Analysis techniques such as powder x-ray diffraction (pXRD), infrared spectroscopy (IRS), Raman spectroscopy were used for the authentication of compounds. An experimental setup for the measurement of adsoprtion capacity, separation efficiency and effectiveness (so-called breakthrough measurements) is under construction. Further steps are including conduction of experiments and selecting most promising structures according to the result of breakthrough measurements. Possible modification of some zeolite and/or MOF structures to improve their separation effectiveness are being considered. A key factor is to achieve a high selectivity and separation efficiency even in mixtures with relatively low ethylene concentrations (1-5% vv.).

Scientific output

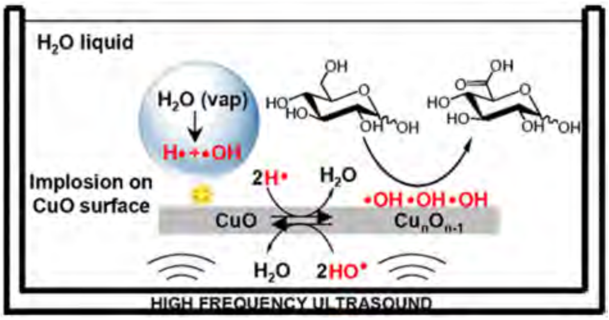
The following are the CREATE-acknowledged publications generated by IRP JPS during the reporting period, excluding those already featured in the Scientific Highlights section on page 11.

Synergistic effect of high-frequency ultrasound with cupric oxide catalyst resulting in a selectivity switch in glucose oxidation under argon

Prince Amaniampong, Quang Thang Trinh, Karine De Oliveira Vigier, Duy Quang Dao, Ngoc Han Tran, Yingqiao Wang, Matthew Sherburne and François Jérôme, *Journal of the American Chemical Society*

DOI: 10.1021/jacs.9b06824

Abstract: We report here, and rationalise, a synergistic effect between a non-noble metal oxide catalyst (CuO) and high-frequency ultrasound (HFUS) on glucose oxidation. While CuO and HFUS are able to independently oxidise glucose to gluconic acid, the combination of CuO with HFUS led to a dramatic change of the reaction selectivity, with glucuronic acid being formed as the major product. By means of density functional theory (DFT) calculations, we show that, under ultrasonic irradiation of water at 550 kHz, the surface lattice oxygen of a CuO catalyst traps H· radicals stemming from the sonolysis of water, making the ring-opening of glucose energetically unfavorable and leaving a high coverage of ·OH radical on the CuO surface, which selectively oxidises glucose to glucuronic acid. This work also points toward a path to optimise the size of the catalyst particle for an ultrasonic frequency that minimises the damage to the catalyst, resulting in its successful reuse.



Predicting CO$_2$ adsorption and reactivity on transition metal surfaces using popular density functional theory methods

Ojus Mohan, Quang Thang Trinh, Arghya Banerjee and Samir Mushrif, *Molecular Simulation*

DOI: 10.1080/08927022.2019.1632448

Abstract: In this work, with Ni (110) as a model catalyst surface and CO$_2$ as an adsorbate, a performance study of Density Functional Theory methods (functionals) is performed. CO being a possible intermediate in CO$_2$ conversion reactions, binding energies of both, CO$_2$ and CO, are calculated on the Ni surface and are compared with experimental data. OptPBE-vdW functional correctly predicts CO$_2$ binding energy on Ni (−62 kJ/mol), whereas CO binding energy is correctly predicted by the rPBE-vdW functional (−138 kJ/mol). The difference in computed adsorption energies by different functionals is attributed to the calculation of gas phase CO$_2$. Three alternate reaction systems based on a different number of C=O double bonds present in the gas phase molecule are considered to replace CO$_2$. The error in computed adsorption energy is directly proportional to the number of C=O double bonds present in the gas phase molecule. Additionally, both functionals predict similar carbon–oxygen activation barrier (40 kJ/mol) and equivalent C1s shifts for probe species (−2.6 eV for CCH$_3$ and +1.5 eV CO$_3^-$), with respect to adsorbed CO$_2$. Thus, by including a correction factor of 28 kJ/mol for the computed CO$_2$ gas phase energy, we suggest using rPBE-vdW functional to investigate CO$_2$ conversion reactions on different metals.

