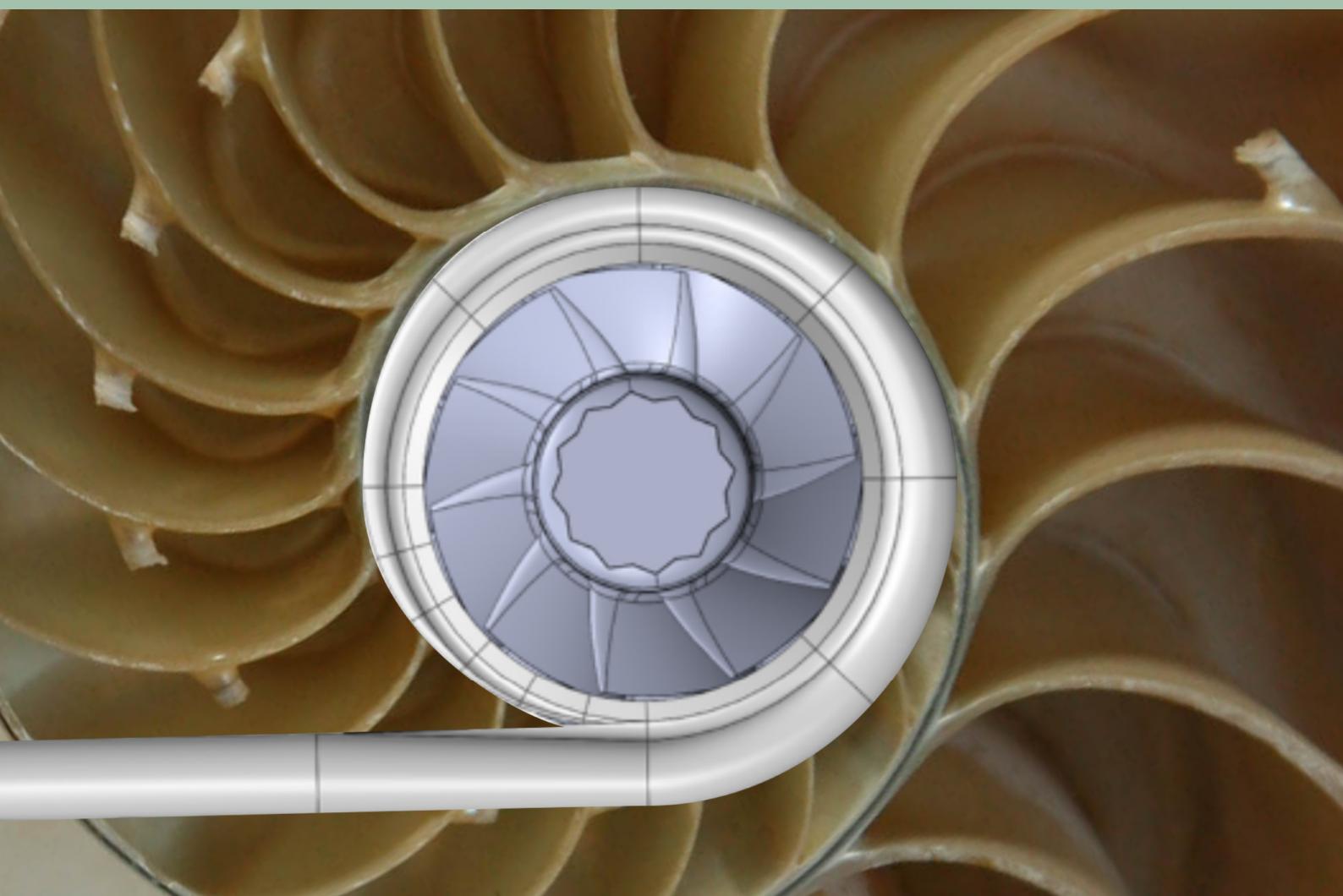


# CAMBRIDGE CARES

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



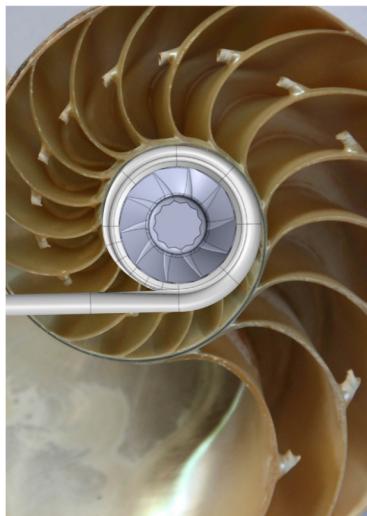
**Biannual Research Report  
November 2019 - March 2020**



**CAMBRIDGE  
CARES**

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EDUCATION IN SINGAPORE LTD

## Cover image



The turbine from the secondary flow injection system combined with an image of a nautilus shell.

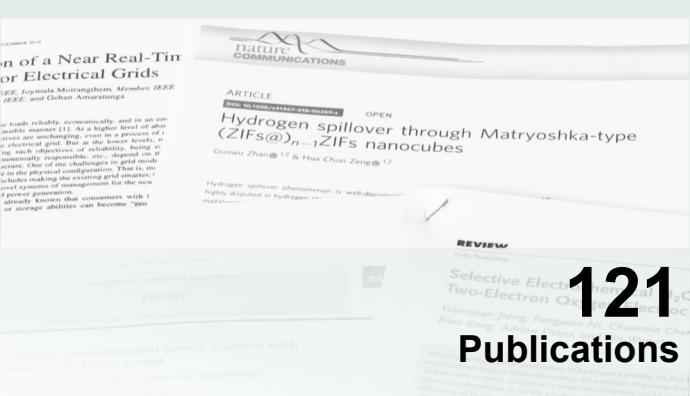
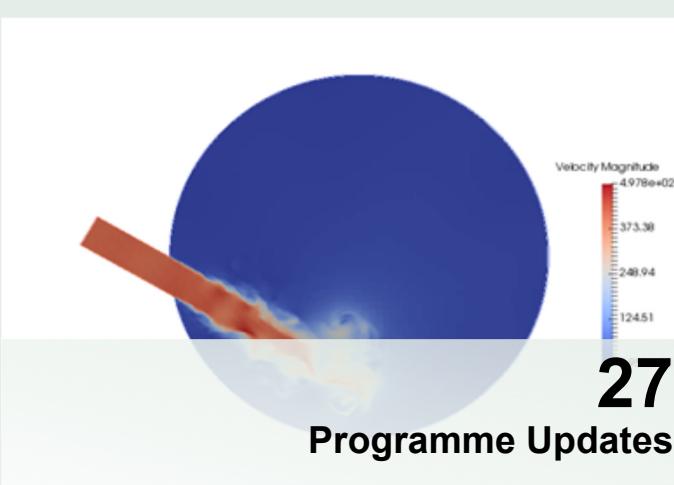
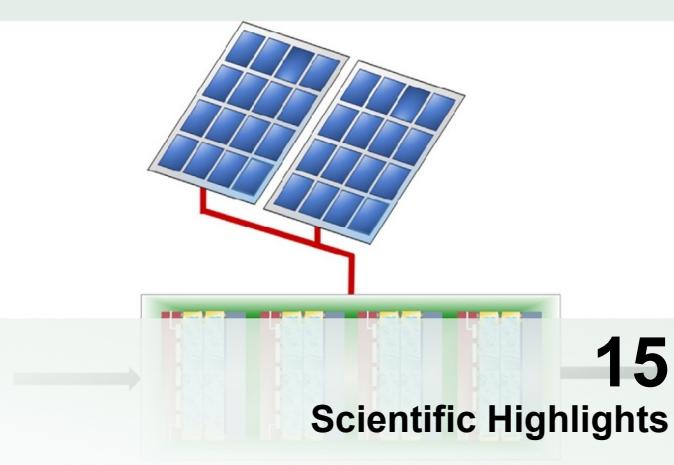
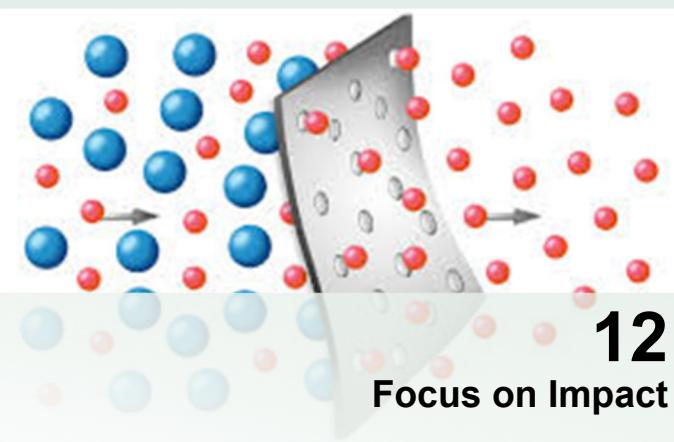
*Image by Zheng LIU, Research Associate, IRP4.*

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1 Create Way, #05-05 CREATE Tower  
Singapore, 138602

[cares@hermes.cam.ac.uk](mailto:cares@hermes.cam.ac.uk)  
[www.caress.cam.ac.uk](http://www.caress.cam.ac.uk)



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# FOREWORD

## EMERGING OPPORTUNITIES FUND

The C4T Emerging Opportunities Fund supports exciting new ideas that have arisen since the start of Phase 2. Some of the EOF projects have now commenced, including an investigation into clean technology initiatives in the shipping industry, new electrocatalysis methods that use machine learning and the production of H<sub>2</sub>O<sub>2</sub> using electrochemistry for lower energy usage and reduction of waste.

## INTELLIGENT DECARBONISATION BOOK

In a culmination of much of the work that CARES has done in this space, following his successful series of visits to Singapore under the CARES Visiting Scientists programme, Oliver Inderwildi and I have secured a book deal with Springer to publish "Intelligent Decarbonisation: Using AI and CPS to Achieve Climate Mitigation Targets". I am delighted Dr Lim Khiang Wee (NRF CREATE) has agreed to write the foreword—most appropriate as the idea for the book has been nurtured in the supportive environment of CREATE!

## CAMBRIDGE-CARES STUDENTS

Many of our Cambridge-CARES students have handed in their PhD theses, and/or graduated over the past few months—Nicholas Jose, Janusz Sikorski, Astrid Boje, Manoel Manuputty, Casper Lindberg and Jacob Martin. We are very proud of them and wish them all the best for their next steps.

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  
April 2020



# 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<sub>2</sub> 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.

The second large programme administered by CARES is eCO<sub>2</sub>EP. 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

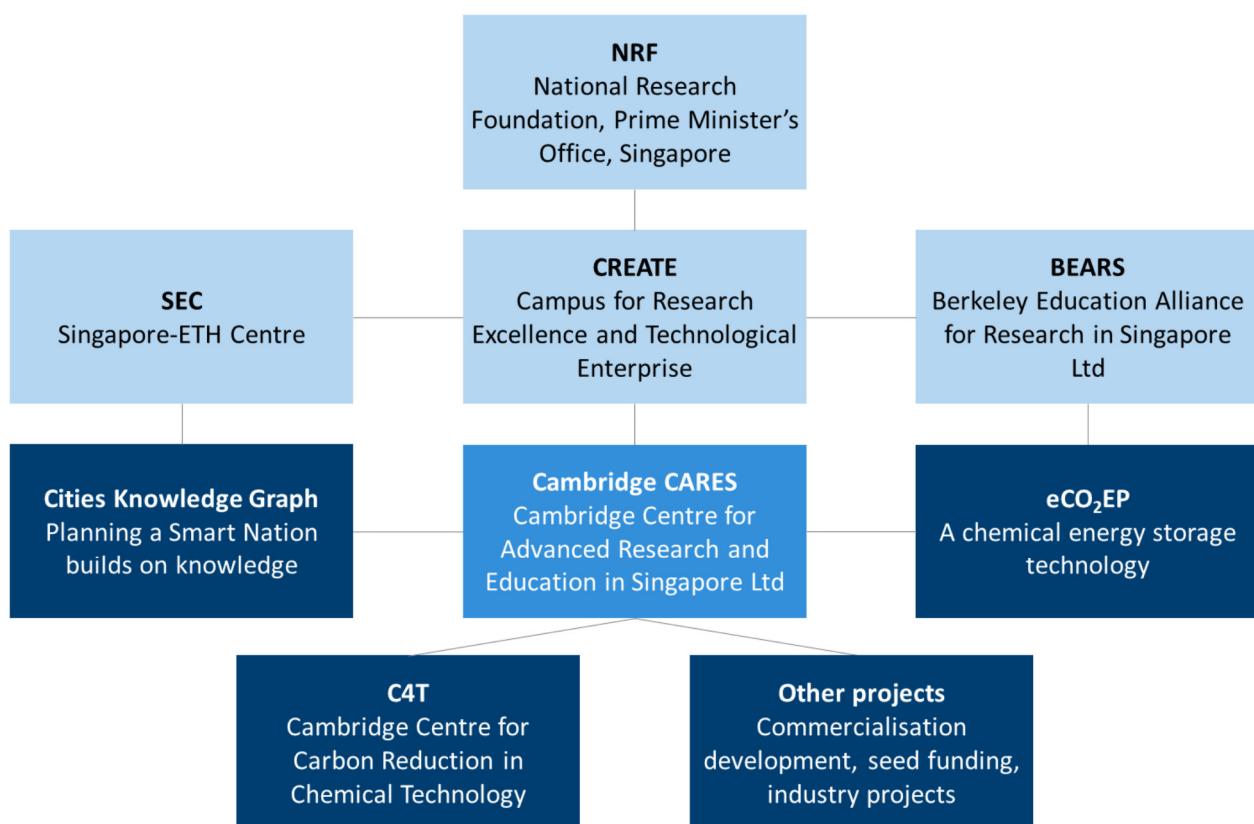
## Cambridge CARES

carbon dioxide emitted as part of the industrial process into compounds that are useful in the chemical industry supply chain. This programme is funded by an Intra-CREATE large grant.

As of 1<sup>st</sup> April 2020, CARES has been awarded a further Intra-CREATE large grant for Cities Knowledge Graph, which brings together researchers from University of Cambridge and ETH Zürich to harness rapidly growing and diversifying data streams to improve the planning and design of cities. Cities Knowledge Graph will do this by developing an innovative digital platform designed to combine data and share knowledge about cities, and to inject new precision and responsiveness to static instruments of planning, such as the city master-plan.

As well as these large Intra-CREATE grants, CARES has several smaller projects ongoing. There is one smaller, seed-funded Intra-CREATE project between CARES and National University of Singapore, and three further projects that involve industry and/or commercial funding. Details and updates for these smaller projects can be found on page 115.

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.



society, research in sustainable and renewable energy sources ranging all the way from wind energy to wind energy has been gaining traction lately. Fuel cells have been extensively studied since the early 20th century.

The main components of fuel cells are the electrolyte, electrodes (anode and cathode), and catalysts. Fuels such as hydrogen, methanol, propane, etc., are supplied to the anode. At the same time, the cathode is provided with an oxidant, usually oxygen. The electrolyte is

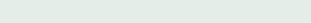
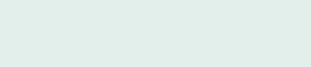
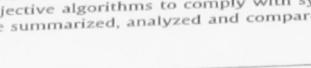
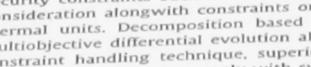
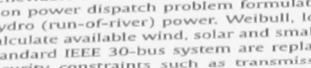
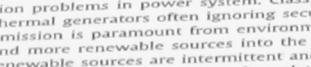
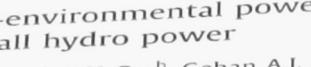
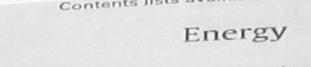
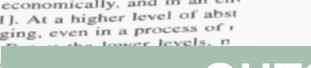
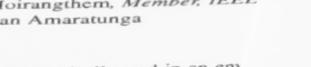
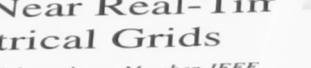
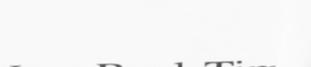
also termed as

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

Kamal Elouarzaki<sup>1,2,3</sup>, Daojian Cheng<sup>3,4</sup>, Adrian C. Fisher<sup>2,3,5</sup> and Jong-Min Lee<sup>1,2\*</sup>

Enzymes are promising electrocatalysts for electron transfer (ET) in many biological processes. Strategies to enhance ET between enzymes and electroactive surfaces include orientation and immobilization of the enzymes and electron mediators. Here, we develop a strategy to couple orientation and electron mediation on electrodes based on carbon nanotubes. This is achieved by the synthesis of a redox mediator with a specific orientation site (pyrene), an electron-carrier redox mediator (ABTS), and an enzyme (cytochrome c oxidase (cyt c)) on the same carbon nanotube (pyrrole-ABTS-pyrene). The coupling of an enzymatic mediator with a redox mediator improved ET in the same chemical structure (pyrrole-ABTS-pyrene). We demonstrate two fuel cells for the synthesized hybrid biofuel cell, which provided a much-improved performance in the hybrid biofuel cell. We demonstrate two fuel cells for the synthesized hybrid biofuel cell, which provided a much-improved performance in the hybrid biofuel cell. We demonstrate two fuel cells for the synthesized hybrid biofuel cell, which provided a much-improved performance in the hybrid biofuel cell. The principle of coupling an enzyme and a redox mediator in a proton-exchange membrane hydrogen/air fuel cell and in a microbial fuel cell is proposed. Our strategy for coupling orientation and a redox mediator allows a great variety of mediators to be engineered and provides vast possibilities for the development of hybrid biofuel cells.

Among these methods, DET is influenced strongly



# FOCUS ON FUNDAMENTAL SCIENCE

## Optimising finned tube heat exchangers for effective heat transfer

Dr Matthew LAW Lee Liong, Research Fellow, C4T IRP4

### What are finned tube heat exchangers?

Finned tube heat exchangers, as the name suggests, consist of tubes – single-pass or multi-pass/coils – with extended outer surface area called fins from the otherwise bare tubes. These fins serve the sole purpose of enhancing the rate of heat exchange by increasing the effective heat transfer area between the tubes and surrounding fluid, usually air.

Finned tube heat exchangers are widely used as industrial heat exchangers in industrial dryers,

power plants, waste heat recovery systems, etc., and in a variety of household applications due to their compactness, ease of implementation and robust construction. For example, an air heat exchanger like the evaporator coil for air conditioning units (shown in Figure 1) and the condenser coil on refrigerators are typically a finned tube heat exchanger. Another common finned tube heat exchanger is the car radiator. The purpose of the car radiator is to remove heat from the hot water that flows inside the tubes to the air blown through it by the fan.



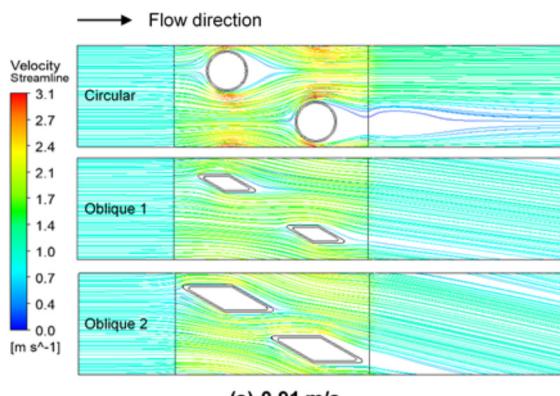
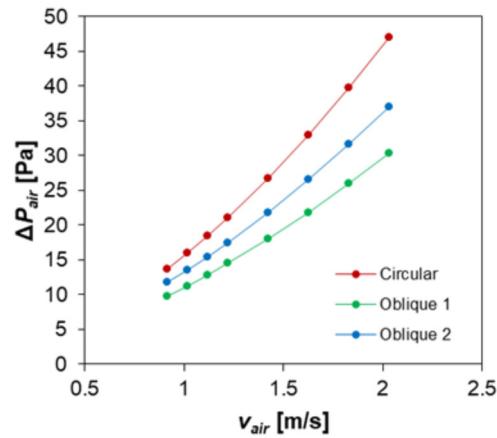
Fig. 1: Evaporator coil inside an air conditioning unit.  
(Image adapted from: <https://skyjuiceiswater.blogspot.com/2018/12/how-to-clean-air-conditioning.html>)

Matthew completed his Bachelor of Engineering (1<sup>st</sup> Class Honours) in Mechanical Engineering at Universiti Malaysia Perlis in 2011 and developed an interest in the area of heat transfer and fluid flow along the way. He joined the workforce as an Engineer for a brief period upon graduation, before being accepted by the National University of Singapore to pursue his Ph.D. in Mechanical Engineering in 2012. His doctoral studies was on two-phase flow boiling heat transfer enhancement in microchannels using novel fin structures under the supervision of Professor Lee Poh Seng. He completed his Ph.D. in 2016 and went on to work with Professor Wang Qing and Professor Lee Poh Seng in the National University of Singapore as a Research Fellow for three years. In 2019, he joined Cambridge CARES as a Research Fellow under the C4T interdisciplinary research group.



One of the main challenges faced by finned tube heat exchangers is the high thermal resistance on the air-side due to the extremely poor heat transfer properties of air. As a result, the focus of most studies are on novel methods to enhance air-side heat transfer of such a heat exchanger, while at the same time, controlling the pressure drop penalty incurred with these new designs.

These efforts can be broadly categorised into two categories: 1) Modifications to the tube geometry [1-3] and 2) Modifications to the fin structure [4-7]. The present work focuses on the first category, which aims to improve the air-side heat transfer performance and control both the air-side and water-side pressure drop by using oblique tubes.



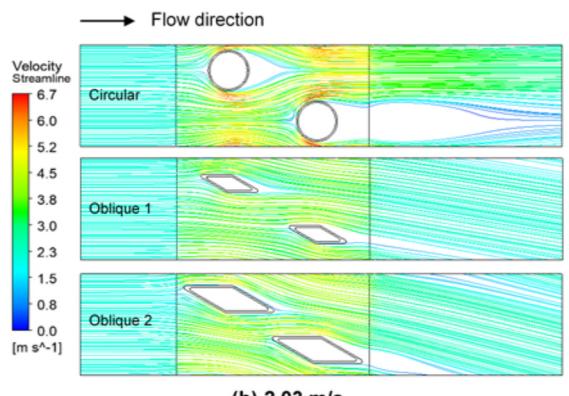
(a) 0.91 m/s

### Air-side performance: pressure drop

Air-side pressure drop across the circular tube is the highest at any given air flow rates, followed by Oblique 2 and Oblique 1, as shown in Figure 2. Streamline profiles are plotted to explain this pressure drop trend.

As seen in Figure 3, the large wake regions in the downstream location of each circular tube contribute to increased pressure drop [8]. Wake regions can also be found downstream of the oblique tubes, but are much smaller due to their more slender shape coupled with a smaller frontal area. On the other hand, the overall smaller footprint of Oblique 1 produces less flow resistance compared to the larger Oblique 2 footprint, which results in lower pressure drop for the former.

Fig. 2: Air-side pressure drop across circular and oblique tubes.



(b) 2.03 m/s

Fig. 3: Streamlines of air flow across the tubes at lowest and highest flow rates.

### Air-side performance: heat transfer

As plotted in Figure 4, the outlet air temperature for both the oblique tube geometries is consistently lower due to smaller wake regions/flow recirculation zones immediately after the tubes [8, 9]. Besides that, the earlier reattachment of the separated flow behind the two oblique tubes gives rise to their more superior heat transfer performance [10]. Oblique 2 has the lowest outlet temperature because of a larger (54%) tube surface area.

As a result of lower pressure drop coupled with more superior heat transfer, it can be shown in Figure 5 that the oblique tubes are able to deliver more cooling per unit fan power (at 80% fan efficiency) compared to their circular counterpart. In other words, a lower fan speed can be used to provide comparable air-side heat transfer performance for the finned oblique tube heat exchanger.

### Water-side performance: Pressure drop comparison between Circular and Oblique 1

As recorded on Table 1, pressure drop along the oblique tube is 13 times higher than circular tube. This extremely high water-side pressure drop penalty is very undesirable, even though there are evident air-side pressure drop and heat transfer improvements. This is because maintaining a comparable tube surface area resulted in a reduction of the oblique tube cross sectional area by 2.7 times. This causes the flow velocity along the oblique tube to increase by the same factor.

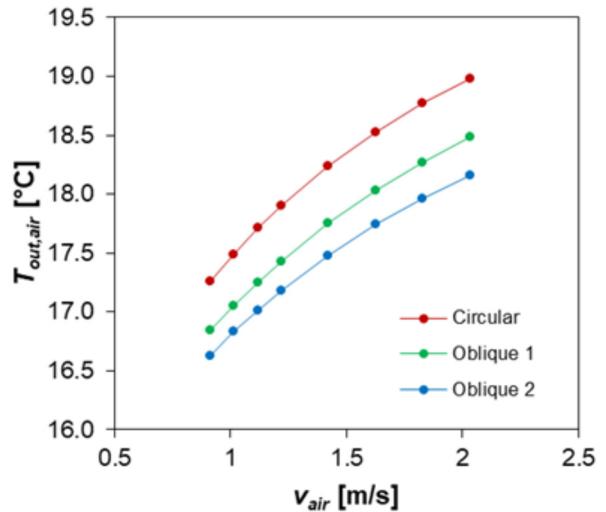


Fig. 4: Outlet air temperature of circular and oblique tubes.

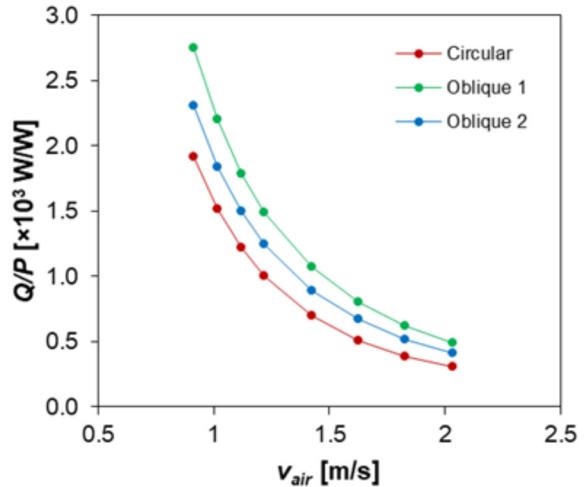


Fig. 5: Cooling per unit fan power of various tube geometries.

Table 1: Comparison of pressure drop and tube size between Circular and Oblique 1

	Circular	Oblique 1	Difference [%]
Pressure drop [Pa]	10.09	130.46	1190
Tube surface area [mm <sup>2</sup> ]	84.19	82.58	1.9 (negligible)
Tube cross section [mm <sup>2</sup> ]	107.51	39.29	63.5

## Water-side performance: Pressure drop comparison between Circular and Oblique 2

Figure 6 shows the pressure drop comparison between circular tube and oblique tube. As the cross sectional area of the oblique tubes is now comparable, its pressure drop is more manageable, with penalties ranging from 55.7 to 58.3% for the flow rates tested.

The higher pressure drop along the oblique tube can be seen in the pressure distribution plots in Figure 7. There are relatively more high pressure regions along the Oblique 2 tubes due to their irregular cross section. On the other hand, high pressure regions are mostly concentrated at the centre of the circular tube where flow velocity is the highest.

To conclude, a series of three-dimensional numerical simulations were carried out on the finned circular and finned oblique tube heat exchangers to study their thermohydraulic performances. From the comparison above, it can be concluded that the finned oblique tubes offer more superior air-side heat transfer with lower pressure drop, which allows the heat exchanger to deliver more cooling per unit fan power.

Employing a more effective waste heat recovery unit, such as the finned oblique tube heat exchanger in waste heat recovery applications is seen as one of the key enablers in achieving high-efficiency engines. These high-efficiency engines contribute to increased energy savings via a reduction in energy consumption and reduced environmental impact by regulating greenhouse gases emission. This, in turn, directly enhances the overall thermal efficiency of a power plant.

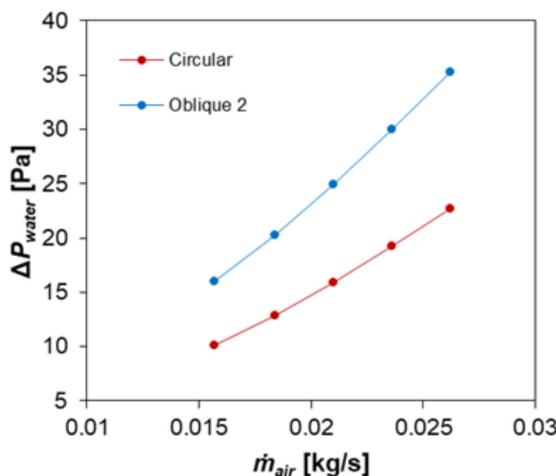


Fig. 6: Pressure drop along Circular and Oblique 2 tube geometries.

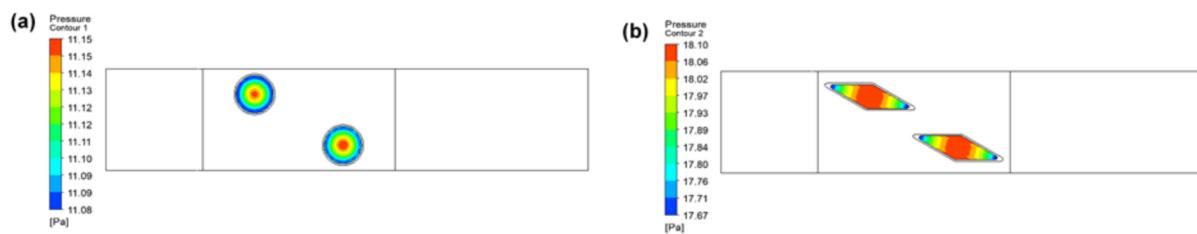


Fig. 7: Pressure distribution along (a) circular and (b) oblique tubes at 0.0262 kg/s.

# FOCUS ON

# IMPACT

## Application of MOFs and zeolites in separation

Dr Alexandre KHUDOROZHKO, Research Fellow, eCO<sub>2</sub>EP

In general, separation is the process of dividing a mixture into constituents or distinct elements.

In chemistry and the chemical industry, separation of mainly gas and liquid mixtures is a common process, used primarily to achieve two results: obtaining a pure compound and increasing the yield of the target product or products. Almost all separation techniques include a combination of physical (gravitation, electromagnetic field, physical adsorption, evaporation/distillation) and chemical (chemisorption, specific chemical reactions) processes.

Separation of a gas mixture containing products of carbon dioxide reduction such as carbon dioxide, hydrogen and hydrocarbons can effectively be done via "molecular sieving", when compounds like zeolites with particular pore size and specific volume may be used as sieves to separate molecules of different sizes from each other (Figure 1).

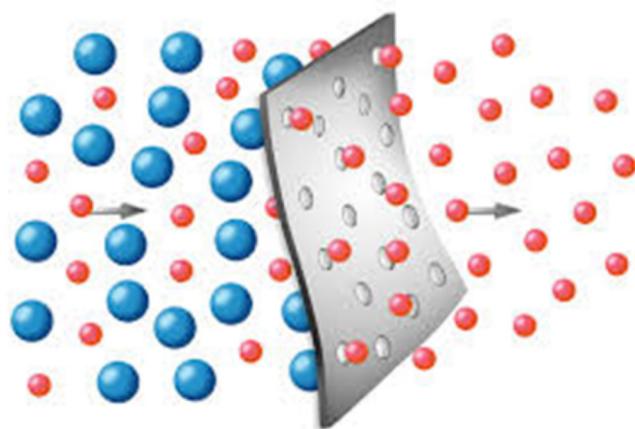


Fig. 1: Molecular sieving effect.

Alexander graduated from Novosibirsk State University in 2011 with a Specialist degree in "Chemistry". He obtained a PhD degree in "Chemical kinetics and catalysis" in 2018 and worked in the Boreskov Institute of Catalysis, Novosibirsk, Russia from 2008 until 2018. He joined CARES at the end of 2018. Alexander's research interests include inorganic chemistry, coordination chemistry, physical chemistry, heterogeneous catalysis, chemical engineering and the programming language Java.



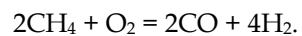
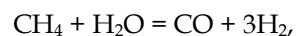
Another promising material for the separation of gas mixtures is metal-organic frameworks (MOFs). The typical MOF molecule (Figure 2) is a central ion (usually metal) surrounded by ligands (organic compounds). It forms “pores” that are used as molecular sieves. The separation efficiency of MOFs can also be enhanced with a chemical interaction between target molecules of a gas mixture and metal ion or ligands of the MOF occur.

Changing the synthesis procedure of MOFs and zeolites can help to obtain structures with different pores and central ions, which may lead to a significant increase of overall performance through better separation efficiency, stability and selectivity.

Besides the utilisation of MOFs and zeolites in the above-mentioned process of the separation of products of carbon dioxide reduction, one of the most promising ways of using of these materials is the refinement of crude oil, which consists of a mixture of hydrocarbons with varying lengths of carbon chain. Separation is necessary to obtain light (petrol, gasoline, naphtha) and heavy (diesel, kerosene, tar) oil fractions with consequent refinement. The most widespread up-to-date technique used for the separation of crude oil is fractional distillation – components are be-

ing separated due to different boiling temperatures and then condensed. Although this process is effective, it is highly energetically unfavourable. Utilisation of specific MOFs and zeolites in crude oil separation as well as in consequent petroleum refining and naphtha cracking may significantly decrease operation costs while providing the same effectiveness and selectivity.

Production of high-purity oxygen and hydrogen for fuel cells and other applications may also be done via separation. Some MOFs and zeolites may efficiently separate air (containing 78% nitrogen and 21% oxygen) to obtain oxygen. Varying the structural properties of these compounds may well help to successfully utilise them in the production of pure hydrogen via its separation from carbon monoxide (CO) in processes of natural gas (containing mainly methane, CH<sub>4</sub>) steam reforming and partial oxidation:



More in-depth investigation of structural and physical-chemical properties of zeolites and MOFs may lead to the development of new and promising materials which could be used in many important industrial separation processes.

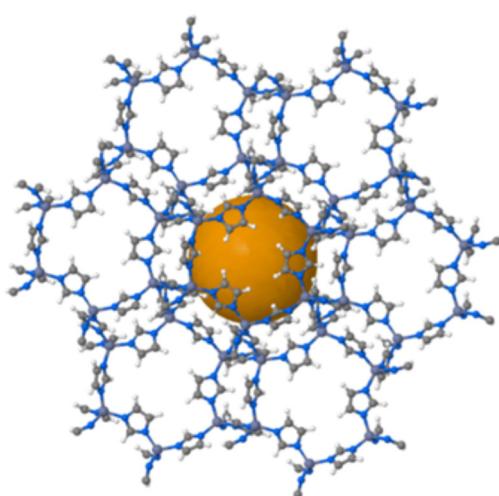


Fig. 2: Structure of a metal-organic framework (MOF).

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## Highlighted research outputs from November 2019 - March 2020

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

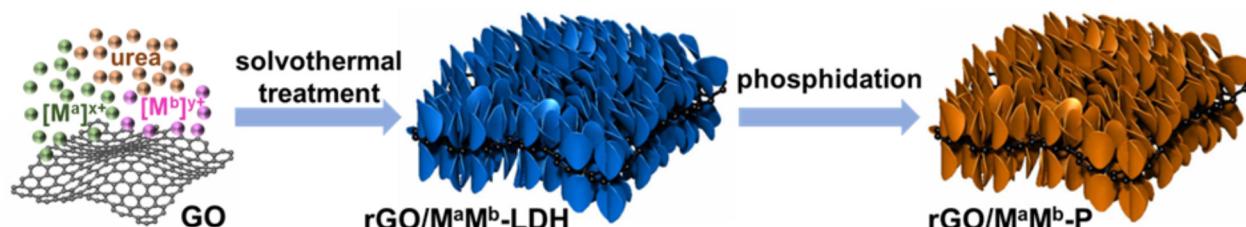
### IRP1: Promoting electrocatalytic oxygen evolution over transition-metal phosphide-based nanocomposites via architectural and electronic engineering

Ping Li and Hua Chun Zeng, *ACS Applied Materials & Interfaces*

DOI: 10.1021/acsami.9b16564

**Abstract:** Exploring noble-metal-free advanced electrocatalysts for oxygen evolution reaction (OER) is of great significance for development of sustainable energy systems. Rationally engineering chemical composition, electronic structure, and micro/nanoarchitecture of these catalysts represent a promising way to achieve their desired performance. Herein, we propose a general synthetic approach to prepare a series of porous nanosheets of bi- and tritransition-metal phosphides with homogeneous compositions supported by reduced graphene oxide (the resultant samples are termed as  $r\text{GO}/\text{M}^{\text{a}}\text{M}^{\text{b}}\text{-P}$  for simplicity, including  $r\text{GO}/\text{CoFe-P}$ ,  $r\text{GO}/\text{NiFe-P}$ ,  $r\text{GO}/\text{CoNi-P}$ , and  $r\text{GO}/\text{CoNiFe-P}$ ). The resultant sheet-on-sheet hierarchical nanocomposites exhibit outstanding OER performance with low overpoten-

tials, small Tafel slopes, and long durability in alkaline electrolyte, which compete favorably with the state-of-the-art OER catalysts reported to date. The remarkable electrocatalytic performances originate from their hierarchical structures and tailorabile compositions with optimized electronic structure modulation and synergistically electroactive sites, together with large active surface area and smooth mass/charge transports. This synthetic route could serve as a facile and controllable process to simultaneously realize the architectural manipulation, compositional regulation, and electronic modulation for low-cost OER electrocatalysts based on earth-abundant metal elements in practical water electrolysis and other energy applications.



*Synthesis procedure for the  $r\text{GO}/\text{M}^{\text{a}}\text{M}^{\text{b}}\text{-P}$  (i.e.,  $r\text{GO}/\text{CoFe-P}$ ,  $r\text{GO}/\text{NiFe-P}$ ,  $r\text{GO}/\text{CoNi-P}$ , and  $r\text{GO}/\text{CoNiFe-P}$ ) nanocomposites with a sheet-on-sheet sandwich-like architecture.*

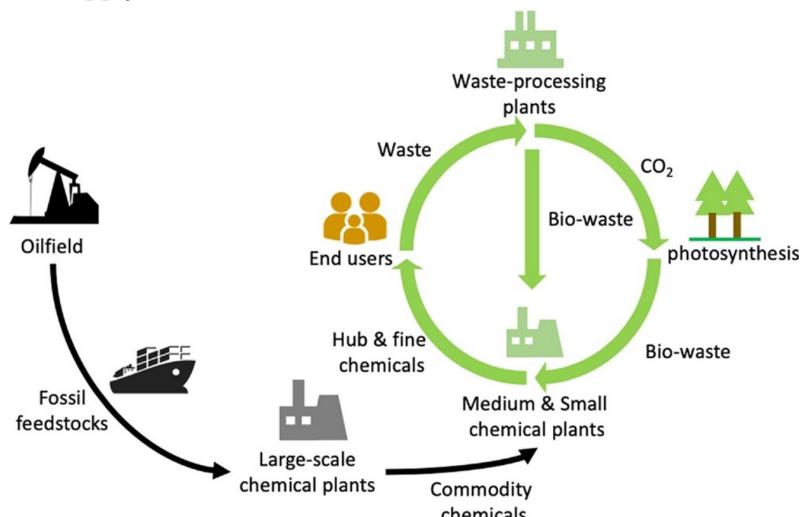
**IRP1: Towards circular economy: integration of bio-waste into chemical supply chain**Zhen Guo, Ning Yan and Alexei A. Lapkin, *Current Opinion in Chemical Engineering*

DOI: 10.1016/j.coche.2019.09.010

**Abstract:** Current chemical industry is heavily reliant on fossil resources as feedstock, resulting in a linear economical model, namely extract-make-use-dispose. In contrast, circular economy, targeting a more sustainable use of materials, aims to construct a loop in which waste is repurposed as feedstock. Circular economy in chemical industry may be achieved by integrating bio-waste into the chemical supply chain. However, bio-waste is different in many ways compared with fossil fuels, such as sparse distribution, geographical diversity, season-dependent supply,

variability and complex composition. This short review highlights recent technological advances in valorization of bio-waste including new processing methods and promising products. Analysis into the specific features of bio-waste suggests that bio-waste could be a promising feedstock for hub and fine chemicals, but not the commodity chemicals. A logic model of bio-waste based circular economy is proposed. Application of data mining and automated chemical routes are envisaged.

*Proposed logic model of circular economy with bio-waste as a key element.*

**IRP2: Electrochemical oxidation of nitrogen towards direct nitrate production on spinel oxides**Chencheng Dai, Yuanmiao Sun, Gao Chen, Adrian C. Fisher and Zhichuan J. Xu, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.202002923

**Abstract:** Nitrates are widely used as fertilizer and oxidizing agents. Commercial nitrate production from nitrogen involves high-temperature -high-pressure multi-step processes. Therefore, an alternative nitrate production method under ambient environment is of importance. Herein, an electrochemical nitrogen oxidation reaction (NOR) approach is developed to produce nitrate catalyzed by  $ZnFe_{x}Co_{2-x}O_4$  spinel oxides. Theoretical and experimental results show Fe aids the

formation of the first N-O bond on the  $^*N$  site, while high oxidation state Co assists in stabilizing the absorbed  $OH^-$  for the generation of the second and third N-O bonds. Owing to the concerted catalysis, the  $ZnFe_{0.4}Co_{1.6}O_4$  oxide demonstrates the highest nitrate production rate of  $130 \pm 12 \mu\text{mol h}^{-1} \text{g}_{\text{MO}}^{-1}$  at an applied potential of 1.6 V versus the reversible hydrogen electrode (RHE).