Capability of *Aganonerion polymorphum* leaf-water extract in protecting hydrochloric acid induced steel corrosion

Pham Van Hien, Nguyen Si Hoai Vu, Lai Xuan Bach, Ngoc Quyen Tran, Vinh Ai Dao, Quang Thang Trinh and Nguyen Dang Nam, *New Journal of Chemistry*

DOI: 10.1039/C9NJ04079J

Abstract: The requirements for an alternative to toxic localised corrosion inhibitors have always been high-performance with localised corrosion inhibition, availability, ease of manufacturing, cost-effectiveness and ecological safety. Due to its reputation in South East Asian countries as a vegetable of low-cost and environmental friendliness, *Aganonerion polymorphum*, or rather its leaf extract, can be a source of environmentally friendly and high-performing inhibitors. The effect of water extract of *Aganonerion polymorphum* leaf (APLWE) on carbon steel in 0.1 M naturally-aerated HCl solution was studied as a potential corrosion inhibitor using electrochemical techniques and surface analyses. The outcome demonstrated the mixed inhibition behavior of APLWE on the steel surface in holding back the electrochemical corrosion reactions by the establishment of a highly resistive layer, resulting in a reduction of the corrosion penetration rate. Surface appraisals indicated the existence of an adsorbed film as a complex between metal ions and an organic film of APLWE components, thereby preventing a case of corrosive degradation on the steel. The details of theoretical methods are in close agreement with experimental results, which confirmed the role of APLWE as an inhibitor through adsorption activities, providing corrosion resistance for steel in a hydrochloric environment.

Other activities and achievements

Dr CHEN Yubo (Research Fellow, NTU) gave a presentation on ’Exceptionally active iridium evolved from a pseudo-cubic perovskite for oxygen evolution in acid) at the *Low-Temperature Fuel Cells, Electrolysers & H_2 Processing* conference (EFCF-2019) in Lucerne, Switzerland in July.

Dr Divya NAGARAJU (Research Fellow, NUS) gave an invited talk on ‘Selected ion flow tube mass spectrometry for real time analysis of electrochemical CO_2 reduction reaction”, at the *Third North American SIFT-MS User Meeting* in September in Cincinnati, Ohio, US.

Dr Divya NAGARAJU presents her work at the Third North American SIFT-MS User Meeting *in the US.*

Dr Quang Thang TRINH (Victor) gave a talk on ‘Synergistic application of XPS and DFT for benchmarking GGA+U’ at the *Southeast Asia Catalysis Conference 2019*, Singapore, in May.

Dr Trinh also gave a talk on ‘Synergistic application of XPS and DFT to investigate metal oxide surface catalysis’, at the workshop *Hands-on DFT and Beyond: High-Throughput Screening and Big-Data Analytics, Towards Exascale Computational Materials Science*, in Barcelona, Spain, in August/September. This work was co-authored by Samir Mushrif and Matthew Sherburne.

Dr Alexandr KHUDOROZHKOV (Research Fellow, CARES) has gained his certificate for the utilisation of the Tip-Enhanced Raman Spectroscopy (TERS) technique for the analysis of solid samples in May.

SMALL PROJECTS

OTHER CARES-FUNDED PROJECTS

CARES is running several smaller projects and collaborations that don't fall entirely under C4T or eCO_2EP. They are often shorter, one to three years, and have only a few researchers working on them. Interns often work on these projects during their time at CARES (such as Aman SINGHAL, pictured above), which gives them a novel experience of research that is less common during their undergraduate degrees.

Many of these projects are the result of long-standing relationships with industry and other organisations, while others are the result of one-off grants from CREATE or the SMART Innovation Centre.

One project is no longer under CARES but sought funding when still part of IRP4 in C4T's Phase 1. There is a comprehensive and final update on this—Power Hardware in the Loop—on the next page.