*Accompanying figure >>*

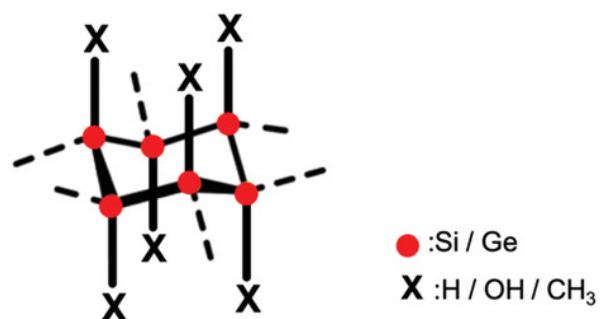
## IRP2: Siloxene, germanane, and methylgermanane: functionalized 2D materials of group 14 for electrochemical applications

Nur Farhanah Rosli, Nasuha Rohaizad, Jiri Sturala, Adrian C. Fisher, Richard D. Webster and Martin Pumera, *Advanced Functional Materials*

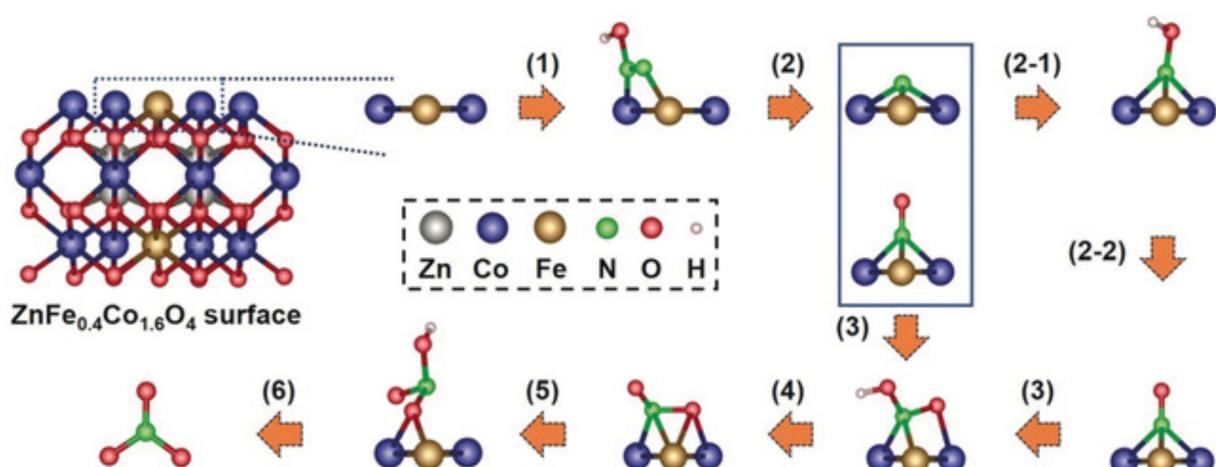
DOI: 10.1002/adfm.201910186

**Abstract:** 2D monoelemental group 14 materials beyond graphene, such as silicene and germanene, have recently gained a lot of attention. Covalent functionalization of group 14 layered materials can lead to significant tuning of their properties. While optical and electronic properties of germanene, silicene, and their derivatives have been studied in detail previously, there is no information on their electrochemistry and toxicity. Herein, electrochemical applications of 2D siloxene, germanane, and methylgermanane, specifically for detection of an important biomarker, dopamine, as well as catalyzation of oxygen reduction and hydrogen evolution reactions, which are important in energy applications, are explored. Among the three materials, germanane portrays most superior properties for the electrochemical applications mentioned. All three materials possess fast heterogeneous electron transfer rates, relative to bare glassy carbon electrodes. In addition, toxicity studies of these materials are conducted to gain insights on their possible

harmful effects toward human health. The results of this study show siloxene nontoxic while germanane and methylgermanane impose dose-dependent toxicity. Interestingly, methylation successfully reduce the toxicity of methylgermanane at lower concentrations. These studies provide fundamental insights into electrochemical and toxic properties of functionalized group 14 layered materials for future electrochemical applications.



Chemical structure of siloxene ( $Si_6H_3(OH)_3$ ), germanane ( $Ge_6H_6$ ), and methylgermanane ( $Ge_6(CH_3)_6$ ).



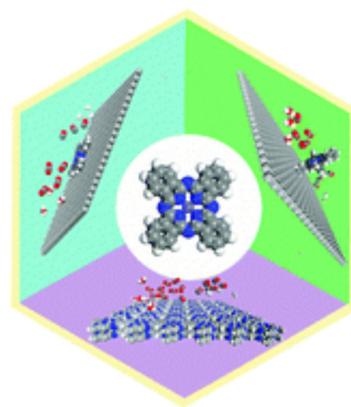
The multistep process of nitrogen oxidation reaction to nitrate on  $ZnFe_{0.4}Co_{1.6}O_4$  spinel oxide.

**IRP2: Electrocatalytic reduction of carbon dioxide: opportunities with heterogeneous molecular catalysts**Libo Sun, Vikas Reddu, Adrian C. Fisher and Xin Wang, *Energy & Environmental Science*

DOI: 10.1039/C9EE03660A

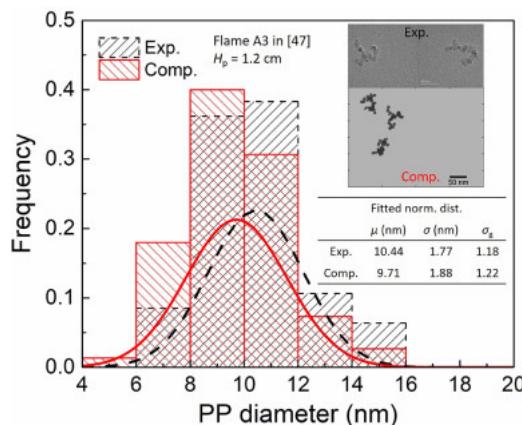
**Abstract:** Electrocatalytic CO<sub>2</sub> reduction by heterogeneous molecular catalysts is emerging as an important area for CO<sub>2</sub> utilization. Unlike commonly used solid heterogeneous catalysts, molecular catalysts possess well-defined structure, which allows the establishment of a precise structural model for better understanding of the CO<sub>2</sub> reduction mechanism. The easy modification of molecular catalysts with designated functional fragments through organic synthesis skills also facilitates the development of novel and efficient molecular catalysts. The direct use of molecular catalysts in the homogeneous phase suffers from poor solubility in some common solvents, low utilization and difficulty in recycling. Heterogeneous immobilization of molecular catalysts onto a substrate can potentially solve these problems. This review summarizes the methods that have

been developed so far for heterogeneous immobilization of homogeneous molecular catalysts, including covalent/non-covalent bonding, and assembling the molecular catalysts into a periodic skeleton. Challenges and factors affecting the activities of such catalysts in electrochemical CO<sub>2</sub> reduction are also discussed.

**IRP3: Simulation of primary particle size distributions in a premixed ethylene stagnation flame**Dingyu Hou, Casper S. Lindberg, Mengda Wang, Manoel Y. Manuputty, Xiaoqing You and Markus Kraft, *Combustion and Flame*

DOI: 10.1016/j.combustflame.2020.02.028

**Abstract:** Numerical simulation of soot formation in a laminar premixed burner-stabilized ethylene stagnation flame was performed with a detailed population balance model (DPBM) capable of tracking full structural details of aggregates as well as their chemical composition. A thorough parametric sensitivity study was carried out to understand the influence of individual sooting processes on the computed primary particle size



distributions (PPSDs). The rate of production of pyrene, coagulation efficiency and surface growth rate were found to have significant effects on the computed PPSDs. Besides, we found that the instantaneous sintering between small primary particles (PP) can affect the computed PPSDs drastically while sintering between large PPs within aggregates only had mild effects. For an ethylene premixed flame with stagnation plate height being 1.2 cm (Combust. Flame, 198:428-435, 2018), good agreement was obtained between both the computed and measured PPSD and fractal dimension, which supports the current mechanisms contributing to the evolution of PPs, i.e. nucleation, coagulation, surface growth and sintering. Moreover, time scale analysis for individual sooting processes was performed to determine the dominant particle processes at different periods of time, which helped explain the evolution of soot morphology.

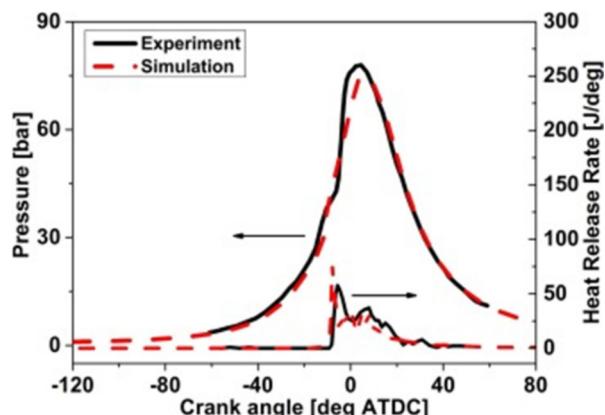
**IRP3: A joint moment projection method and maximum entropy approach for simulation of soot formation and oxidation in diesel engines**

Shaohua Wu, Chung Ting Lao, Jethro Akroyd, Sebastian Mosbach, Wenming Yang and Markus Kraft, *Applied Energy*

DOI: 10.1016/j.apenergy.2019.114083

**Abstract:** A joint moment projection method and maximum entropy approach for treating the soot population balance equations is developed and presented in this work. The moment projection method is used to solve the population balance equations and generate moments that are supplied to the maximum entropy approach as a post-processing technique to reconstruct the soot particle size distribution. The particle size range required by the maximum entropy for particle size distribution reconstruction is determined based on the weighted particles generated in the moment projection method. The performance of the joint approach is first evaluated by solving a set of simplified population balance equations in MatLab, then it is implemented into a Stochastic Reactor Model engine code to simulate the formation and oxidation of soot particles in a single-cylinder direct injection diesel engine. Results

suggest that the joint approach has the advantages of ease of implementation, high accuracy and low computational cost. It enables a detailed analysis on the soot formation and oxidation processes in diesel engines. Complete information on the soot particle size distribution can be provided with little CPU cost induced.



**IRP3: Reactivity of polycyclic aromatic hydrocarbon soot precursors: implications of localized  $\pi$ -radicals on rim-based pentagonal rings**

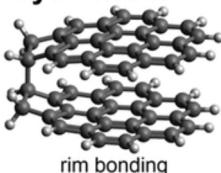
Jacob W. Martin, Dingyu Hou, Angiras Menon, Laura Pascazio, Jethro Akroyd, Xiaoqing You and Markus Kraft, *The Journal of Physical Chemistry C*

DOI: 10.1021/acs.jpcc.9b07558

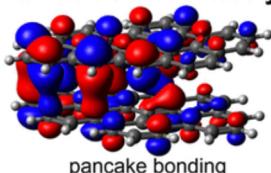
**Abstract:** This paper presents a systematic study of the reactivity of polycyclic aromatic hydrocarbons (PAH), identifying crosslinks that permit the combination of physical  $\pi$ -stacking interactions and covalent bonding. Hybrid density functional theory was used to identify the location of reactive sites on PAHs using the average local ionization potential. The bond energies formed between these various reactive sites were then computed.  $\sigma$ -Radicals were found to be the most reactive, forming bonds with other radicals and some reactive closed shell edge types. Partially saturated rim-based pentagonal rings were found to form localized  $\pi$ -radicals with high reactivity.

This site, in addition to resonantly stabilized  $\pi$ -radicals, was found to be capable of bonding and stacking, which is explored for a variety of larger species. Localized  $\pi$ -radicals on rim-based pentagonal rings, in particular, were found to form strongly bound stacked complexes, indicating a potentially important role in soot formation.

**Systematic study of aromatic reactivity**



$\pi$ -radicals combine bonding and stacking



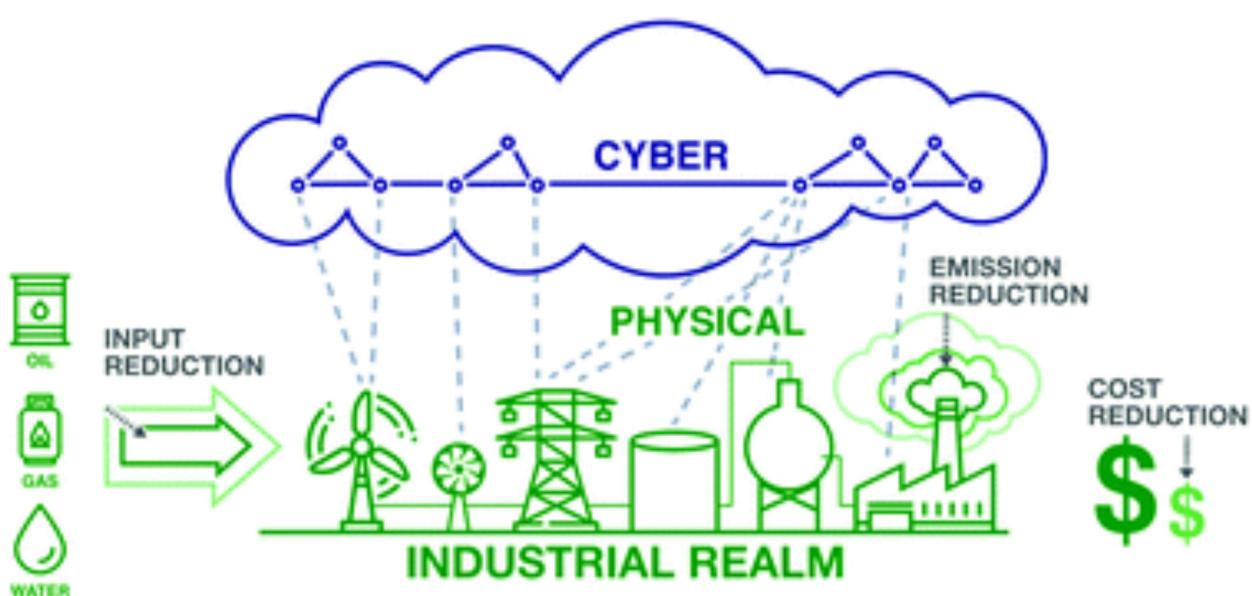
## IRP JPS: The impact of intelligent cyber-physical systems on the decarbonization of energy

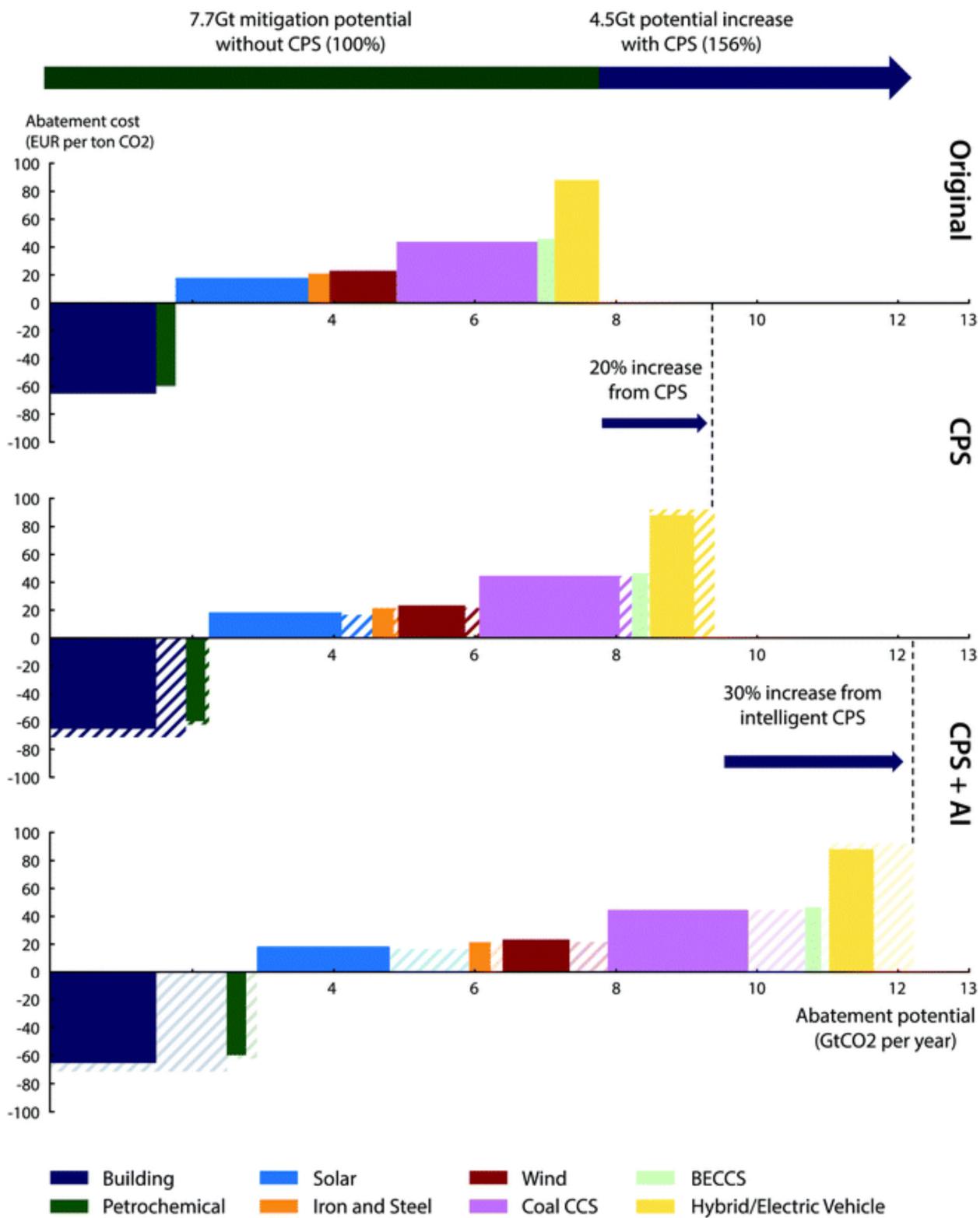
Oliver Inderwildi, Chuan Zhang, Xiaonan Wang and Markus Kraft, *Energy & Environmental Science*

DOI: 10.1039/C9EE01919G

**Abstract:** The decarbonisation of energy provision is key to managing global greenhouse gas emissions and hence mitigating climate change. Digital technologies such as big data, machine learning, and the Internet of Things are receiving more and more attention as they can aid the decarbonisation process while requiring limited investments. The orchestration of these novel technologies, so-called cyber-physical systems (CPS), provides further, synergistic effects that increase efficiency of energy provision and industrial production, thereby optimising economic feasibility and environmental impact. This comprehensive review article assesses the current as well as the potential impact of digital technologies within CPS on the decarbonisation of energy systems. *Ad hoc* calculation for selected applications of CPS and its subsystems estimates not

only the economic impact but also the emission reduction potential. This assessment clearly shows that digitalisation of energy systems using CPS completely alters the marginal abatement cost curve (MACC) and creates novel pathways for the transition to a low-carbon energy system. Moreover, the assessment concludes that when CPS are combined with artificial intelligence (AI), decarbonisation could potentially progress at an unforeseeable pace while introducing unpredictable and potentially existential risks. Therefore, the impact of intelligent CPS on systemic resilience and energy security is discussed and policy recommendations are deducted. The assessment shows that the potential benefits clearly outweigh the latent risks as long as these are managed by policy makers.





*Impact of CPS technologies on the marginal abatement cost of selected decarbonization technologies in energy transition. Shown in the figure is the marginal abatement cost of selected decarbonization technologies (represented by different colours) without CPS technologies (top), with CPS technologies (middle), and with intelligent CPS technologies (below).*

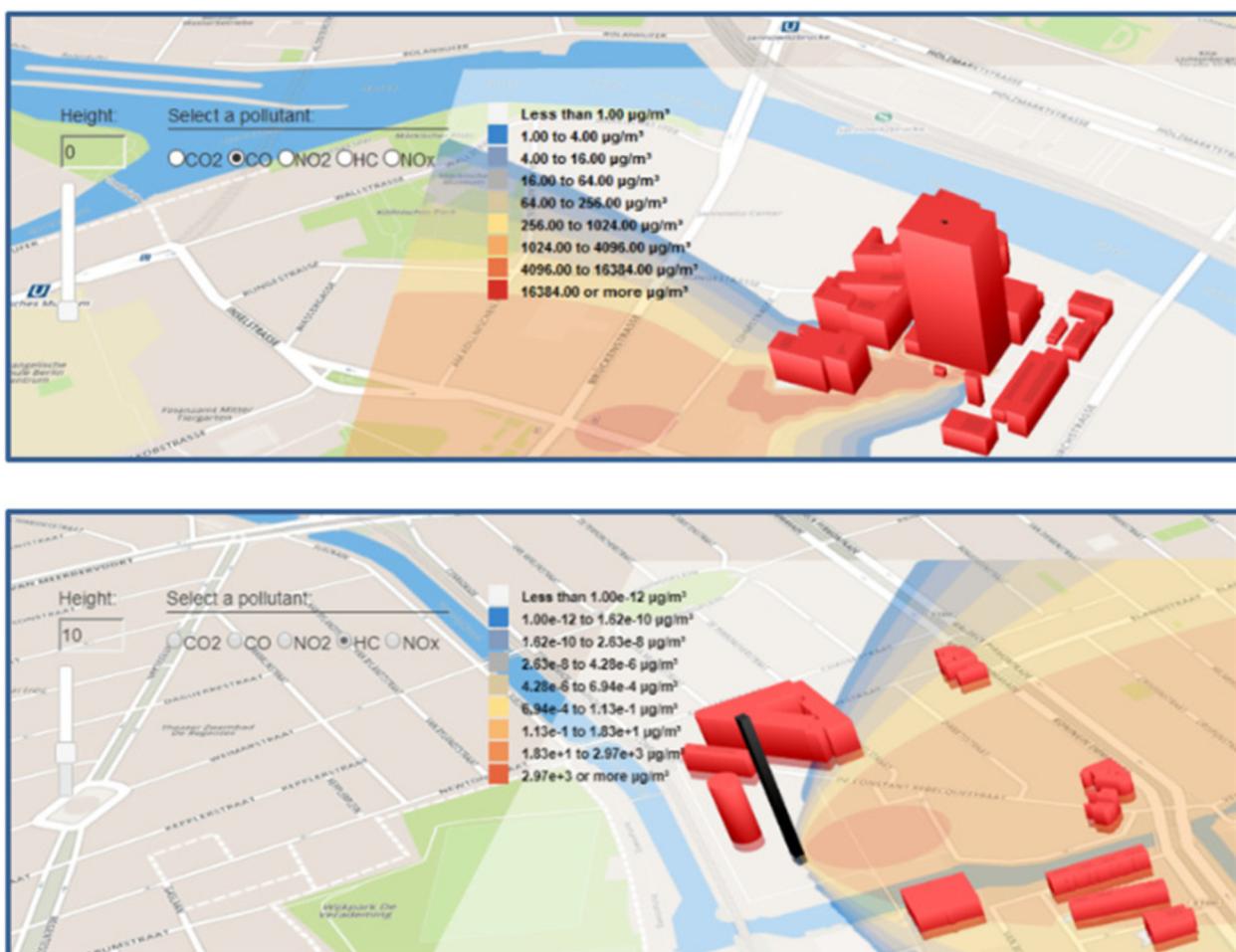
## IRP JPS: J-Park Simulator: an ontology-based platform for cross-domain scenarios in process industry

Andreas Eibeck, Mei Qi Lim and Markus Kraft, *Computers & Chemical Engineering*

DOI: 10.1016/j.compchemeng.2019.106586

**Abstract:** The J-Park Simulator (JPS) acts as a continuously growing platform for integrating real-time data, knowledge, models, and tools related to process industry. It aims at simulation and optimization in cross-domain and multi-level scenarios and relies heavily on ontologies and semantic technologies. In this paper, we demonstrate the interoperability between different applications in JPS, introduce new domain ontologies into the JPS, and integrate live data. For this, we utilize a knowledge graph to store and link semantically described data and models and cre-

ate agents wrapping the applications and updating the data in the knowledge graph dynamically. We present a comprehensive industrial air pollution scenario, which has been implemented as part of the JPS, to show how knowledge graphs and modular domain ontologies support the interoperability between agents. We show that the architecture of JPS increases the interoperability and flexibility in cross-domain scenarios and conclude that the potential of ontologies outweighs additional wrapping efforts.