Power Hardware in the Loop Testing Facility in the Clean Energy Research Laboratory

This work was part of the former, Phase 1 IRP4—Integrated chemicals and electrical systems operation. Prof. GOOI Hoay Beng (former Co-PI, NTU) had applied for 300,000 USD funding from the US Office of Naval Research in 2018. This was successful and the three-year project commenced in February.

Work packages

WP1: Development of a Universal HIL Platform for Hybrid AC/DC Microgrid

- Build a universal HIL platform for the hyrbid AC/DC microgrid using the OPAL-RT real time simulators OP5600 and OP5607, dspace MicroLabBox controller and Spitzenberger & Spies power amplifiers.
- Integrate and testing of PHIL system with clean energy research lab (CERL) microgrid.

WP2: Regulation and Optimisation for Hybrid AC/DC Microgrids Based on the Universal HIL Platform

- To develop the regulation and optimisation strategies for hybrid AC/DC microgrid.
- To verify developed control strategies on the universal HIL platform for the hybrid AC/DC microgrid.

WP3: Advanced power converter design for hybrid AC/DC microgrids

- To design a high reliability, high stability and high performance AC-AC power converter.
- Use the designed converter for integration of wind turbine into hybrid AC/DC microgrid.

WP4: Improved virtual synchronous machine technologies for the hybrid AC/DC microgrids

- Develop improved VSM technologies.
- Study of VSM technologies with fast dynamic performance for the hybrid AC/DC microgrid.

Work update

Introduction

In recent days, the power system and power electronics technologies have been developing rapidly. Thus, the need for the validation of the proposed concept is getting tougher due to various limitations such as the cost to set up the required hardware systems, experiments, etc. The proper validation method requires a large amount of resources and time. There are various methods for validation as shown in Figure 8.1. The simulation method is the basic one and is limited to proof of concept. It might give different results during the actual implementation of an idea. This

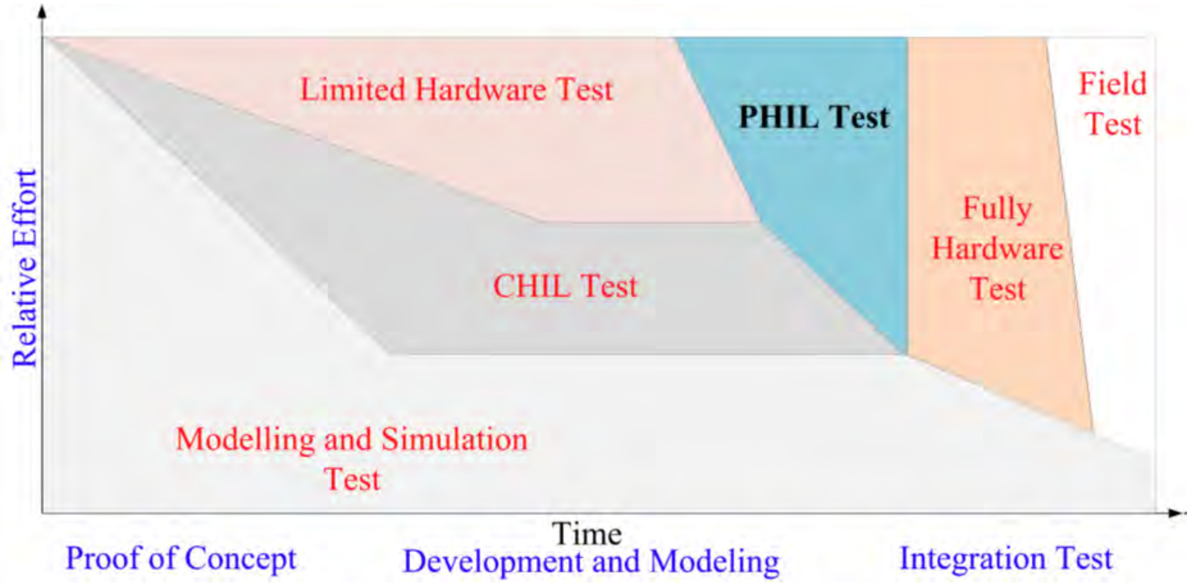


Fig. 8.1: Comparison of different verification methods.

makes some testing methods unreliable and time consuming. The full hardware test is the most effective one but it is hampered by the huge component cost and the effort to conduct the hardware experiments.

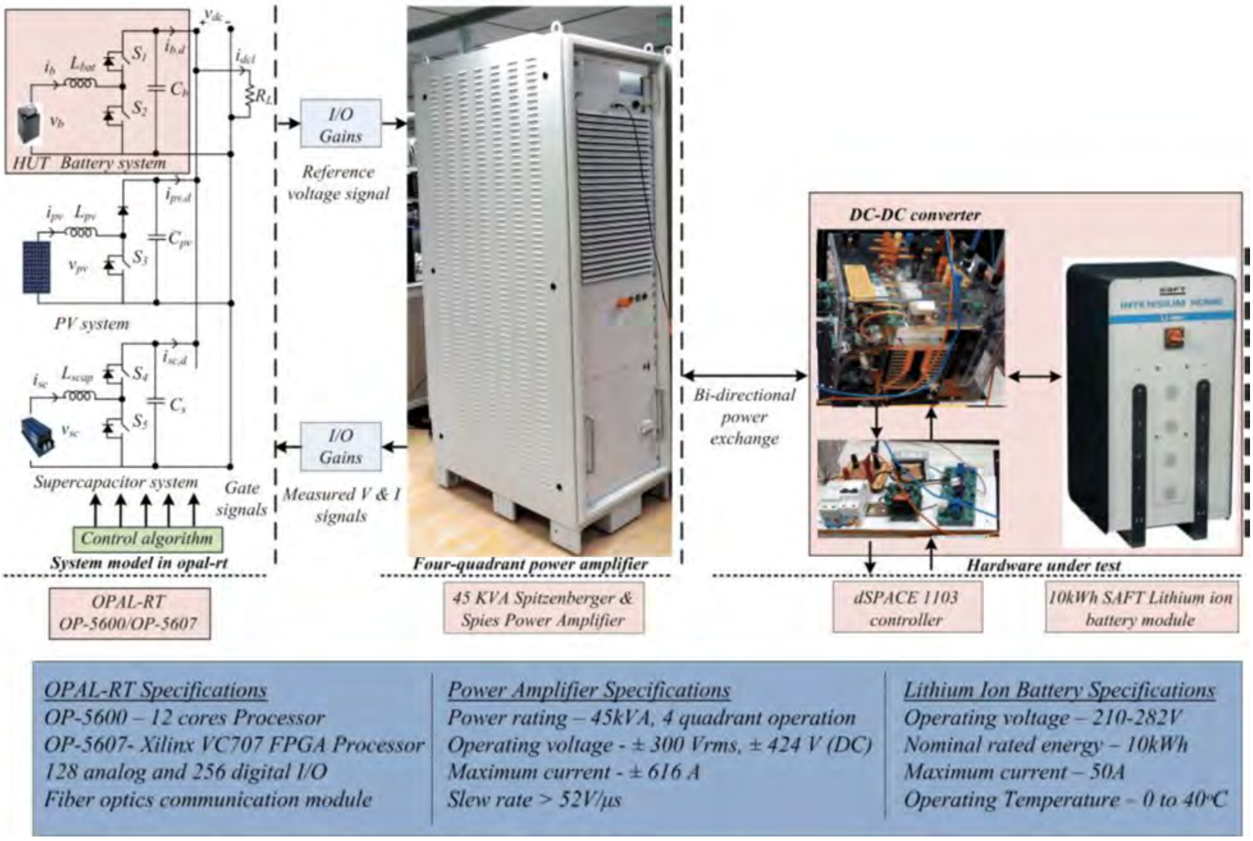
Power hardware in the loop (PHIL) is a unique way to validate the proposed system. In PHIL, the total system is divided into two parts. The numerical simulation is done in the real-time (RT) simulation platform, and the hardware under test (HUT) is interfaced through a power amplifier. The three key components for the PHIL test are RT simulator, power amplifier, and HUT. The advantages of the PHIL testing are (i) reduces system development cost, (ii) easy reconfiguration, (iii) easy to build experimental setup, (iv) provides results similar to the real hardware testing and (iv) safe to operate.