*Simulated dispersion profile of CO emissions estimated for "Heizkraftwerk Mitte" in Berlin at a height of zero meters (upper picture) and of unburned hydrocarbons emissions estimated for "Energiecentrale" in The Hague at a height of ten meters (lower picture). Both simulations take into consideration the effects of surrounding buildings and real-time weather conditions.*

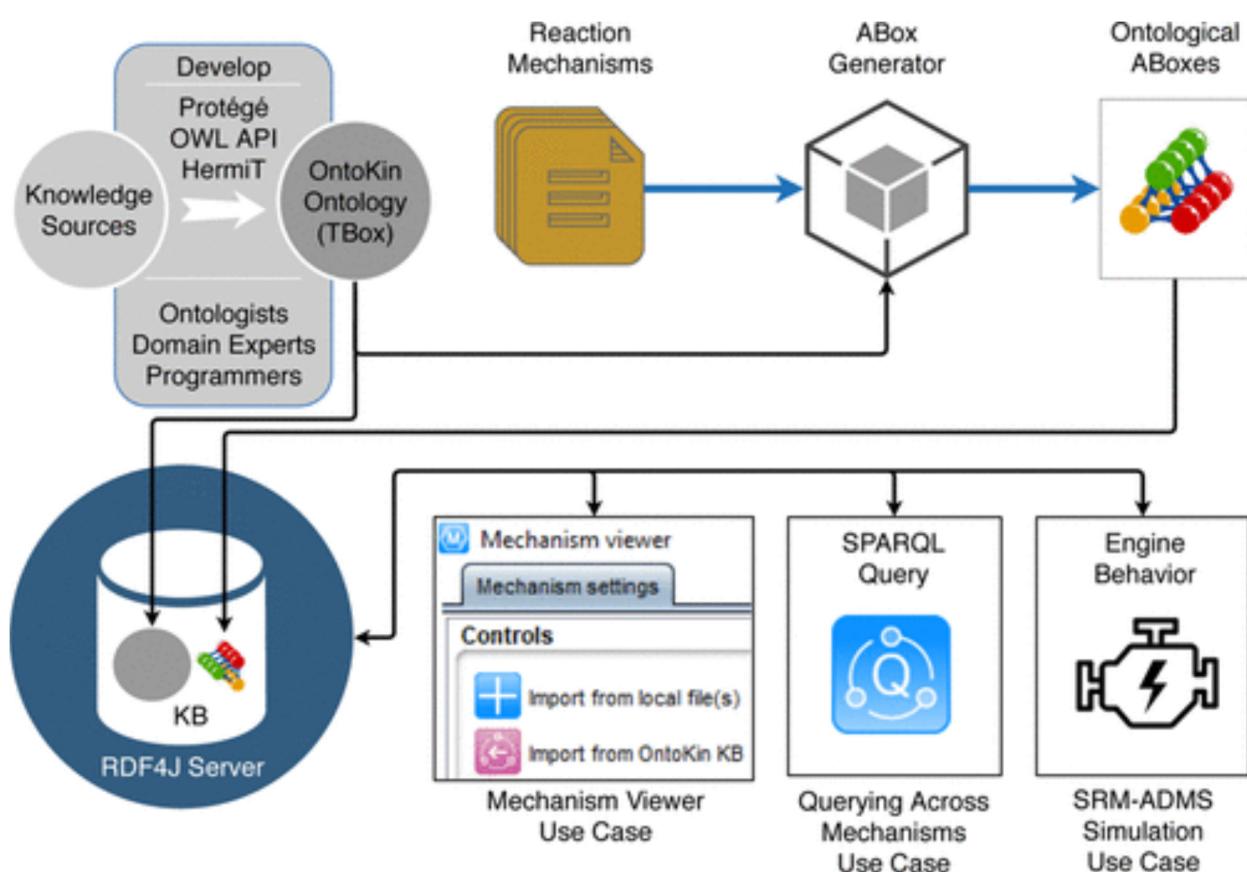
## IRPs JPS &amp; 3: OntoKin: an ontology for chemical kinetic reaction mechanisms

Feroz Farazi, Jethro Akroyd, Sebastian Mosbach, Philipp Buerger, Daniel Nurkowski, Maurin Salamanca and Markus Kraft, *Energy & Environmental Science*

DOI: 10.1021/acs.jcim.9b00960

**Abstract:** An ontology for capturing both data and the semantics of chemical kinetic reaction mechanisms has been developed. Such mechanisms can be applied to simulate and understand the behavior of chemical processes, for example, the emission of pollutants from internal combustion engines. An ontology development methodology was used to produce the semantic model of the mechanisms, and a tool was developed to automate the assertion process. As part of the development methodology, the ontology is formally represented using a web ontology language (OWL), assessed by domain experts, and validated by applying a reasoning tool. The re-

sulting ontology, termed OntoKin, has been used to represent example mechanisms from the literature. OntoKin and its instantiations are integrated to create a knowledge base (KB), which is deployed using the RDF4J triple store. The use of the OntoKin ontology and the KB is demonstrated for three use cases—querying across mechanisms, modeling atmospheric pollution dispersion, and as a mechanism browser tool. As part of the query use case, the OntoKin tools have been applied by a chemist to identify variations in the rate of a prompt NO<sub>x</sub> formation reaction in the combustion of ammonia as represented by four mechanisms in the literature.



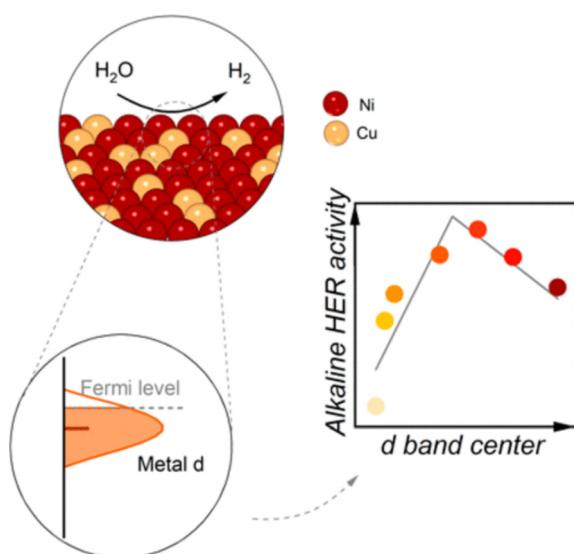
**eCO<sub>2</sub>EP: Surface composition dependent ligand effect in tuning the activity of nickel-copper bimetallic electrocatalysts toward hydrogen evolution in alkaline**

Chao Wei, Yuanmiao Sun, Günther G. Scherer, Adrian C. Fisher, Matthew Sherburne, Joel W. Ager and Zhichuan J. Xu, *Journal of the American Chemical Society*

DOI: 10.1021/jacs.9b12005

**Abstract:** Exploring efficient and low-cost electrocatalysts for hydrogen evolution reaction (HER) in alkaline media is critical for developing anion exchange membrane electrolyzers. The key to a rational catalyst design is understanding the descriptors that govern the alkaline HER activity. Unfortunately, the principles that govern the alkaline HER performance remain unclear and are still under debate. By studying the alkaline HER at a series of NiCu bimetallic surfaces, where the electronic structure is modulated by the ligand effect, we demonstrate that alkaline HER activity can be correlated with either the calculated or the experimental-measured d band center (an indicator of hydrogen binding energy) via a volcano-type relationship. Such correlation indicates the descriptor role of the d band center, and this hypothesis is further supported by the evidence that combining Ni and Cu produces a variety of adsorption sites, which possess near-optimal hydro-

gen binding energy. Our finding broadens the applicability of d band theory to activity prediction of metal electrocatalysts and may offer an insightful understanding of alkaline HER mechanism.



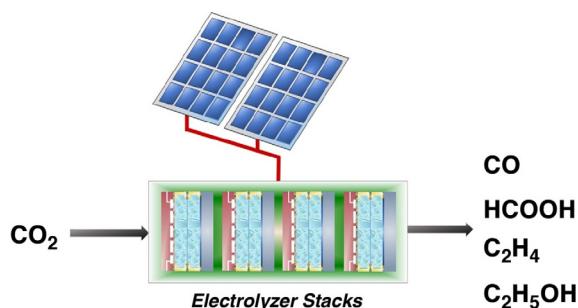
**eCO<sub>2</sub>EP: Electrochemical conversion of carbon dioxide to high value chemicals using gas-diffusion electrodes**

Souradip Mukhundi and Boon Siang Yeo, *Current Opinion in Chemical Engineering*

DOI: 10.1016/j.coche.2019.09.008

**Abstract:** The synthesis of value-added chemicals from the electrochemical reduction of carbon dioxide is attractive from the perspectives of both sustainable manufacturing and environmental protection. In this review article, we first discussed the electrochemical CO<sub>2</sub> reduction reaction, relevant figures-of-merit, and configurations for electrolyzers and gas diffusion electrodes. We

then summarized important developments towards the scaled-up synthesis of commercially valuable carbon monoxide, formic acid, hydrocarbons and alcohols. Among all these developments, electrolyzers for generating carbon monoxide and formic acid appear to be approaching close to practical realization in the industry. In contrast, electrolyzers for producing hydrocarbons and alcohols need to be further improved. Finally, directions for future research are suggested.



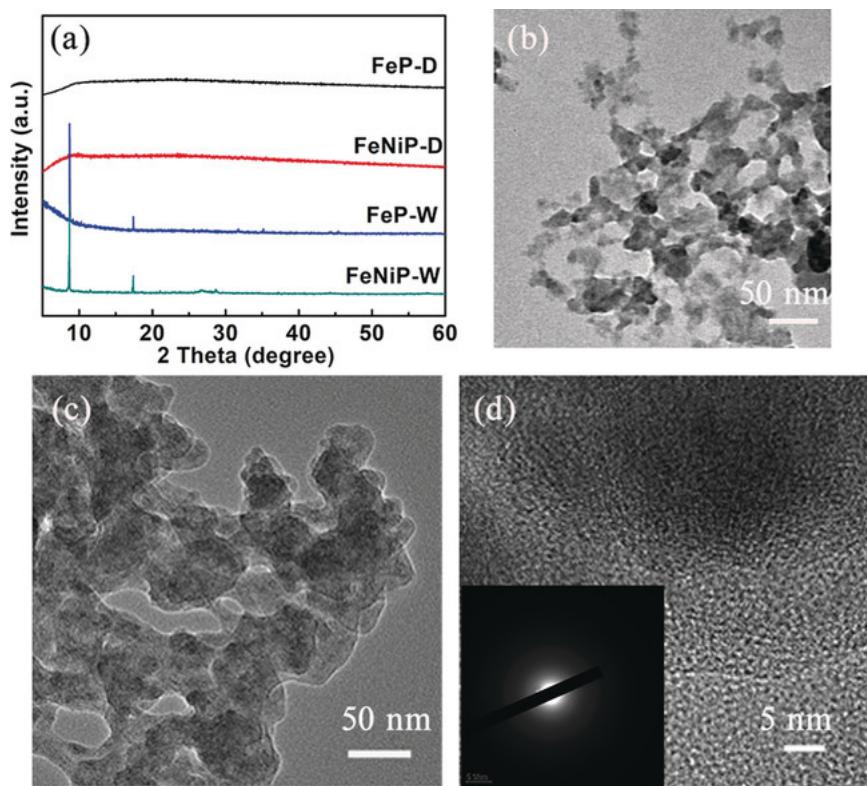
**eCO<sub>2</sub>EP: Rational synthesis of amorphous iron-nickel phosphonates for highly efficient photocatalytic water oxidation with almost 100 % yield**

Weinan Xing, Shengming Yin, Wenguang Tu, Guanyu Liu, Shuyang Wu, Haojing Wang, Markus Kraft and Guangyu Wu, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.201912552

**Abstract:** A simple solvent ligation effect was successfully used to disrupt the growth of a model compound,  $\text{Fe}[(\text{OH})(\text{O}_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{H})]\cdot\text{H}_2\text{O}$  (MIL-37), into an extended 2D structure by replacing water with dimethylformamide (DMF) as the solvent during the synthesis. Owing to the lack of -OH group, which provides the corner-sharing (binding) oxygen atoms for the octahedra, an amorphous and porous structure is formed.

When  $\text{Fe}^{3+}$  is partially replaced by  $\text{Ni}^{2+}$ , the amorphous structure remains and the resultant binary metal catalyst displays excellent photocatalytic oxygen evolution activity with almost 100 % yield achieved under visible light irradiation using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as the photosensitizer. This study opens up new possibilities of using the simple solvent effect to synthesize high surface area metal phosphonates for catalytic and other applications.



a) XRD patterns of various samples, b),c) TEM images of FeP-D (b) and FeNiP-D (c), and d) HRTEM and SAED pattern (inset) of FeNiP-D.

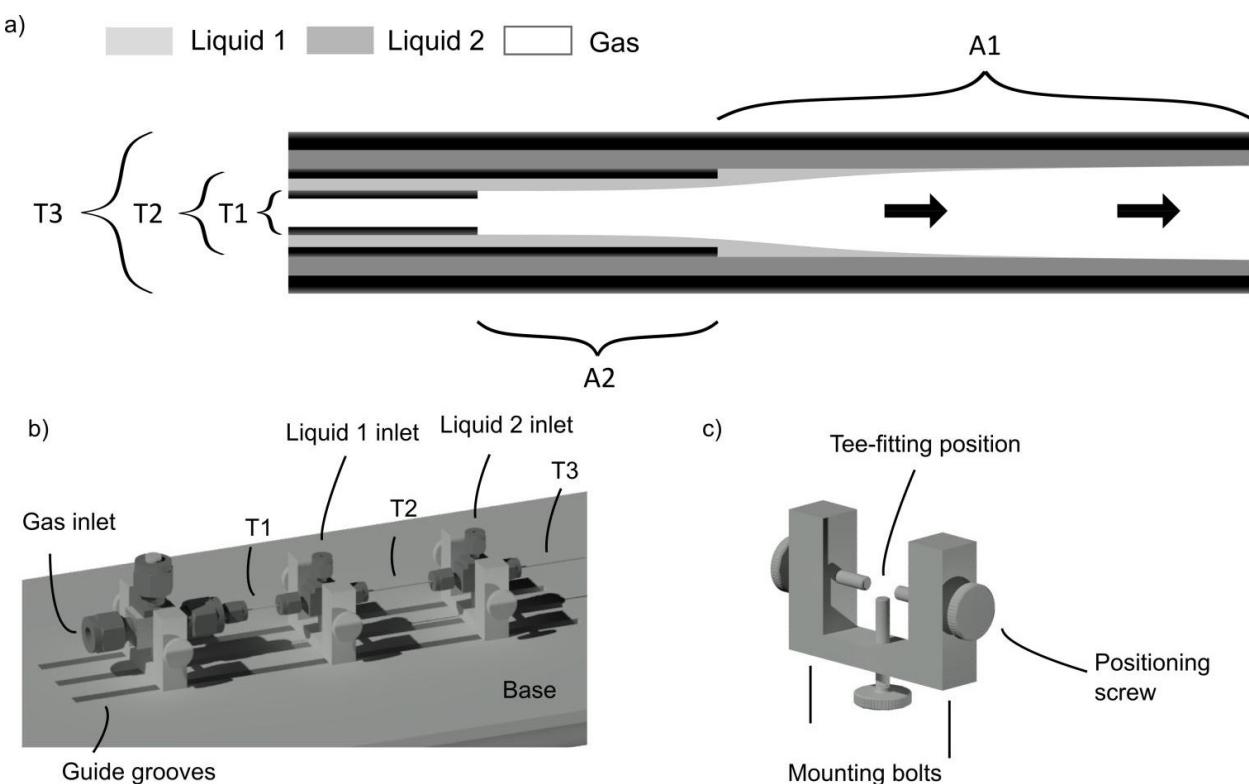
**RINGS project: Scalable and precise synthesis of two-dimensional metal organic framework nanosheets in a high shear annular microreactor**

Nicholas A. Jose, Hua Chun Zeng and Alexei A. Lapkin, *Chemical Engineering Journal*

DOI: 10.1016/j.cej.2020.124133

**Abstract:** Despite their promise as next generation materials for adsorbents, membranes and sensors, two-dimensional metal organic frameworks (2D MOFs) are far from commercial adoption. Current synthesis methods are neither scalable nor precise enough to use at industrial scales. Furthermore, the characterization of 2D MOF nanostructure is problematic due to aggregation in post-processing. By accelerating precipitation kinetics and using the recently developed annular flow microreactor, we synthesized copper benzene-dicarboxylic acid nanosheets with signif-

icantly higher efficiency and precision than conventional batch methods. The reactor space-time yield was five orders of magnitude higher than the previously published batch methods. We used liquid cell transmission electron microscopy to reduce drying-induced aggregation and revealed a monodisperse particle size distribution. These developments are step-changes in the synthesis and analysis of 2D MOF structures, and may accelerate the commercialization of innovative 2D MOF technologies.



*Microreactor schematic and construction. Representation of microreactor axial cross section showing direction of flow and fluid profile and labeled regions in (a), where T1, T2, and T3 are the three coaxial tubes, and regions A1 and A2 are the annular flow regions created by the flow of the gas phase (white). In A2, mixing of liquid 1 (light grey) and liquid 2 (dark grey) occur. (b) Assembly of capillary tubes using compression fittings mounted on a base. The use of positioning clamps (c) and guiding grooves allow precise positioning of capillaries.*



# 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

**P**hase 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.

During the last period in WP2 Dr Zhen GUO delivered the final report to BASF on the specific industrial project and in WP2 the new Emerging Opportunities project has started, led by Prof. Ning YAN. In WP1 remarkably selective new catalytic materials were developed and in WP3 a new mode of activity in methanol synthesis is being studied.

**Professor Alexei Lapkin, PI**  
**University of Cambridge**

## Update on work package 1.1

### Design of nano-structured catalysts

Zeolite materials have been widely adopted in many catalysis applications, acting as both active catalysts and catalyst supports. By constructing different secondary building blocks and hence the final zeolite structures, a series of mesoporous zeolites could be synthesised with controlled pore dimensions and composition dependent acidity. In particular, hollow zeolites have attracted much interest in recent years. Their unique morphology is advantageous in catalysis, providing better material utilisation, a shorter diffusion-al barrier, enhanced stability and product selectivity, etc.

In the past six months, **LI Bowen (PhD student, NUS)** and **Prof. ZENG Hua Chun (PI, NUS)** have developed a general synthetic approach to synthesise an integrated catalyst consisting of hollow ZSM-5 support and multiple metal nanoparticles. To achieve hollow ZSM-5 crystals with a thinner shell and smaller dimensions, the dissolution-recrystallisation method was adopted. In our synthesis, solid ZSM-5 crystals were first prepared from Stöber silica. The solid samples were treated in hydrothermal conditions with the presence of structural directing units. Due to local inhomogeneity of Al distribution, inner regions of the solid sample dissolved and the released silicate species were then recrystallised on the outer surface. As such, a central cavity is formed,

producing the desired hollow morphology. Loading of various transition metals has been achieved with solid ZSM-5 using the impregnation method. After the hollow process, these loaded metal nanoparticles were well confined within the hollow ZSM-5 support.

Targeting the CO<sub>2</sub> hydrogenation reaction, Cu and Zn were confined within hollow ZSM-5 with further integration of Pt nanoparticles at the exterior surface of the hollow support. By having Pt at the exterior surface, it is possible to create a localised environment with enhanced CO concentration to the CuZn catalyst, thus increasing the production efficiency of methanol. The hollow zeolite support could then convert methanol to higher hydrocarbons and the product selectivity is controlled by the well-defined pore dimensions. This integrated catalyst could directly produce light olefins from CO<sub>2</sub> hydrogenation and its performance will be further evaluated with more test runs.

**WANG Jingjing (PhD student, NUS)** and **Prof. ZENG Hua Chun** report that metal-organic frameworks (MOFs), constructed by joining metal ions with organic ligands, have emerged as a class of versatile porous materials for a wide range of applications. However, MOFs are generally considered to be poor electrocatalysts for

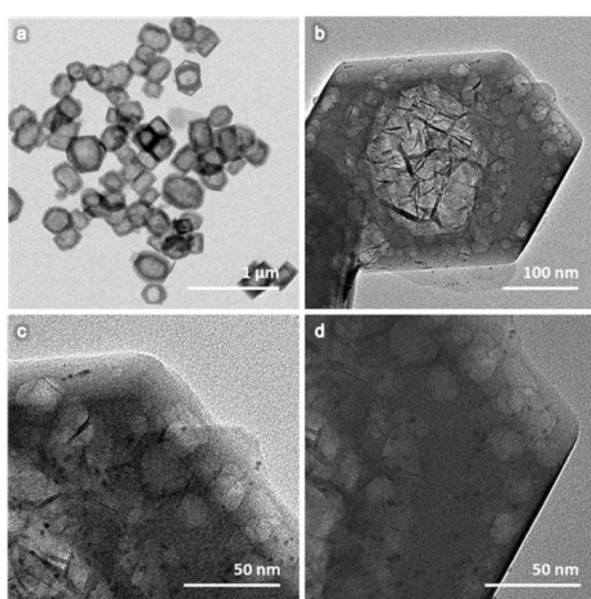


Fig. 1.1: HRTEM images (at different magnifications (a) to (d)) of hollow ZSM-5 loaded with catalytic CuZn particles (interior) and Pt particles (exterior).

LI Bowen

electrochemical reactions such as the water splitting or CO<sub>2</sub> reduction.

The activity of an electrocatalyst is usually dependent on, among many other factors, accessible active centres, electrical conductivity and electrode geometry. Improvement in catalytic efficiency requires each of these parameters to be optimised. For example, MOFs have abundant intrinsic molecularly coordinated metal sites, but few of them are utilised for electrocatalysis because of their poor electrical conductivity and small pore size (usually in the sub-nanometre regime; microporosity). Very recently, a few two-dimensional (2D) MOFs have been synthesised, but the majority of 2D MOFs reported to date have been prepared in powder form, and little effort has been devoted to increasing the macro-/meso-porosity, conductivity or number of catalytic centres.

During this report period, a strategy was developed for the *in situ* growth of nanosheet arrays of 2D MOFs (Ni-BDC) on nickel foams. The material was prepared via a facile one-step chemical bath deposition method by using the nickel foam as the metal source and introducing the corresponding organic ligand(s) for the above 2D MOF. We will further investigate the electrochemical performances of this prepared sample such as water splitting or CO<sub>2</sub> reduction.

**Alvin LIM Ming Hao (PhD student, NUS) and Prof. ZENG Hua Chun** explain that in addition to the selective formation of methanol, calcined layered double hydroxide (LDH) materials can also be used as catalysts to produce CH<sub>4</sub> and CO. Expanding on his group's previous work using calcined LDH materials to perform other CO<sub>2</sub> hydrogenation reactions, MgAl-LDO (layered double oxide) was introduced into dilute nickel (II) nitrate and iron (II) nitrate solution in varying amounts in order to produce methane at high conversion. However, when too much iron was added, the nanoflower morphology was destroyed (Figure 1.3b). From the preliminary CO<sub>2</sub>

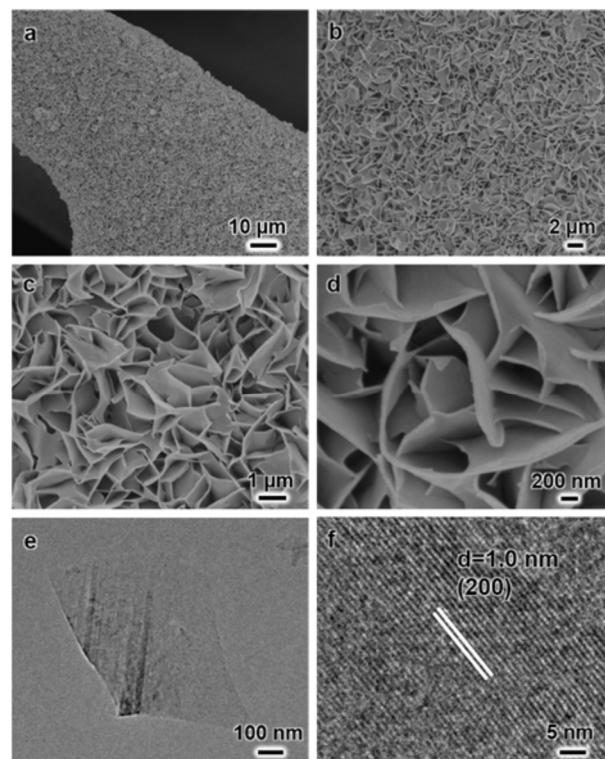


Fig. 1.2: SEM and TEM images (at different magnifications (a) to (f)) of Ni-BDC grown on the nickel foam.

WANG Jingjing

hydrogenation results, it was found that temperatures over 300 °C significantly increase the CH<sub>4</sub> production as indicated by the red line in the space-time yield (STY) graph (Figure 1.3c), while higher pressure at 30 barg helps to improve CH<sub>4</sub> production (yellow to red line) and to suppress CO production (green to blue line). The selectivity graph (Figure 1.3d) shows that CH<sub>4</sub> selectivity improves from 89.14% to 98.56%. ICP-OES result shows that there are around 20 wt% Ni and 2.5 wt% Fe present in the as-prepared catalyst (LDOH-8Ni<sub>2</sub>Fe).

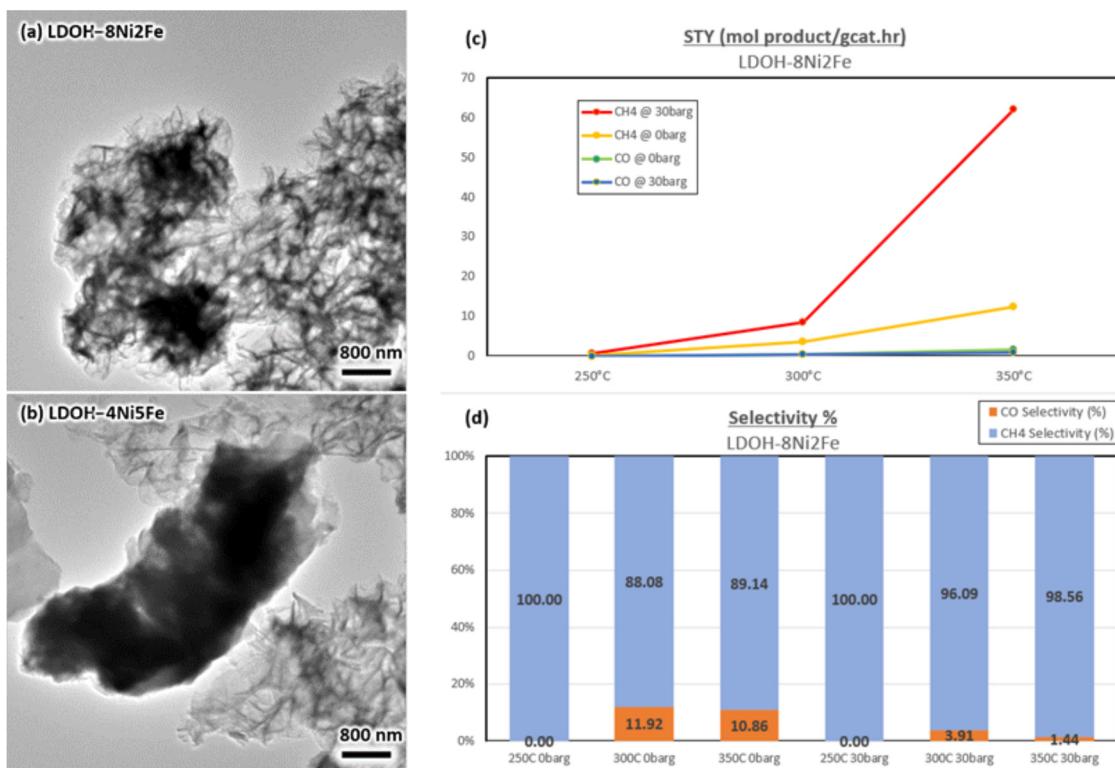


Fig. 1.3: (a) TEM of LDOH-8Ni<sub>2</sub>Fe, (b) TEM of LDOH-4Ni<sub>5</sub>Fe, (c) Space Time Yield Performance of LDOH-8Ni<sub>2</sub>Fe, and (d) Selectivity of product using catalyst LDOH-8Ni<sub>2</sub>Fe at different temperatures and pressure at 0 barg and 30 barg.

Alvin LIM Ming Hao

## Update on work package 1.2

### Novel reactions and functional molecules

**Perman JORAYEV (PhD student, CAM)** has been working on developing novel, industrially relevant processes. The main motivation behind the research is to utilise data driven approaches (e.g. machine learning) and automation tools to speed up and ease difficult and repetitive tasks. The methodology consists of three main parts: generation and incorporation of chemical knowledge (cheminformatics), development or implementation of machine learning algorithms to guide the model development and optimisation process, and robotic tools to carry out hundreds, if not thousands, of experiments. Recently, Perman JORAYEV has focused on gathering and

testing the prior information about the chemical system to be developed. This required generation of descriptors to define the chemical space and finalising the input parameter space. Jointly with Dr Simon SUNG and Dr Mohammed JERAAL, he has been working on building Vapourtec based automated continuous flow systems to carry out dozens of reactions without human intervention. This required setting up communication between the reactor systems, online analysis tools (e.g. HPLC), and Bayesian based machine learning algorithms. The system was tested for compatibility of different chemicals and states (e.g. handling suspension) under various reaction conditions.

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 have allowed for the extraction of several of these platform chemicals in viable yields. Of particular importance is p-coumaric acid and its related analogue methyl p-coumarate, which could be chemically transformed to several high value added chemicals

commonly found in the cosmetics and pharmaceutical industries.

Methyl p-coumarate and its derivatives have been used previously in the synthesis of several platform chemicals and drugs. In this project, Dr SEE Jie Yang and colleagues are investigating the construction of pyrazoles from the reaction of methyl p-coumarate with a diazomethane functionalisation reagent. Pyrazoles are five-membered nitrogen containing heterocycles commonly observed in the structures of antifungals and drugs. Studies are currently underway to determine the full extent of this reaction, catalytic pathway and the structure of the other isomeric side products.

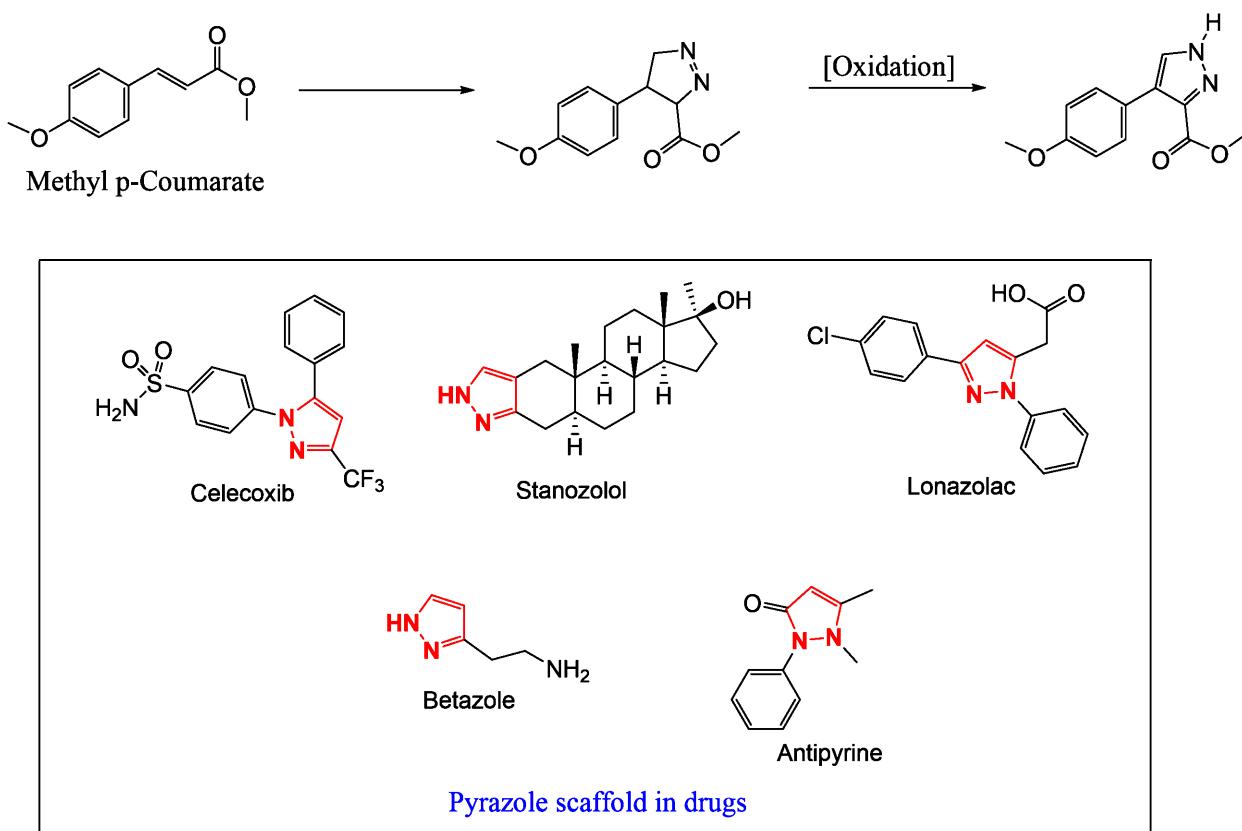


Fig. 1.4: The reaction of methyl p-coumarate with a diazomethane functionalisation reagent to form a pyrazole scaffold.

Dr SEE Jie Yang

## Update on work package 1.3

### Novel reactors and process technology

**Dr YAN Yong (Research Fellow, NTU)** reports that Cu nanoparticles have been synthesised and several different oxides adopted as the support to disperse the metal particles, including  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$ . Among all the supported mono-metallic Cu catalysts,  $\text{CeO}_2$ -based catalysts showed the best performance for the catalytic hydrogenation of  $\text{CO}_2$  into methanol, with a TOF of  $0.28 \times 10^{-3} \text{ s}^{-1}$  at a temperature of  $250^\circ\text{C}$  and a total pressure of 35 bar. Subsequently, Pd addition was carried out over the Cu/ $\text{CeO}_2$  samples by a galvanic replacement process at the Cu:Pd ratio of 160, 80, 40 and 20, respectively. The catalytic results clearly pointed out to an increase of  $\text{CO}_2$  conversion with 1/160 Pd addition and similar selectivity to methanol if compared to the undoped catalyst. Further increase of the Pd content led to an obvious decrease in both activity and selectivity. X-ray photoelectron spectroscopy was carried out to study the chemical nature of Pd species. With the smallest replace ratio, only one doublet can be identified at 337.6 eV/343.4 eV, while another pair appeared over the catalysts with higher Pd replacement ratio. This result suggested that these two kinds of different Pd species may have played different roles in the activation of  $\text{CO}_2$  and/or  $\text{H}_2$ . Further studies are needed to help establish the structure and performance relation.

**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 established the equilibrium and kinetics for diffusion of pure components of wet flue gas ( $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ ) and binary mixture of  $\text{CO}_2/\text{N}_2$  on silica gel. The next step involved determining the adsorption and kinetics of a mixture of  $\text{CO}_2$  and  $\text{N}_2$  in the presence of moisture. She conducted binary mixture experiments of  $\text{N}_2/\text{H}_2\text{O}$  and  $\text{CO}_2/\text{H}_2\text{O}$  on a pre-saturated moisture bed to ascertain the equilibrium of these gases ( $\text{N}_2$  and  $\text{CO}_2$ ) in the presence of moisture and the mixture equilibrium models necessary to simulate the VSA process for drying of wet flue gas. She observed a considerable reduction in  $\text{N}_2$  and  $\text{CO}_2$  adsorption capacity on silica gel in the moisture saturated bed as compared to the corresponding dry conditions. She undertook co-adsorption runs of wet flue gas mixture on a clean silica gel bed to study the ternary breakthrough behaviour of the dry gases ( $\text{CO}_2$  and  $\text{N}_2$ ) in the presence of moisture. This is also important for simulating the Vacuum Swing Adsorption (VSA) process aimed at drying wet flue gas.

## 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 15.

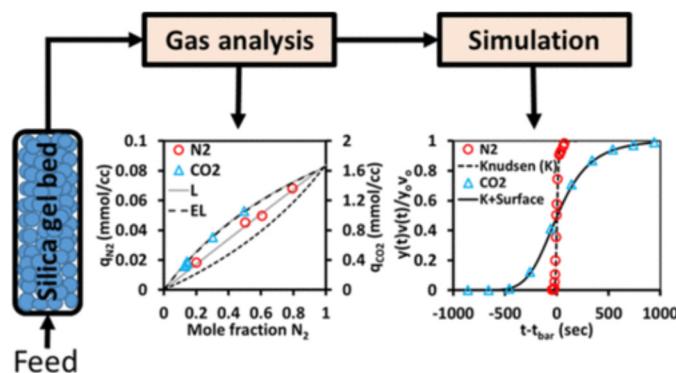
### Adsorption and diffusion of N<sub>2</sub> and CO<sub>2</sub> and their mixture on silica gel

Prerna Goyal, Mark J. Purdue and Shamsuzzaman Farooq, *Industrial & Engineering Chemistry Research*

DOI: 10.1021/acs.iecr.9b02685

**Abstract:** The rising concentration of CO<sub>2</sub>, emitted into the atmosphere from power plant flue gas, is a major contributor to global warming. Silica gel is an important adsorbent to dry wet flue gas prior to sending the dried gas (CO<sub>2</sub>/N<sub>2</sub> mixture) for carbon capture. In the present work, a comprehensive experimental and simulation study is undertaken to establish the adsorption and diffusion of N<sub>2</sub> and CO<sub>2</sub> and their mixture on silica gel at pressures and temperatures relevant to vacuum swing adsorption (VSA) processes. The adsorption equilibrium of pure N<sub>2</sub> and CO<sub>2</sub> is captured well by the single component Langmuir isotherm model. Carefully designed controlled experiments are conducted to show that the transport mechanism for the adsorption of pure N<sub>2</sub> in silica gel pores is governed

by Knudsen flow, while for CO<sub>2</sub>, it is a combination of Knudsen and surface flow. Binary mixture experiments are performed to confirm the mixture equilibrium and kinetic models necessary to simulate the dry product end of a column in a VSA process for drying wet flue gas. For binary mixture equilibrium of these gases, there is no effect of competition from the other gas present in the mixture, implying that they exhibit non-competitive adsorption on silica gel. Transport of CO<sub>2</sub>/N<sub>2</sub> mixture in silica gel pores is well captured by the mechanism established from the single component study.



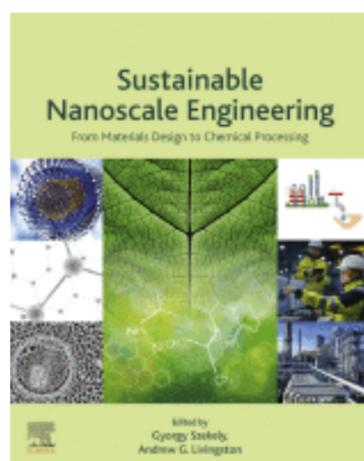
### Rational design of continuous flow processes for synthesis of functional molecules [book chapter]

Alexei A. Lapkin, in *Sustainable Nanoscale Engineering: From Materials Design to Chemical Processing*

DOI: 10.1016/B978-0-12-814681-1.00016-3

**Abstract:** In the chapter, we present an overview of continuous process technology, focusing on generic features of the technology, illustrated by few specific examples. We develop the concepts of digital molecular technology and Molecular Context, as the emerging underpinning methodologies that would allow rational design of continuous processes. Finally, we argue that environmental impacts of continuous processes, when evaluated correctly within the framework of life

cycle assessment, may not necessarily be significantly better than the batch technology, but the sustainability impacts, which include also economic and social impacts, are enormously beneficial.