In the Clean Energy Research Lab (CERL), OPAL-RT OP-5600 and OP-5607 are used as the RT simulator. A 45-kVA four-quadrant linear three-phase power amplifier from the Spitzenberger & Spies is used to interface the RT simulator and the HUT.

With PHIL facility in the CERL, we have successfully demonstrated the two PHIL applications during the short course entitled ‘Novel hierarchical transactive energy management system incorporating predictive assessment techniques for enhanced community market participation (HTEMS)’ held in April 2019. The two demonstrations presented during the short course are briefly described below.

II. Operation of PHIL for the DC Microgrid Testing

The overall system architecture for the PHIL experiment for DC microgrid is shown in Figure 8.2. It consists of the OPAL-RT as RT simulation platform. The power amplifier is used as an interface between the OPAL-RT and HUT. The lithium-ion battery with a bi-directional DC-DC converter serves as the HUT. The DC microgrid with HESS and the PV system model are developed in the OPAL-RT platform. The voltage reference



OPAL-RT Specifications	*Power Amplifier Specifications*	*Lithium Ion Battery Specifications*
OP-5600 – 12 cores Processor	Power rating – 45kVA, 4 quadrant operation	Operating voltage – 210-282V
OP-5607- Xilinx VC707 FPGA Processor	Operating voltage - ± 300 Vrms, ± 424 V (DC)	Nominal rated energy – 10kWh
128 analog and 256 digital I/O	Maximum current - ± 616 A	Maximum current – 50A
Fiber optics communication module	Slew rate > 52V/µs	Operating Temperature – 0 to 40°C

Fig. 8.2: Architecture of the PHIL experiment for DC microgrid.

from the OPAL-RT simulation is sent to the power amplifier through an optical fiber link. The output current profile from the battery is changed based on the voltage output from the power amplifier. The real voltage and current measurements from the battery are sent back to the OPAL -RT simulation for updating the real-time simulation with necessary control actions. In this experiment, the power amplifier is operated under voltage control mode.

III. Operation of PHIL for the AC Microgrid Testing

CERL in Nanyang Technological University, Singapore has a three-phase, 400V (L-L), 50 Hz microgrid testbed to perform real-time studies associated with power systems and power electronics. It comprises 2 x 18-kVA Chroma programmable AC sources, a 6-kvar capacitor bank, a 5-kW solar photovoltaic system, 2 x 13.5-kW wind simulators, 2 x 10-kWh lithium-ion battery systems, 2 x 15-kVA Triphase power converter systems, a 5-kW fuel cell system, a 45-kVA power amplifier, a 13.5-kW programmable load, a 13.5-kVA synchronous generator and a 10-kW simulated industrial load. The microgrid is reconfigurable and can be operated in standalone mode or grid-connected mode.

The general system architecture and connections for the operation of the power amplifier together with CERL microgrid are presented in Figure 8.3. The system model is simulated in the OPAL RT simulator (OP5600 and OP5607). In the OPAL-RT simulator, the current and voltage measurements from the power amplifier are obtained through a high-speed optical link. The CERL microgrid voltage reference signal is measured using LM-55 external voltage transducer. The analog-in channel is used for the measurement of the microgrid voltage. The current reference signal for the power amplifier is calculated based on the system requirement or the simulated system in the OPAL-RT. In this experiment, the power amplifier is operated under current control mode.

The preliminary test results for voltage control mode operation, current control mode operation and the synchronisation of the power amplifier with the CERL microgrid are discussed during the short course demonstration.