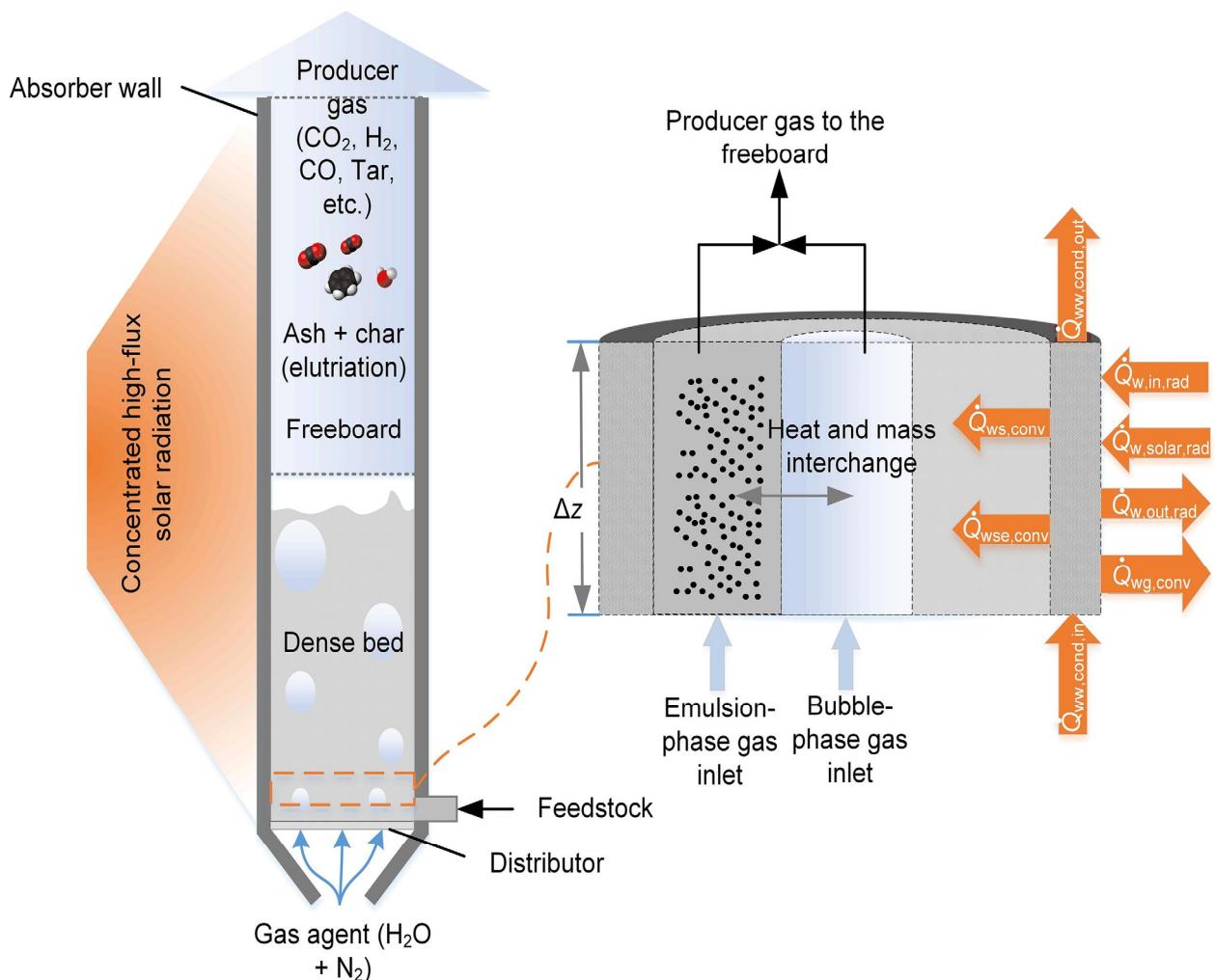
## Hydrogen production of solar-driven steam gasification of sewage sludge in an indirectly irradiated fluidized-bed reactor

Xian Li, Ye Shen, Liping Wei, Chao He, Alexei A. Lapkin, Wojciech Lipiński, Yanjun Dai and Chi-Hwa Wang, *Applied Energy*

DOI: 10.1016/j.apenergy.2019.114229

**Abstract:** A fluidized-bed based solar steam gasification of sewage sludge for production of high-quality syngas with a high content of hydrogen is numerically modeled and validated by experimental data generated from a lab-scale fluidized bed. The solar gasifier is mainly composed of a fluidized bed and a concentrically tubular cavity. A transient model coupling a two-phase fluidization model (in terms of reaction kinetics and hydrodynamics) and a solar cavity receiver model is established to conduct the parametric investiga-

tion of the proposed solar gasifier, including the effects of the direct normal irradiance, gasifying agent composition, and spatial flux distribution at the freeboard wall on the performance criteria of solar gasification i.e. solar upgraded ratio and solar-to-fuel efficiency. The transient simulation of the solar gasifier with ~2.2 MW solar power input is performed. A H<sub>2</sub> yield range of 61.2–67.6 g/kg(sludge) can be achieved through solar steam gasification of sewage sludge, which can be adjusted by modifying the steam content of the gasifying agent and the direct normal irradiance. Under the condition of the direct normal irradiation of 1000 W/m<sup>2</sup>, the mean concentration ratio of 1000 suns at the dense bed, and 100 vol% N<sub>2</sub> content, a maximum solar upgraded ratio of 1.0 and solar-to-fuel efficiency of 0.26 can be achieved.



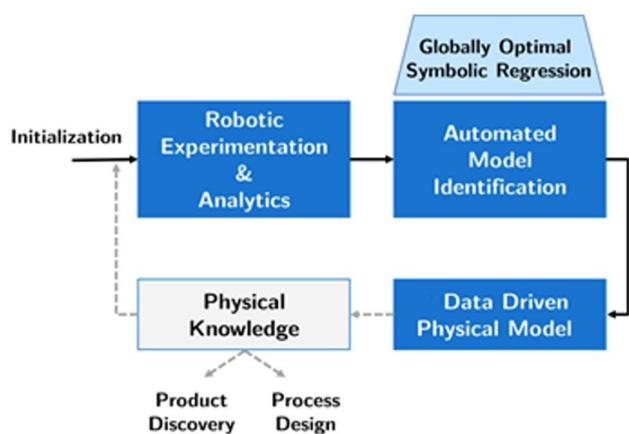
*Schematics of a two-phase flow model of the bubbling fluidised bed driven by concentrated solar radiation.*

**A new formulation for symbolic regression to identify physico-chemical laws from experimental data**

Pascal Neumann, Liwei Cao, Danilo Russo, Vassiliadis and Alexei A. Lapkin, *Chemical Engineering Journal*

DOI: 10.1016/j.cej.2019.123412

Abstract: A modification to the mixed-integer nonlinear programming (MINLP) formulation for symbolic regression was proposed with the aim of identification of physical models from noisy



experimental data. In the proposed formulation, a binary tree in which equations are represented as directed, acyclic graphs, is fully constructed for a pre-defined number of layers. The introduced modification results in the reduction in the number of required binary variables and removal of redundancy due to possible symmetry of the tree formulation. The formulation was tested using numerical models and was found to be more efficient than the previous literature example with respect to the numbers of predictor variables and training data points. The globally optimal search was extended to identify physical models and to cope with noise in the experimental data predictor variable. The methodology was proven to be successful in identifying the correct physical models describing the relationship between shear stress and shear rate for both Newtonian and non-Newtonian fluids, and simple kinetic laws of chemical reactions. Future work will focus on addressing the limitations of the present formulation and solver to enable extension of target problems to larger, more complex physical models.

## Other activities and achievements

**PI Prof. ZENG Hua Chun** gave a keynote presentation, "Integration of Nanocomposites and Nanohybrids for Catalytic Applications" at the *International Conference on Nanoscience and Nanotechnology*, University of Queensland, Brisbane, Australia, 13-15 February 2020.

**Prof. ZENG Hua Chun** gave an invited talk, "Rational Design of Integrated Nanocatalysts for Heterogeneous Catalysis" at Xiamen University, Xiamen, China, 12 December 2019.

**Prof. ZENG Hua Chun** gave an invited talk, "Synthetic Architecture of Catalytic Materials" at *The Congress of Asia Pacific Academy of Materials 2019 (APAM 2019)*, Chinese Academy of Sciences and Asia Pacific Academy of Materials, Guangzhou, China, 15-18 November 2019.

**Prof. ZENG Hua Chun** was elected as an Academician of the Asia Pacific Academy of Materials, 2019.

**PhD student CAO Liwei** gave two oral presentations, "Symbolic regression for automated physical model identification in reaction engineering" and "Machine learning and molecular descriptors enable rational solvent selection in asymmetric catalysis" at the AIChE annual meeting, Orlando, US, 10-15 November 2019.

**Research Fellow Dr GUO Zhen** and **PI Prof. Alexei LAPKIN** incorporated a Singapore company to exploit the technology for reaction networks analysis.



## 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 focused on novel electrosynthetic paths for nitrogen oxidation and carbon dioxide reduction. In the case of nitrogen oxidation the new strategy for nitrate generation offers a significant low carbon alternative synthesis route for production of this important product. Current commercial approaches utilise high-temperature-high-pressure processes, with the associated high levels of carbon dioxide emissions. We are currently developing the strategy further for application in the micro-variable pressure and temperature electrosynthesis plant in the IRP2 laboratories. Dr Dai Chencheng has been working with Dr Zeng Minyu to design the reactor and flow infrastructure required for demonstration and evaluation of the nitrate synthesis approach.

In collaboration with Prof. Jim Yang Lee, 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. Dr Zhang has recently explored the use of an electrode-integrated membrane (EIM) technology to mitigate the operational problem and to extend the membrane lifetime. The EIM consists of a porous titanium foil at the back of the membrane and a counter electrode in front of the membrane and is being tested for reverse osmosis (RO). He evaluated two common types of foulants (Alginate and BSA-FITC) and found the anti-fouling performance of the EIM to be better than that of the standard membrane.

In further electrocatalysis research developments Dr Sun Libo has been exploring new strategies

for single atom catalysts (SACs) applications in eCO<sub>2</sub>RR reactions. In this work it has been observed that the CO partial current density curves exhibit greatly enhanced j<sub>CO</sub> compared with Ni-N-C which suggests that the Cu-N-C fabricated in this system is not a good catalyst toward eCO<sub>2</sub>RR.

The recently launched start-up company Datum Electronix, between Dr Kamal Elouarzaki and Dr Adrian Fisher, has been active in developing further industrial partnerships and is in advanced discussions with a Chinese company to develop a first-generation water treatment facility for mining applications.

In collaboration with Prof. Erik Birgersson, Dr Kuppa Ashoke Raman and Vishvak Kannan, work has continued in the area of electrosynthetic reactors. Vishvak Kannan has established a generic approach for numerical multi-scale electrochemical modelling and analysis. In this report, a summary of the progress in quantifying the uncertainties around the safety of a commercially available 18650 Sony Li-ion battery is presented. The safety of this battery is evaluated with respect to simultaneous change in various properties of the battery and a thermal management system using phase change materials (PCM). This study was performed for a hypothetical application in a Tesla Model S (P90D) AWD Performance car at its peak and 70% motor capacities.

**Dr Adrian Fisher, PI**  
**University of Cambridge**

## Update on work package 2.1

### Advanced electrode architectures

Dr Kamal ELOUARZAKI's (Senior Research Fellow, NTU) recent work focuses on a chemical inactivation/redox reactivation process (IAP) based on surface-confined rhodium-porphyrinic catalyst on multi-walled carbon nanotubes surface, which presents an excellent and stable electron transfer. A chronoamperometric method was used with mathematical models and digital simulation to investigate the IAP at the catalytic metallic site. A mechanistic analysis of the non-catalytic and catalytic responses exhibited by this complex is presented, enabling a deep understanding of the thermodynamic and kinetic pa-

rameters that govern the IAP. These studies support a mechanism for sugar oxidation that proceeds through a complex EC'CECE scheme with catalytic steps similar to the ones reported for hydrogenases. The overall mechanism was detailed based on both electrochemical experiments and experimentally validated models. The high activity of this catalyst allows integration of this molecular nanomaterial in a fully molecular fuel cell together with phthalocyanine cobalt at the cathode. As shown in Figure 2.1 below, the resulting fuel cell reaches  $0.3 \text{ mW cm}^{-2}$  with a possible regeneration of initial performance.

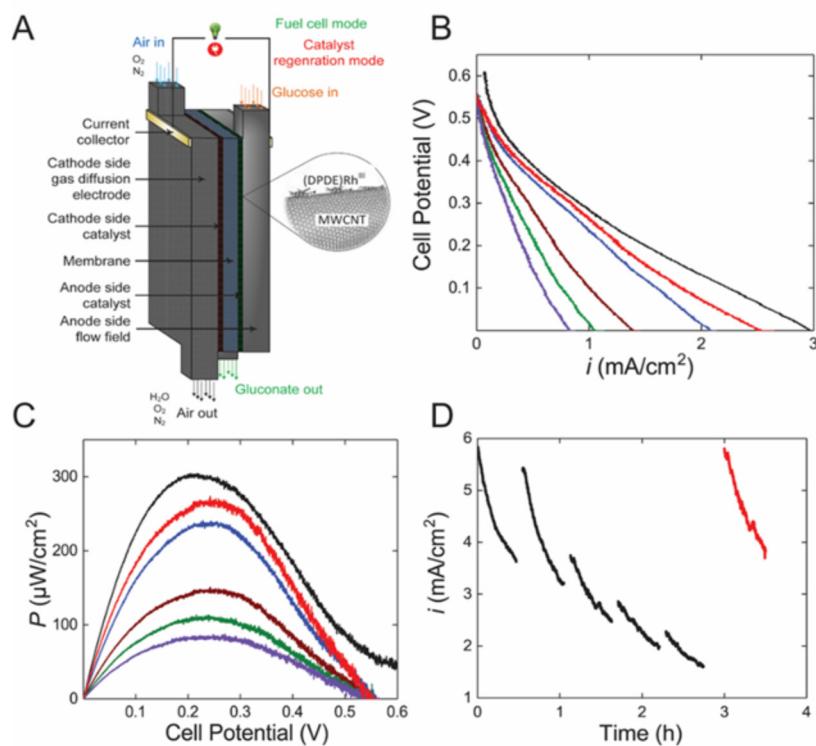


Fig. 2.1: (a) Schematic of the glucose fuel cell (GFC).

(b) Polarisation curves measured at a scan rate of  $2 \text{ mV s}^{-1}$  with the initial measurement in black and the final measurement in purple; the red curve represents the polarisation curve after the application of  $-1.0 \text{ V}$ .

(c) Power curves corresponding to the polarisation curves with the red curve representing the measurement performed after applying  $-1.0 \text{ V}$ .

(d) Galvanostatic measurements recorded at  $0.2 \text{ V}$  for 30 minutes each with a relaxation time of 4 minutes; the red curve corresponds to the galvanostatic measurement recorded after the application of  $-1.0 \text{ V}$ .

Dr Kamal ELOUARZAKI

**Dr DAI Chencheng (Research Fellow, NTU)** has been working on the development of electrocatalysts for electrochemical preparation of nitrate from direct nitrogen oxidation reaction (NOR). A series of  $ZnFe_xCo_{2-x}O_4$  ( $x = 0, 0.4, 1, 1.4$ , and  $2$ ) spinel oxides were synthesised and characterised as the electrocatalysts for NOR tests in  $N_2$ -saturated  $1\text{ M KOH}$  electrolyte. The  $ZnFe_{0.4}Co_{1.6}O_4$  oxide with the highest Co oxidation state demonstrates the highest nitrate production rate of  $130 \pm 12 \mu\text{mol h}^{-1} \text{ g}_{\text{Mo}}^{-1}$  throughout the chronoamperometry test at an applied potential of  $1.6\text{ V}$  vs. reversible hydrogen electrode (RHE) for 24 hours. DFT calculations were also conducted to further understand the synergistic effect of Fe and Co atoms on the NOR performance. The calculation results show that Fe facilitates the formation of the first N-O bond on the  $^*N$  site, while Co assists in stabilising the absorbed  $\text{OH}^-$  for the successful generation of the second and third N-O bonds. Hence, the synergistic effect of Co and Fe atoms in the spinel oxide catalyst improves the NOR activity by lowering the energy barrier. This work provides a choice for energy-efficient and environmentally friendly production of nitrate.

**Nur Farhanah's BTE ROSLI's (PhD student, NTU)** recent work explores group 14 functionalised materials: germanane, methylgermanane and siloxene. 2D monoelemental group 14 materials beyond graphene, such as silicene and germanene, have recently gained a lot of attention. Covalent functionalisation of group 14 layered materials can lead to significant tuning of their properties. While optical and electronic properties of germanene, silicene and their derivatives have been studied in detail previously, there is no information on their electrochemistry and toxicity. Hence, electrochemical applications of 2D si-

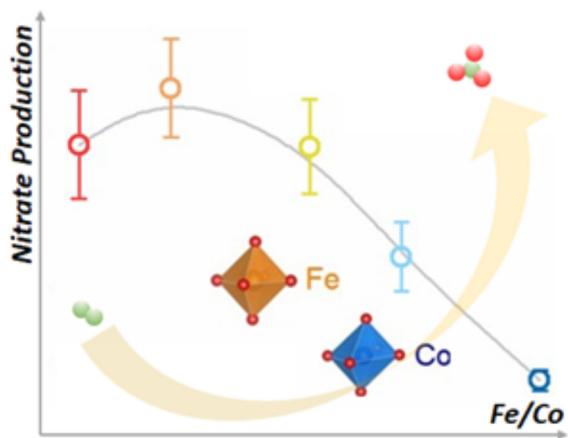


Fig. 2.2: A diagram showing impact of the Fe:Co ratio on the production of nitrates from  $N_2$ .

Dr DAI Chencheng

loxene, germanane and methylgermanane, specifically for the detection of an important biomarker, dopamine, as well as catalysis of the oxygen reduction and hydrogen evolution reactions (which are important in energy applications) are explored. In addition, toxicity studies of these materials are conducted to gain insights on their possible harmful effects toward human health. These studies provide fundamental insights into electrochemical and toxic properties of functionalised group 14 layered materials for future electrochemical applications.

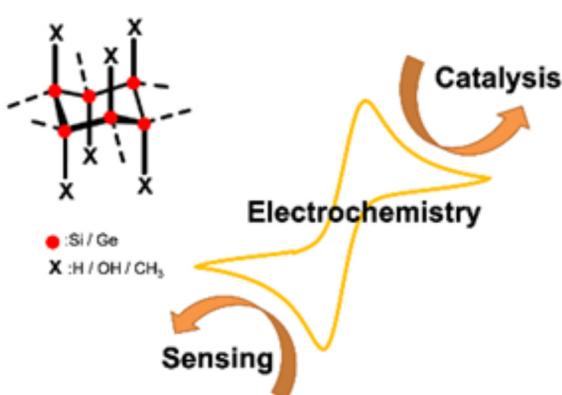


Fig. 2.3: Diagram of the molecular structure and electrochemistry allowing for catalysis and sensing.

Nur Farhanah BTE ROSLI

**THAM Guo Xiong (PhD student, NTU)** has carried out voltammetric studies of functionalised carbon nanotubes (fCNTs) dispersions in various solvents and surfactants with the drop casting of the fCNT suspensions on a cleanly polished glassy carbon electrode surface. A number of factors such as the type of fCNTs (single and multi-walled fCNTs), amount of fCNTs, type of fCNTs and variable scan rates are also studied with further quantitative analysis of the experimental results. Regardless of the type of fCNTs, fCNT % wt and dispersing solvent used, thin layer diffusion and semi-infinite diffusion are determined to be predominant at slow and fast scan rates respectively when fCNT/GCE film electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM fer-

ri/ferrocyanide redox couple. Investigation of the fCNT/GCE film electrodes immersed in the presence of cationic, anionic or nonionic surfactants in the bulk solution have unsurprisingly revealed that the cationic surfactant DDAB provides the best current responses. Optimum current responses with the least  $\Delta E_{pp}$  values are obtained with the film electrodes immersed in bulk solutions containing DDAB concentrations at the cmc value.

His thesis titled 'Electrochemistry of Thin Film Electrodes via Surface Modification' has been completed and submitted to the examiners board, pending for oral defence.

## Update on work package 2.2

### Co-generation and electrolytic synthesis reactor engineering

**Dr ZHANG Tianran (Research Fellow, NUS)** reports that fouling is a perennial issue in membrane applications for seawater treatment. He is exploring the use of an electrode-integrated membrane (EIM) technology to mitigate the operational problem and to extend the membrane lifetime. The EIM consists of a porous titanium foil at the back of the membrane and a counter electrode in front of the membrane and is being tested for reverse osmosis (RO). He evaluated two common types of foulants (Alginate and BSA-FITC) and found the anti-fouling performance of the EIM to be better than that of the standard membrane. The water fluxes after prolonged fouling were reduced by ~ 4% for both Alginate

and BSA-FITC, while the values were > 10% for the standard membrane (Figure 2.4). Furthermore, he discovered that the counter electrode plays an important role in the anti-fouling performance. An Ag wire counter electrode performs better than a Ti wire counter electrode, possibly because of additional Ag electro-reactions with the foulants. With these reactions, the applied voltage needed to deliver similar anti-fouling performance is smaller for the Ag wire and the energy consumption of the EIM can be reduced. Dr ZHANG Tianran now seeks to understand the mechanism of Ag electro-reactions and also to test other metals as counter electrodes.

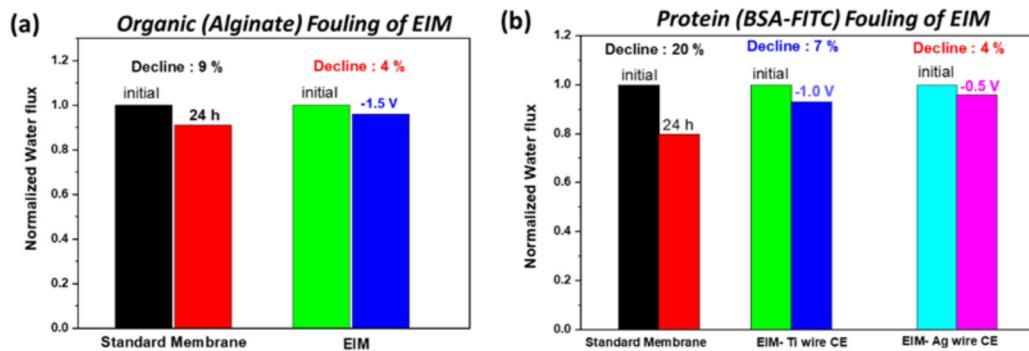


Fig. 2.4: The anti-fouling performance of the EIM for (a) Alginate and (b) BSA-FITC. The standard membrane was used as a reference.

Dr ZHANG Tianran

**Dr SUN Libo (Research Fellow, NTU)** has used a precursor directed method to develop isolated double atom catalysts (DACs). To clarify the merits of using DACs rather than single atom catalysts (SACs) towards eCO<sub>2</sub>RR, the contrast experiments of Ni-N-C and Cu-N-C were further performed for comparison. From Figure 2.5b, the Ni-N-C only shows the FECO higher than 90% from -0.60 V vs. RHE ( $92.28 \pm 1.09\%$ ), and the value at -0.55 V vs. RHE is  $80.58 \pm 1.68\%$ , while NiCu-N-C could reach ca. 90% at -0.55 V vs. RHE ( $89.10 \pm 1.49\%$ ). In contrast, Cu-N-C exhibits the opposite trend toward CO production, and decreased FECO with increased applied potential could be observed. From the CO partial current density curves (Figure 2.5c), it is obvious that NiCu-N-C exhibits greatly enhanced jCO compared with Ni-

N-C. For instance, at -0.85 V vs. RHE, the jCO for NiCu-N-C is  $-17.21 \pm 0.13 \text{ mA cm}^{-2}$ , while that for Ni-N-C is  $-10.52 \pm 0.13 \text{ mA cm}^{-2}$ . However, as shown in Figure 2.5b, the activity for Cu-N-C is rather low, which suggests that the Cu-N-C fabricated in this system is not a good catalyst toward eCO<sub>2</sub>RR. Furthermore, when the activity of the SACs and DACs were compared in Figure 2.5d, it is noticed that the TOFCO for Cu-N-C is the poorest among these catalysts. However, the TOFCO for NiCu-N-C is significantly improved; as discussed in the previous section, the TOFCO value for NiCu-N-C is  $36.20 \pm 0.17 \text{ s}^{-1}$  at -0.85 V vs. RHE. For comparison, Ni-N-C and Cu-N-C exhibit a TOFCO value of  $22.51 \pm 0.22 \text{ s}^{-1}$  and  $1.37 \pm 0.05 \text{ s}^{-1}$  at the same applied potential.

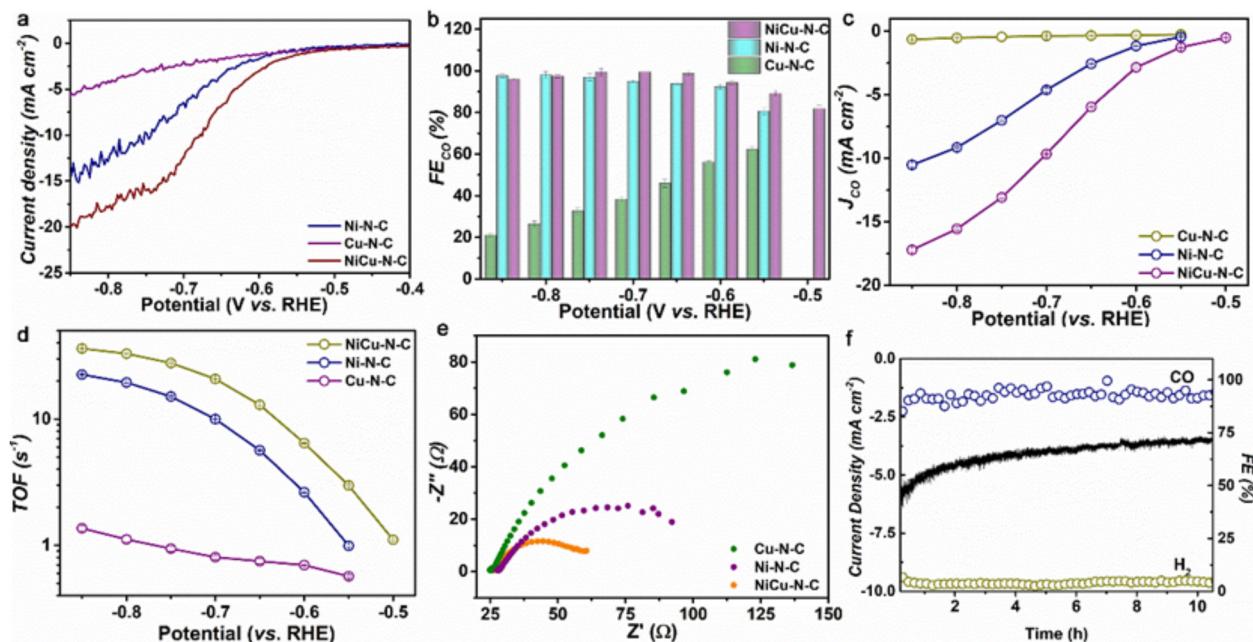


Fig. 2.5: (a) The LSV curves. (b) Faradaic efficiency of CO. (c) Partial current density of CO. (d) Turnover frequency. (e) EIS spectra. (f) Stability test of NiCu-N-C.

Dr SUN Libo

**Vishvak KANNAN (PhD Student, NUS)** is working on numerical multi-scale electrochemical modelling and analysis. In this report, a summary of the progress in quantifying the uncertainties around the safety of a commercially available 18650 Sony Li-ion battery is presented. The safety of this battery is evaluated with respect to simultaneous change in various properties of the battery and a thermal management system using phase change materials (PCM). This study was performed for a hypothetical application in a Tesla Model S (P90D) AWD Performance car at its peak and 70% motor capacities.

The safety of Li-ion batteries is as important, if not more, as their performance because their use in contemporary transport applications can otherwise lead to catastrophic scenarios. Owing to the exothermic reactions and complex heat transfer within Li-ion batteries, they are prone to overheating and possible thermal runaway in the absence of adequate thermal management systems. Therefore, to ensure safe operation it is key to evaluate the uncertainties with respect to a thermal management system along with the uncer-

tainties in the intricate multiphysical phenomena within the system. To achieve this, Vishvak KANNAN conducted Monte Carlo simulations followed by sensitivity analysis to correlate the variability of 14 different factors with the safety of the 18650 Sony cell with a PCM in stressed conditions. He identified the ambient temperature to have most influence on the safety of the battery. The effect of the ambient temperature on the safety of the battery, characterised by its maximum temperature, is illustrated in Figure 2.6. It can be observed that despite having a PCM, it is probable to encounter unsafe scenarios like thermal runaways for ambient temperatures greater than 327 K.

In addition, the probability of the sub-optimal unsafe scenarios occurring was also estimated by examining the distribution of the maximum temperature within the battery. Finally, reduced surrogate models were obtained with an accuracy of about 91% through supervised machine learning algorithms.

In January, Vishvak KANNAN submitted his thesis to NUS for evaluation.

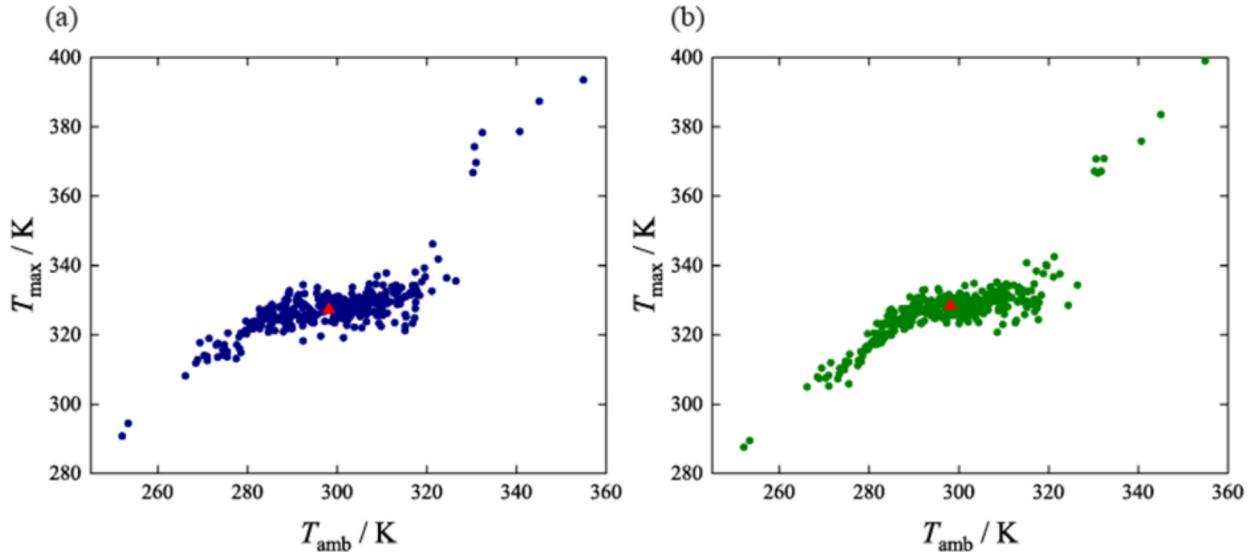


Fig. 2.6: Effect of  $T_{\text{amb}}$  on  $T_{\text{max}}$  when the battery was discharged at (a) 70% motor capacity and (b) peak motor capacity. The red triangles represent the  $T_{\text{max}}$  for the mean conditions.

Vishvak KANNAN

**ZHANG Shengliang (PhD student, NUS)** has been working on dual-band electrochromic smart windows capable of independent control of near-infrared (NIR) and visible (VIS) light transmittance. His most recent work was focused on the controllable synthesis of oxygen deficient  $\text{TiO}_{2-x}$  nanocrystals (NCs) with good uniformity and tuneable LSPR performance, and their application for dual-band electrochromic modulation. A series of  $\text{TiO}_{2-x}$  NCs with different oxygen vacancy concentration, morphology and particle size were prepared by varying F to Ti atomic ratio in the precursor mix. The  $\text{TiO}_{2-x}$  NCs with the strongest LSPR absorption and smallest particle size are selected for dual-band electrochromic

application. The optimised  $\text{TiO}_{2-x}$  NC film is not only able to modulate the NIR and VIS light transmittance independently and effectively through three distinct operating modes, but also delivers an impressive electrochromic performance – high optical modulation of the full solar spectrum (95.5%, 98.8%, 90.5% and 77.5% at 633, 800, 1200 and 1600 nm respectively), fast switching speed, high bistability and long cycle life (95.6% capacity retention after 2000 cycles). These measurements demonstrate the great potential of that single-component  $\text{TiO}_{2-x}$  NC with abundant oxygen vacancy for spectrally-selective electrochromic modulation of VIS light and NIR.

## Update on work package 2.3

### Micro-variable pressure and temperature electrosynthesis plant

**Dr ZENG Minyu (Research Fellow, CAM)** has designed and is constructing a temperature/pressure flow rig with the aim to 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. The rig has been installed in the clean room and is ready to launch imminently. A similar yet smaller scale rig is currently under construction in Cambridge's Department of Chemical Engineering and Biotechnology.

Dr ZENG Minyu also reports on novel anode electrode design and synthesis for environmentally friendly bio-photovoltaic applications. Bio-photovoltaics, or BPVs, are green and environmentally friendly ways to harvest solar energy. They utilise oxygenic photosynthetic microorganisms, such as microalgae and cyanobacteria, to harness light energy for the generation of electric current through the photolysis of water. When

the microorganisms undergo photosynthesis, water is split into electrons, protons and oxygen in the anodic chamber. The electrons obtained from photosynthesis flow through an external circuit to recombine with protons and oxygen to form water at the cathode. BPVs, however, generally produce lower power densities as compared to other solar power systems. One of the strategies adopted widely to overcome this shortcoming is to enhance the transfer of electrons that are generated within the photosynthetic microorganisms to a working electrode poised as anode by looking at appropriate anode materials. The latter will have a major impact on current and power outputs in a BPV. As general guidance, the anode material in a BPV device needs to be stable, biocompatible, conductive, inexpensive and suitable for cell adhesion. It has been proven that some previously developed electrodes for inorganic fuel cell application function well in a BPV environment. Carbon-based materials are examples. Work has been conducted to explore potential carbon materials for BPV anode applications. Titanium based materials follow.

## 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 15.

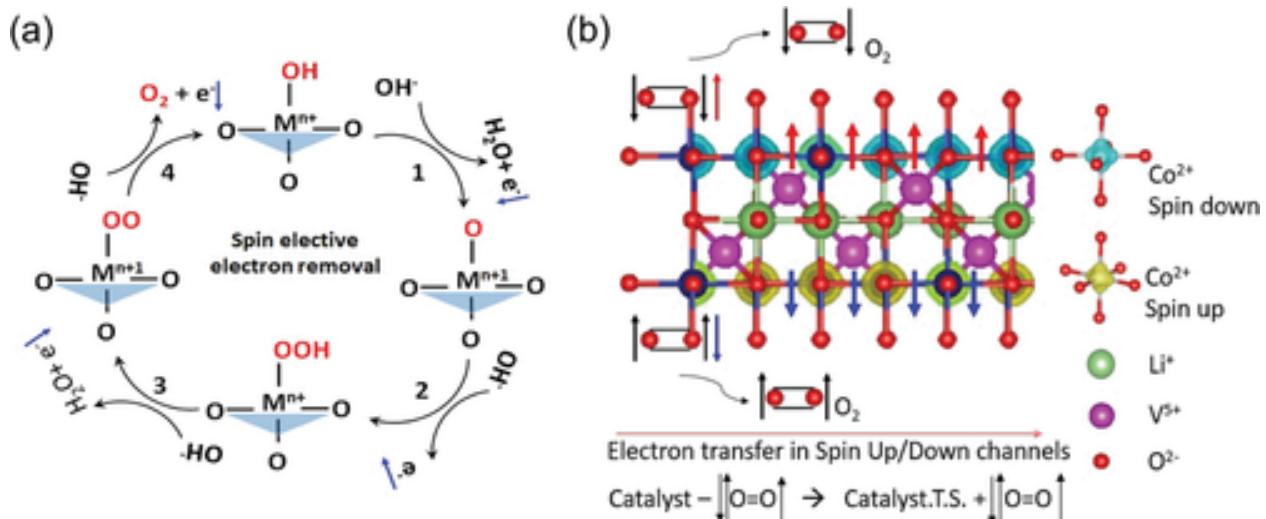
### Antiferromagnetic inverse spinel oxide $\text{LiCoVO}_4$ with spin-polarized channels for water oxidation

Riccardo Ruixi Chen, Yuanmiao Sun, Samuel Jun Hoong Ong, Shibo Xi, Yonghua Du, Chuntai Liu, Ovadia Lev and Zhichuan J. Xu, *Advanced Materials*

DOI: 10.1002/adma.201907976

**Abstract:** Exploring highly efficient catalysts for the oxygen evolution reaction (OER) is essential for water electrolysis. Cost-effective transition-metal oxides with reasonable activity are raising attention. Recently, OER reactants' and products' differing spin configurations have been thought to cause slow reaction kinetics. Catalysts with magnetically polarized channels could selectively remove electrons with opposite magnetic moment and conserve overall spin during OER, enhancing triplet state oxygen molecule evolution. Herein, antiferromagnetic inverse spinel oxide

$\text{LiCoVO}_4$  is found to contain  $\text{d}^7 \text{Co}^{2+}$  ions that can be stabilized under active octahedral sites, possessing high spin states  $S = 3/2$  ( $t_{2g}^5 e_g^2$ ). With high spin configuration, each  $\text{Co}^{2+}$  ion has an ideal magnetic moment of  $3 \mu_B$ , allowing the edge-shared  $\text{Co}^{2+}$  octahedra in spinel to be magnetically polarized. Density functional theory simulation results show that the layered antiferromagnetic  $\text{LiCoVO}_4$  studied contains magnetically polarized channels. The average magnetic moment ( $\mu_{\text{ave}}$ ) per transition-metal atom in the spin conduction channel is around  $2.66 \mu_B$ . Such channels are able to enhance the selective removal of spin-oriented electrons from the reactants during the OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution. In addition, the  $\text{LiCoVO}_4$  reported has been identified as an oxide catalyst with excellent OER activity.



a) The spin selective OER reaction mechanism. b) Spin selective electron transfer in layered antiferromagnetic  $\text{LiCoVO}_4$ .

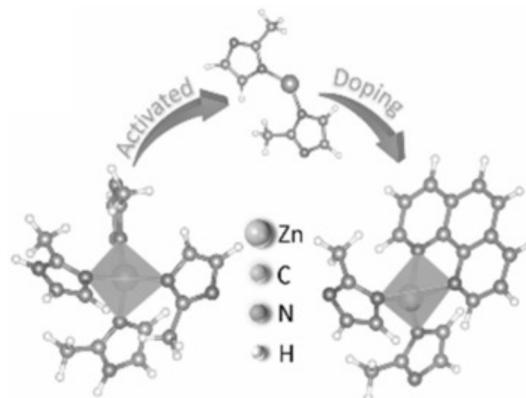
## Boosting electrochemical CO<sub>2</sub> reduction on metal-organic frameworks via ligand doping

Shuo Dou, Jiajia Song, Shibo Xi, Yonghua Du, Jiong Wang, Zhen-Feng Huang, Zhichuan J. Xu and Xin Wang, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.201814711

**Abstract:** Electrochemical CO<sub>2</sub> reduction relies on the availability of highly efficient and selective catalysts. Herein, we report a general strategy to boost the activity of metal-organic frameworks (MOFs) towards CO<sub>2</sub> reduction via ligand doping. A strong electron-donating molecule of 1,10-phenanthroline was doped into Zn-based MOFs of zeolitic imidazolate framework-8 (ZIF-8) as CO<sub>2</sub> reduction electrocatalyst. Experimental and theoretical evidences reveal that the electron-

donating nature of phenanthroline enables a charge transfer, which induces adjacent active sites at the sp<sup>2</sup> C atoms in the imidazole ligand possessing more electrons, and facilitates the generation of \*COOH, hence leading to improved activity and Faradaic efficiency towards CO production.



## Chemical and structural origin of lattice oxygen oxidation in Co-Zn oxyhydroxide oxygen evolution electrocatalysts

Zhen-Feng Huang, Jiajia Song, Yonghua Du, Shibo Xi, Shuo Dou, Jean Marie Vianney Nsanizimana, Cheng Wang, Zhichuan J. Xu and Xin Wang, *Nature Energy*

DOI: 10.1038/s41560-019-0355-9

**Abstract:** The oxygen evolution reaction (OER) is a key process in electrochemical energy conversion devices. Understanding the origins of the lattice oxygen oxidation mechanism is crucial because OER catalysts operating via this mechanism could bypass certain limitations associated with those operating by the conventional adsorbate evolution mechanism. Transition metal oxy-

hydroxides are often considered to be the real catalytic species in a variety of OER catalysts and their low-dimensional layered structures readily allow direct formation of the O-O bond. Here, we incorporate catalytically inactive Zn<sup>2+</sup> into CoOOH and suggest that the OER mechanism is dependent on the amount of Zn<sup>2+</sup> in the catalyst. The inclusion of the Zn<sup>2+</sup> ions gives rise to oxygen non-bonding states with different local configurations that depend on the quantity of Zn<sup>2+</sup>. We propose that the OER proceeds via the lattice oxygen oxidation mechanism pathway on the metal oxyhydroxides only if two neighbouring oxidized oxygens can hybridize their oxygen holes without sacrificing metal–oxygen hybridization significantly, finding that Zn<sub>0.2</sub>Co<sub>0.8</sub>OOH has the optimum activity.



*a) Schematic of the preparation process for zinc-substituted CoOOH. (b) SEM image of Zn<sub>0.2</sub>Co<sub>0.8</sub>OOH.*

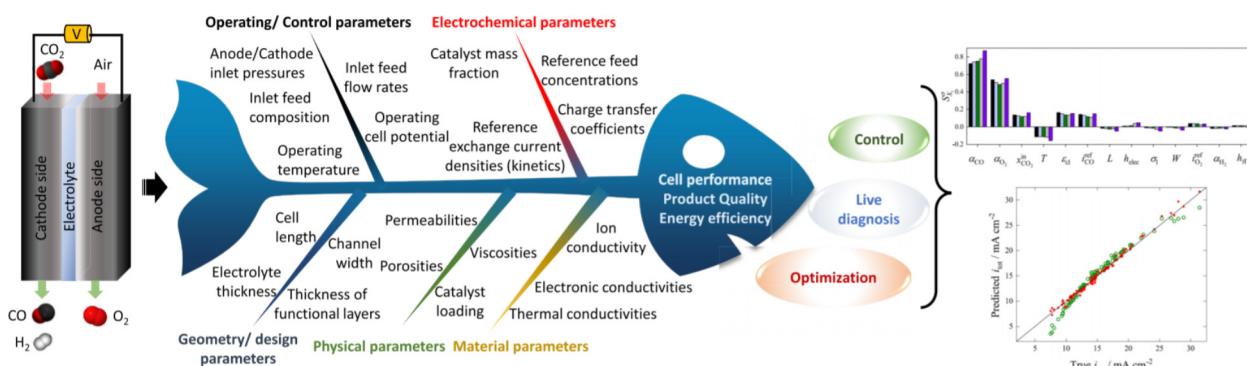
## Correlating uncertainties of a CO<sub>2</sub> to CO microfluidic electrochemical reactor: a Monte Carlo simulation

Vishvak Kannan, K. Ashoke Raman, Adrian Fisher and Erik Birgersson, *Industrial & Engineering Chemistry Research*

DOI: 10.1021/acs.iecr.9b04596

**Abstract:** The electrochemical conversion of CO<sub>2</sub> into useful chemicals in a microfluidic flow cell (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, we carry out a Monte Carlo simulation (MCS) based on a mechanistic mathematical model for the electrochemical conversion of CO<sub>2</sub> to CO. The MCS is conducted in two scenarios: first, by varying the stochastic parameters

individually (IND), and second, by varying all of the stochastic parameters simultaneously (SIM), at different cell potentials. These parameters are then ranked on the basis of their contributions to the cell performance, the conversion efficiency, and the selectivity, thereby providing insights into optimum ranges of operation. The charge-transfer coefficient toward CO and H<sub>2</sub> formation, catalyst properties, are the most sensitive parameters toward the cell performance and conversion efficiency and the 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 cell potentials. Furthermore, we derive 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.