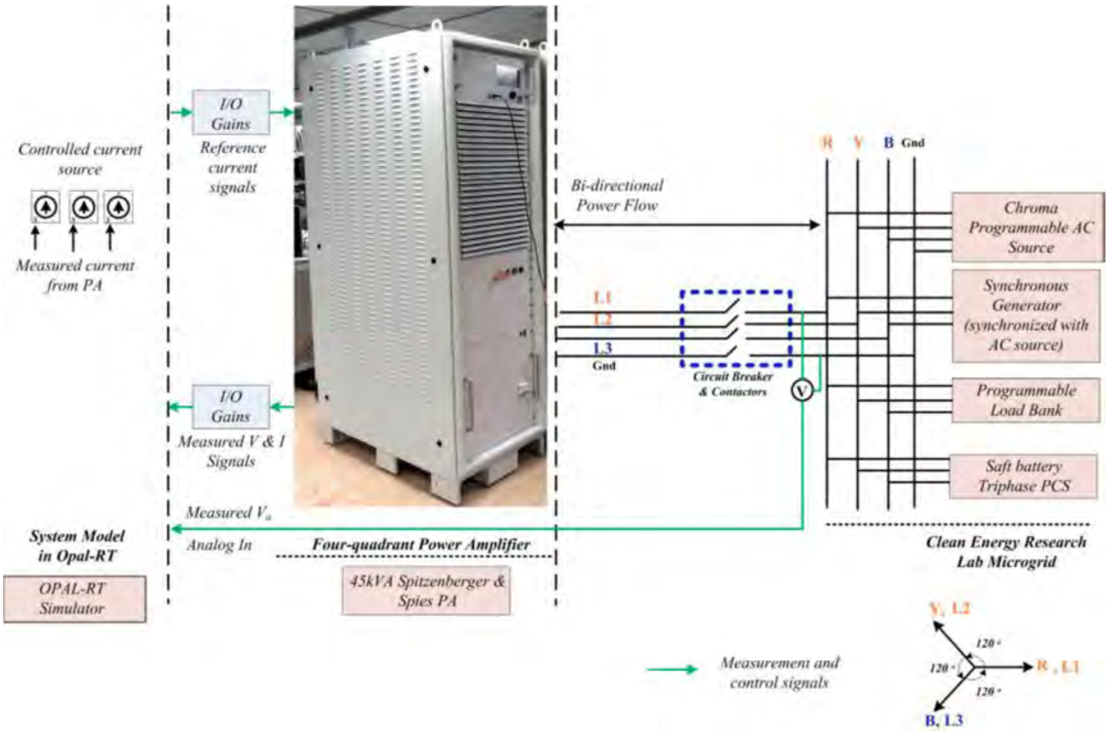


Fig. 8.3: System architecture for integration of OPAL-RT, power amplifier and CERL microgrid.

Prof. GOOI Hoay Beng

Automated Chemical Routes

With funding from BASF

Guided by Prof. Alexei Lapkin (PI, CAM), **Dr Zhen Guo (Research Fellow, CARES)** continues to work this collaborative industrial project with BASF. In this project, the automated chemical route (ACR) technique developed by Prof. Lapkin's group has been applied to search new chemical routes towards two target compounds of interest to the industrial sponsor. Compared to conventional manual design of chemical routes, ACR, as a data-driven searching technique, is much faster and more comprehensive. The aim is to find novel, efficient and green chemical routes to replace the current industrial routes which present a number of problems, such as undesired solvents, long and expensive synthesis paths and use of non-renewable starting materials. In the past six months, two promising routes for each of the target compounds were found, and the industrial collaborators are working on validation of these routes in their labs. Along the progress in the project, several topics emerged as technical motivations for further research:

1. Developing similarity based reaction network for compounds with limited synthesis records;
2. Clustering structurally similar chemicals over large chemical database;
3. Searching suitable feedstocks for targeted compound based on graph-theory and chemoinformatics.
4. Develop new molecular descriptors to cover more molecular features, such as similarity, chirality and spatial conformation;
5. Develop metrics to evaluate the feasibility of a reaction route based on molecular structures.

When the project shifted from the fine chemical target to the drug target, two challenges were identified:

1) compared to fine chemicals with rich literature records, this specific drug has only a handful of reported records in the database. This issue could be common for pharmaceuticals with unique structures;

2) Unlike the fine chemical with preferred starting compounds as requested by our industrial partner, the choice of starting compounds for the drug was open, which means any compound out of almost 1 million compounds in the reaction network stemmed from this drug can potentially be used as a starting compound.

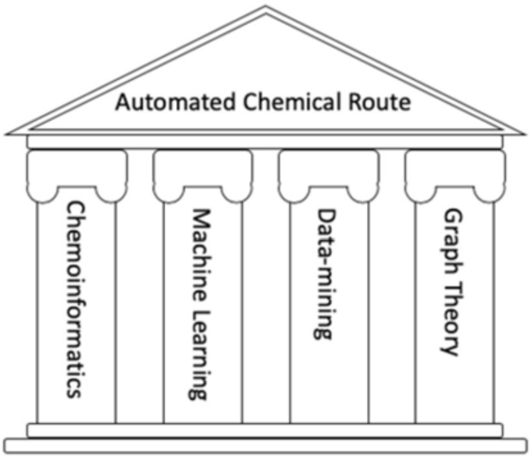


Fig. 8.4: The development of Automated Chemical Route relies on four pillars: chemoinformatics, machine learning, data-mining and graph theory.

Challenge 1 was envisaged by Prof. Alexei Lapkin (PI, CAM, IRP1) who proposed to build a similarity based reaction network on top of the current type of reaction network, at the beginning of this project. In the proposed network, a node contains molecules sharing similar structures, while a edge covers a type of reaction instead of a single reaction records. As a results, synthesis information can be largely enriched by using the similarity based network which could be essential for the target compounds with limited synthesis reports, e.g., the drug we are working on. Construction of similarity based reaction network is ongoing, some progress has been made, such as building similarity database over millions of compounds and similarity search for a one-step reaction.

To overcome challenge 2, three technical strategies have been implemented, including: 1) identify strategic molecules using graph algorithms; 2) molecular structure analysis by finding shared scaffolds and calculating similarities; 3) accelerating path searching by using multiprocessing technique. These approaches made the searching open starting compounds in large reaction network viable.

Development of Multiphase Processes in Pharma

With funding from the Pharma Innovation Programme (PIPS)

This project is led by Prof. Alexei LAPKIN. It commenced in June of this year and is due to run for three years. Within the first quarter the project has recruited three post-doctoral researchers and is in the process of recruiting a fourth. During this quarter a discussion of the chemical case study for the project between PI and industry leads has taken place and currently two industrial partners will soon start to share information with the researchers. Two post-docs—Dr Simon SUNG and Dr Mohammed JERAAL—have spent one month in intensive training in Prof. Lapkin's team in Cambridge.

Rapid Industrialisation of Next Generation Nanomaterials

With funding from the SMART Innovation Centre

This project is funded by the SMART Innovation Centre and focuses on developing an accelerated platform for developing new nanomaterials and scaling them up. This interdisciplinary project, in collaboration with A*STAR SIMTECH, combines continuous microreactors, automation, machine learning, materials science and biology. The end goal of this project is to build the platform and demonstrate its commercial application in the development of ZnO nanoparticles for antimicrobial coatings.

Swee Tong CHONG (Research Engineer, CARES) has joined the RINGs team to assist in this effort, and has been responsible for automation of various laboratory processes, 3D printing of custom-designed equipment and the synthesis and testing of nano-ZnO.

Aman SINGHAL (Research Intern, CARES) worked with Swee Tong and Nick to build a low -cost fraction collection system to be incorporated into the automated development platform.

In RINGs Nick is currently working on new manifolding strategies for microreactor scale-up, business model development and laboratory automation. He is also expanding upon previous studies for the flow synthesis of precipitation of quantum dots and pharmaceutical nanocrystals.

PUBLICATIONS

ALL C4T PUBLICATIONS WITH CREATE ACKNOWLEDGEMENT

The following list includes all the C4T publications from the beginning of Phase 2 (November 2018). Those in bold are new for this reporting period.
For a full record of Phase 1 publications (April 2013—October 2018) please visit our Publications page on the CARES website: www.cares.cam.ac.uk/publications/

C4T joint IRP publications

IRP1 and IRP3

- Kan, Xiang, Xiaoping Chen, Ye Shen, Alexei Lapkin, Markus Kraft, and Chi-Hwa Wang. 2019. "Box-Behnken Design Based CO_2 Co-Gasification of Horticultural Waste and Sewage Sludge with Addition of Ash from Waste as Catalyst." *Applied Energy* 242 (May): 1549–61. https://doi.org/10.1016/j.apenergy.2019.03.176.

IRP3 and IRP JPS

- Chhabra, Pulkit, Sebastian Mosbach, Iftekhar A. Karimi, and Markus Kraft. 2019. "Practically Useful Models for Kinetics of Biodiesel Production." *ACS Sustainable Chemistry & Engineering* 7 (5): 4983–92. https://doi.org/10.1021/acssuschemeng.8b05636.
- **Krdzavac, Nenad, Sebastian Mosbach, Daniel Nurkowski, Philipp Buerger, Jethro Akroyd, Jacob Martin, Angiras Menon, and Markus Kraft. 2019. "An Ontology and Semantic Web Service for Quantum Chemistry Calculations."** ***Journal of Chemical Information and Modeling*** **59 (7): 3154–65. https://doi.org/10.1021/acs.jcim.9b00227.**
- **Menon, Angiras, Nenad B Krdzavac, and Markus Kraft. 2019. "From Database to Knowledge Graph — Using Data in Chemistry."** ***Current Opinion in Chemical Engineering*** **26 (December): 33–37. https://doi.org/10.1016/j.coche.2019.08.004.**

C4T IRP1: Sustainable reaction engineering

- **Amar, Yehia, Artur M. Schweidtmann, Paul Deutsch, Liwei Cao, and Alexei Lapkin. 2019. "Machine Learning and Molecular Descriptors Enable Rational Solvent Selection in Asymmetric Catalysis."** ***Chemical Science*** **10 (27): 6697–6706. https://doi.org/10.1039/C9SC01844A.**
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- **Li, Bowen, and Hua Chun Zeng. 2019. "Synthetic Chemistry and Multifunctionality of an Amorphous Ni-MOF-74 Shell on a Ni/SiO_2 Hollow Catalyst for Efficient Tandem Reactions."** ***Chemistry of Materials*** **31 (14): 5320–30. https://doi.org/10.1021/acs.chemmater.9b02070.**
- **Qin, Runze, and Hua Chun Zeng. 2019. "Confined Transformation of UiO-66 Nanocrystals to Yttria-Stabilized Zirconia with Hierarchical Pore Structures for Catalytic Applications."** ***Advanced Functional Materials*** **29 (39): 1903264. https://doi.org/10.1002/adfm.201903264.**
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C4T IRP2: Electrosynthetic pathways

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C4T IRP3: Combustion for cleaner fuels and better catalysts

- **Boje, Astrid, Jethro Akroyd, and Markus Kraft. 2019. "A Hybrid Particle-Number and Particle Model for Efficient Solution of Population Balance Equations."** ***Journal of Computational Physics*** **389 (July): 189–218. https://doi.org/10.1016/j.jcp.2019.03.033.**
- **Bowal, Kimberly, Peter Grančič, Jacob W. Martin, and Markus Kraft. 2019. "Sphere Encapsulated Monte Carlo: Obtaining Minimum Energy Configurations of Large Aromatic Systems."** ***The Journal of Physical Chemistry A*** **123 (33): 7303–13. https://doi.org/10.1021/acs.jpca.9b04821.**
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IRP4 (Better, cleaner heat usage) and IRP BB (Pathways to industrial decarbonisation) are new projects in Phase 2, so there are no publications from these IRPs at the present time.

C4T IRP JPS: The J-Park Simulator

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eCO$_2$EP: Carbon capture and utilisation

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This research is funded by the National Research Foundation, Prime Minister’s Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme.

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