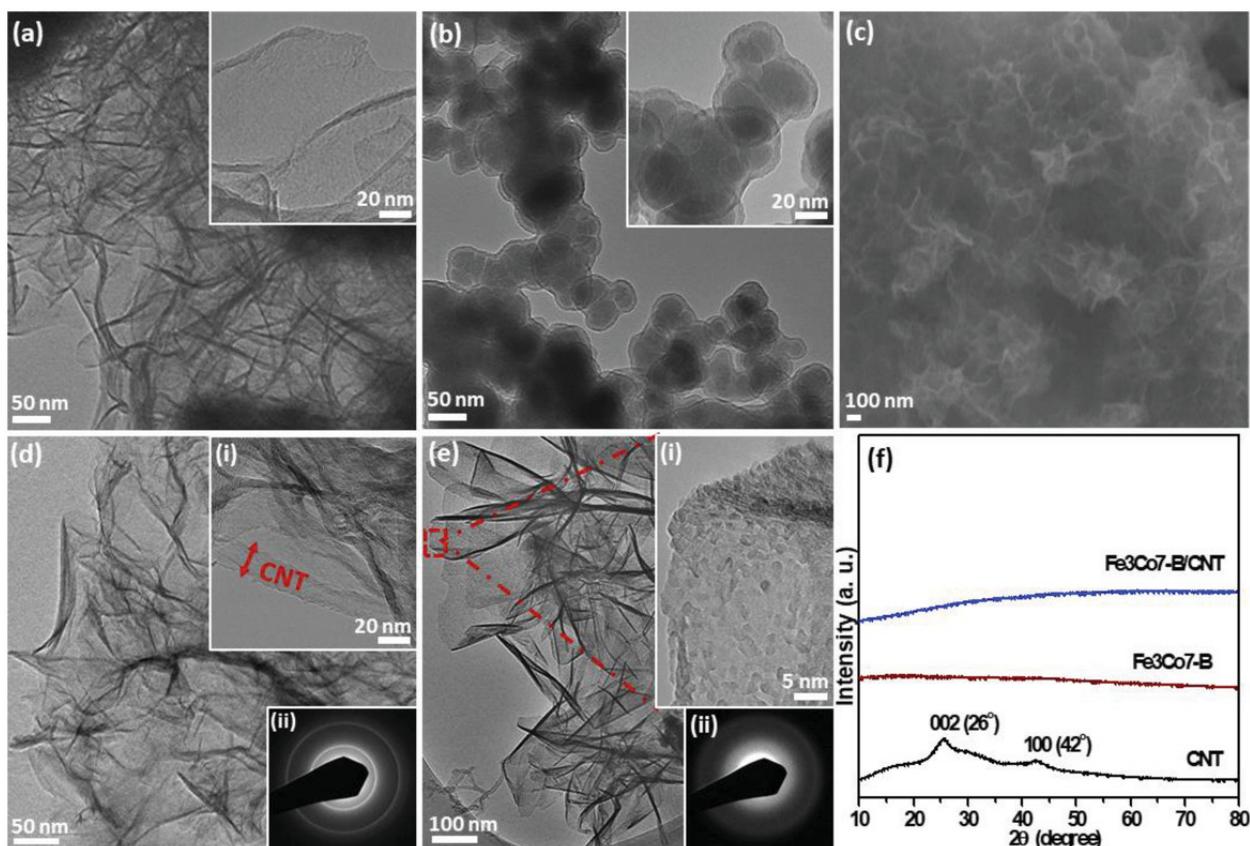
## Tailoring of metal boride morphology via anion for efficient water oxidation

Jean Marie Vianney Nsanzimana, Lanqian Gong, Raksha Dangol, Vikas Reddu, Vishal Jose, Bao Yu Xia, Qingyu Yan, Jong-Min Lee and Xin Wang, *Advanced Energy Materials*

DOI: 10.1002/aenm.201901503

**Abstract:** The metal-metalloid materials have received a massive interest as oxygen-evolving catalysts due to their ability for charge transfer between different elements and modified electronic structures lowering the kinetic energy barriers of the electrochemical processes. Herein, a facile and

systematic preparation of metal borides by chemical reduction is reported, with morphologies ranging from nanoparticles to nanosheets which is driven by a careful selection of metal salts solution. The iron doping in cobalt boride nanosheets is found to be an effective approach to further tune the water oxidation activity. The as-prepared catalyst exhibited superior oxygen evolution performance in 1.0 m KOH as the optimized ternary CoFe boride needs an overpotential of 265 mV to achieve a current density of 10 mA cm<sup>-2</sup> at a mass loading of 0.3 mg cm<sup>-2</sup>.



a) TEM image of pristine Co-B and b) pristine Co-B(Cl). c) SEM image of Co-B/CNT hybrid. TEM images of d) Co-B/CNT and e) Fe5Co5-B/CNT. The insets: i) at high-magnificence and ii) SAED pattern. f) XRD patterns of Fe3Co7-B/CNT, Fe3Co7-B, and CNT.

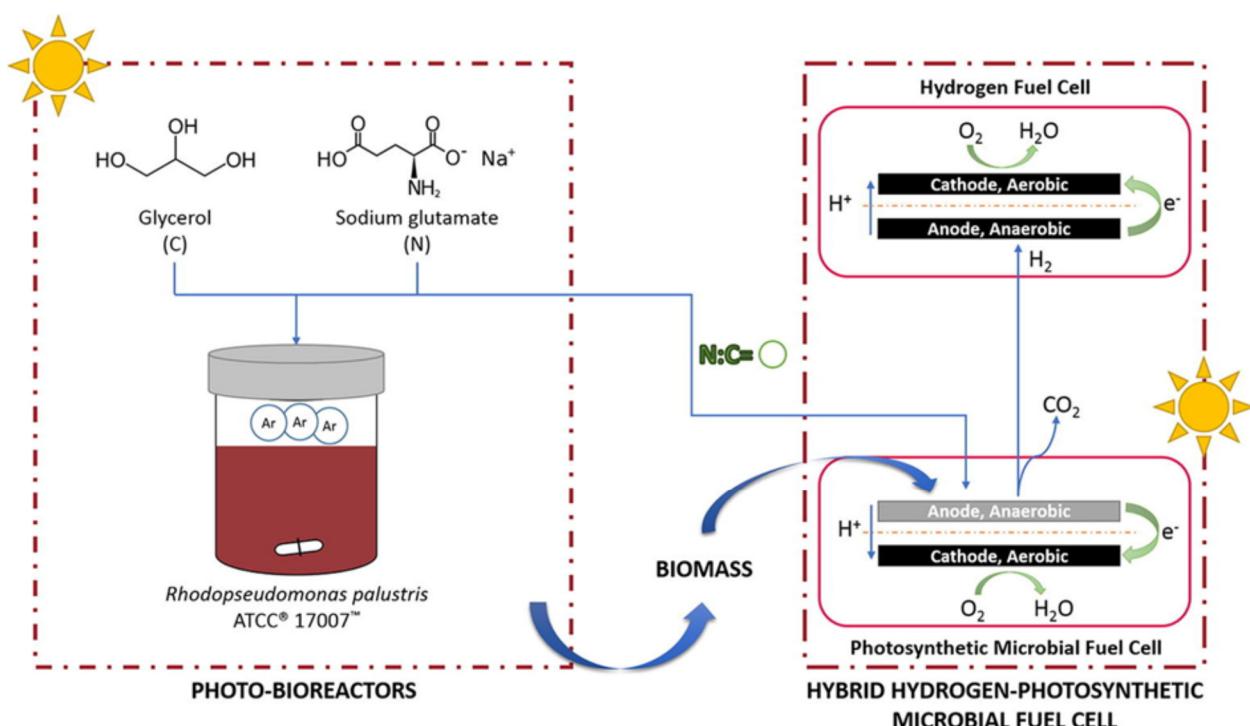
## Mechanistic evaluation of the exoelectrogenic activity of *Rhodopseudomonas palustris* under different nitrogen regimes

Aazraa O. Pankhan, Kamran Yunus and Adrian C. Fisher, *Bioresource Technology*

DOI: 10.1016/j.biortech.2019.122637

**Abstract:** The operation of bioelectrochemical systems (BESs) relies on the ability of microbes to export electrons outside of their cells. However, microorganisms are not evolutionary conceived to power BESs as most of the redox processes occur within. In this study, a low cost strategy equivalent to the one used to improve hydrogen production is employed to divert electrons from

the metabolism to an electrode. Varying the ratio of nitrogen to carbon concentration (0, 0.20 and 0.54) determines what fraction of the electron flux is directed towards biosynthesis, biohydrogen generation and extracellular electron transfer. The ratio of 0.54 produced a higher specific growth rate while the ratio of 0.20 resulted in combined higher maximum specific hydrogen production and exoelectrogenic activity, translating into a maximum power density of  $2.39 \pm 0.13$  mW m<sup>-2</sup> in a novel hybrid hydrogen-photosynthetic microbial fuel cell. The current work sets a framework for the optimisation of *R. palustris* for bioenergy recovery.



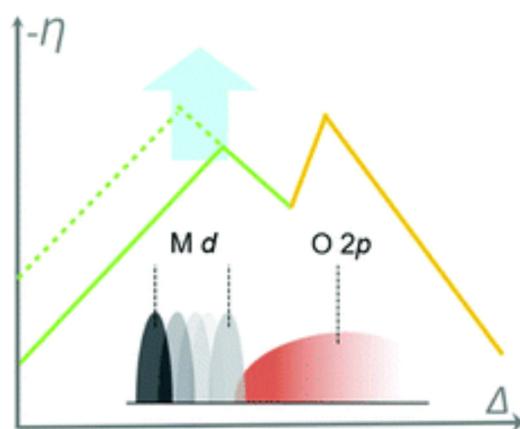
## A review on fundamentals for designing oxygen evolution electrocatalysts

Jiajia Song, Chao Wei, Zhen-Feng Huang, Chun-tai Liu, Lin Zeng, Xin Wang and Zhichuan J. Xu, *Chemical Society Reviews*

DOI: 10.1039/C9CS00607A

**Abstract:** Electricity-driven water splitting can facilitate the storage of electrical energy in the form of hydrogen gas. As a half-reaction of electricity-driven water splitting, the oxygen evolution reaction (OER) is the major bottleneck due to the sluggish kinetics of this four-electron transfer reaction. Developing low-cost and robust OER catalysts is critical to solving this efficiency problem in water splitting. The catalyst design has to be built based on the fundamental understanding of the OER mechanism and the origin of the reaction overpotential. In this article, we summarize the recent progress in understanding OER mechanisms, which include the conventional adsorbate evolution mechanism (AEM) and lattice-oxygen-mediated mechanism (LOM) from both theoretical and experimental aspects. We start with the discussion on the AEM and its linked

scaling relations among various reaction intermediates. The strategies to reduce overpotential based on the AEM and its derived descriptors are then introduced. To further reduce the OER overpotential, it is necessary to break the scaling relation of  $\text{HOO}^*$  and  $\text{HO}^*$  intermediates in conventional AEM to go beyond the activity limitation of the volcano relationship. Strategies such as stabilization of  $\text{HOO}^*$ , proton acceptor functionality, and switching the OER pathway to LOM are discussed. The remaining questions on the OER and related perspectives are also presented at the end.



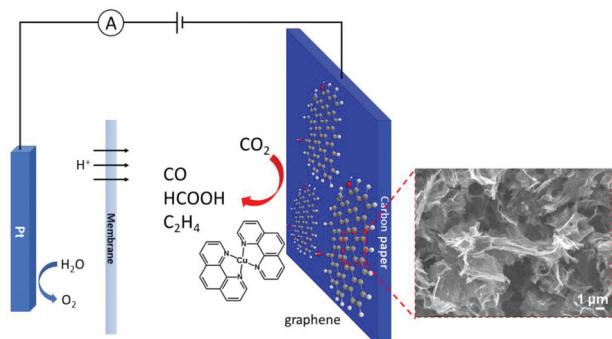
## A water-soluble Cu complex as molecular catalyst for electrocatalytic $\text{CO}_2$ reduction on graphene-based electrodes

Jiong Wang, Liyong Gan, Qianwen Zhang, Vikas Reddu, Yuecheng Peng, Zhichao Liu, Xinghua Xia, Cheng Wang and Xin Wang, *Advanced Energy Materials*

DOI: 10.1002/aenm.201803151

**Abstract:** A structurally simple molecular 1,10-phenanthroline-Cu complex on a mesostructured graphene matrix that can be active and selective toward  $\text{CO}_2$  reduction over  $\text{H}_2$  evolution in an aqueous solution is reported. The active sites con-

sist of Cu(I) center in a distorted trigonal bipyramidal geometry, which enables the adsorption of  $\text{CO}_2$  with  $\eta^1\text{-COO}$ -like configuration to commence the catalysis, with a turnover frequency of  $\approx 45 \text{ s}^{-1}$  at  $-1 \text{ V}$  versus reversible hydrogen electrode. Using *in situ* infrared spectroelectrochemical investigation, it is demonstrated that the Cu complex can be reversibly heterogenized near the graphene surface via potential control. An increase of electron density in the complex is observed as a result of the interaction from the electric field, which further tunes the electron distribution in the neighboring  $\text{CO}_2$ . It is also found that the mesostructure of graphene matrix favored  $\text{CO}_2$  reduction on the Cu center over hydrogen evolution by limiting mass transport from the bulk solution to the electrode surface.



*A phen-Cu complex applied as  $\text{CO}_2\text{RR}$  molecular catalyst on mesoporous graphene electrode in  $\text{CO}_2$  saturated  $0.1 \text{ M}$   $\text{KHCO}_3$ . A representative SEM image of the graphene surface is included.*

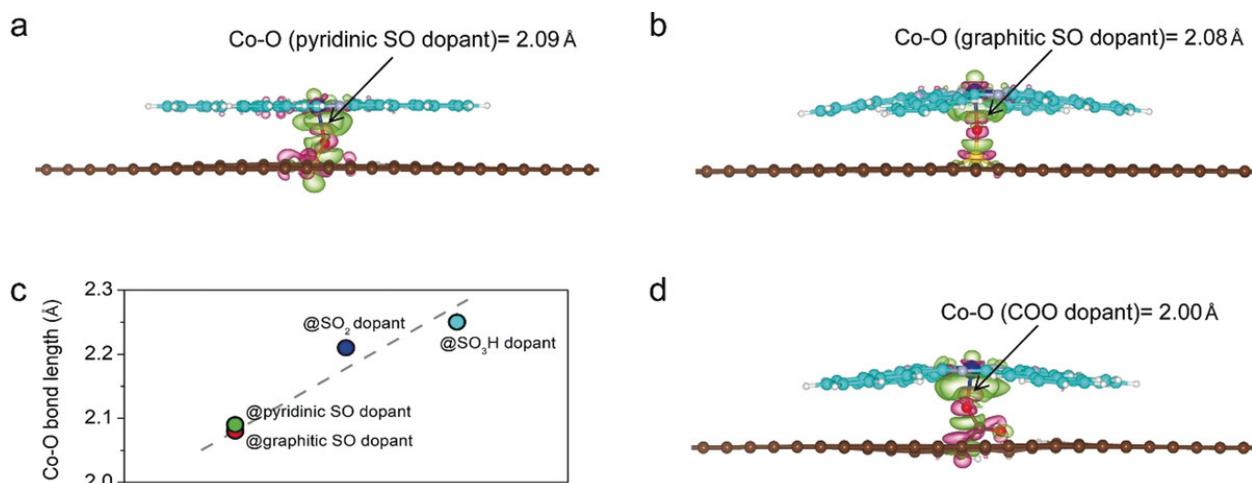
## Linkage effect in the heterogenization of cobalt complexes by doped graphene for electrocatalytic CO<sub>2</sub> reduction

Jiong Wang, Xiang Huang, Shibo Xi, Jong-Min Lee, Cheng Wang, Yonghua Du and Xin Wang, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.201906475

**Abstract:** Immobilization of planar Co<sup>II</sup>-2,3-naphthalocyanine (NapCo) complexes onto doped graphene resulted in a heterogeneous molecular Co electrocatalyst that was active and selective to reduce CO<sub>2</sub> into CO in aqueous solution. A systematic study revealed that graphitic sulfoxide and carboxyl dopants of graphene were

the efficient binding sites for the immobilization of NapCo through axial coordination and resulted in active Co sites for CO<sub>2</sub> reduction. Compared to carboxyl dopants, the sulfoxide dopants further improved the electron communication between NapCo and graphene, which led to the increase of turnover frequency of the Co sites by about 3 times for CO production with a Faradic efficiency up to 97 %. Pristine NapCo in the absence of a graphene support did not display efficient electron communication with the electrode and thus failed to serve as the electrochemical active site for CO<sub>2</sub> reduction under the identical conditions.



*Charge density difference of NapCo immobilized on pyridinic SO (a) and graphitic SO (b) dopants of graphene. c) The Co-O bond lengths for NapCo on SO, SO<sub>2</sub>, and SO<sub>3</sub>H dopants of graphene. d) Charge density difference of NapCo on a COO dopant of graphene. The charge accumulation regions are in pink and charge depletion regions are in green. The charge density difference was obtained via subtracting the total charge densities of adsorbed NapCo and graphene from that of NapCo@graphene. Iso-surface level was set to  $\pm 0.001$  e/bohr<sup>3</sup>. Brown C atoms of graphene, cyan C atoms of NapCo, white H, yellow S, red O, blue Co and light blue N atoms.*

## Electrocatalysis: a core technique for a sustainable future [editorial]

Zhichuan J. Xu and Xun Wang, *Chemistry – A European Journal*

DOI: 10.1002/chem.202000909

**Abstract:** Electrocatalysis will play a key role in a proposed man-made, sustainable future. An energy infrastructure without using fossil fuels is a

blue map. It can be a hydrogen-based energy system, involving the hydrogen production from solar-driven water electrolysis and the hydrogen fuel cell, or it can be a closed carbon cycle using carbon dioxide electrolysis techniques. Zero-carbon emission cannot be achieved without electrocatalysis.

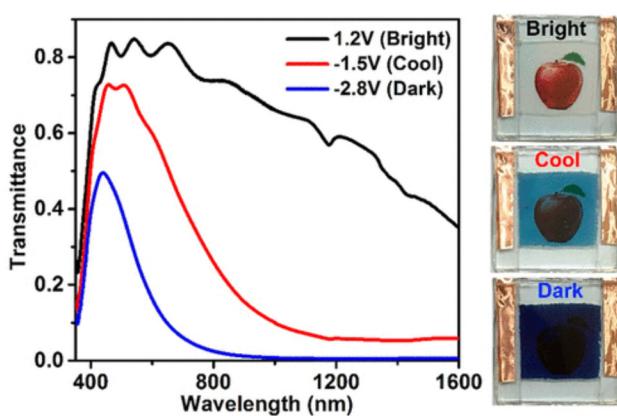
## Dual-band electrochromic devices with a transparent conductive capacitive charge-balancing anode

Shengliang Zhang, Yang Li, Tianran Zhang, Sheng Cao, Qiaofeng Yao, Haibin Lin, Hualin Ye, Adrian C. Fisher and Jim Yang Lee, *ACS Applied Materials & Interfaces*

DOI: 10.1021/acsami.9b17678

**Abstract:** Dual-band electrochromic devices (DBEDs), which can selectively modulate near-infrared (NIR) and visible (VIS) light transmittance through electrochromism, have gained increasing interest as a building energy saving technology. The technology is strongly dependent on the progress in electrochromic materials. Most current research has focused on the dual-band properties of the cathode materials, leaving the charge-balancing anode materials under-explored by comparison. This is a report of our study on the suitability of tin-doped indium oxide (ITO) nanocrystals (NCs) as a capacitive anode material for DBEDs. The ITO NCs are electrically conductive and VIS light transparent throughout the device operating range. As a result, they would not affect the NIR-selective modulation of the

electrochromic device like most other anode materials do. The high surface area and good conductivity of the ITO NCs facilitate the adsorption/desorption of anions; thereby increasing their effectiveness as an ion storage thin film on the anode to balance the cathode charge. The best DBED prototype assembled from an ITO NC anode and a  $\text{WO}_{3-x}$  cathode showed effective and independent control of VIS light and NIR transmittance with high optical modulation (71.1% at 633 nm, 58.1% at 1200 nm), high coloration efficiency ( $95 \text{ cm}^2 \text{ C}^{-1}$  at 633 nm,  $220 \text{ cm}^2 \text{ C}^{-1}$  at 1200 nm), fast switching speed, good bistability, and cycle stability.



## Other activities and achievements

**PI Dr Adrian FISHER and Research Fellow Dr ZENG Minyu** have been interviewed by the Cambridge Alumni Magazine on the electrochemistry research taking place in IRP2. The article, 'Super Power', was published in the Lent issue of CAM.

Dr Adrian FISHER and Dr ZENG Minyu have enhanced the collaboration with Project Dignity in Singapore by involving them as one of participants in a recent Intra-CREATE application. Although not awarded, momentum persists for further collaboration opportunities. Project Dignity is an organisation which aims to restore dignity to the differently-abled and disadvantaged by providing sponsored training for unemployed adults with special needs and places them with employment partners.

Dr Adrian FISHER and Dr ZENG Minyu further explored the relationship with Chinese Organisation for Rare Disorders (CORD). Potential collaboration for research has been identified and outreach programme has been drafted. CORD is a Chinese NPO which works to promote exchange and cooperation among rare disease patients and organisations, medical specialists, pharmaceutical companies and governmental agencies.

Featured on BBC on Rare Disease Day 2020, Dr Adrian FISHER and Dr ZENG Minyu have launched the CamRareEd programme through the network in Cambridge and the collaborations between Project Dignity and CORD. The CamRareEd programme aims to help bridge this gap for those with rare diseases through a series of educational outreach activities in schools and other public education environments.



# 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

**I**n recent months, we have further expanded our portfolio of soot particle characterisation techniques for laboratory burners and now internal combustion engines as well to include not only particle sizing through Differential Mobility Spectrometry (DMS) and laser-induced incandescence (LII), but also Soot Particle Aerosol Mass Spectrometry (SP-AMS) for single-particle chemical composition.

Continuing our investigations into how the presence of oxygenated hydrocarbons in a fuel affects soot formation as a potential mitigation strategy, we have been doping a laminar coflow ethylene diffusion flame with dimethyl carbonate, dimethoxymethane, and iso-propanol. We have studied the soot-reducing effects of these compounds by means of colour ratio pyrometry and DMS, revealing non-linear blending behaviour.

Computationally, we have been investigating the reactivity of aromatic soot precursors in order to identify the main species involved in soot inception - the least well-understood aspect in the formation of soot. Comparing bond energies, our analysis indicates which species are not likely to fragment in the high-temperature conditions found in a flame. Using density functional theory calculations and kinetic Monte Carlo simulations, we were able to show that these species can exist at appreciable concentrations in a flame.

In the area of flame-synthesised inorganic nanocatalytic materials, we have continued to study our long-time favourite material, titanium dioxide, but also other metals and composites with

other organic and inorganic materials. Our focus has been on gaining an understanding of how synthesis methods and conditions affect the physical and chemical properties of the produced films using a variety of diagnostic and characterisation techniques. For example, we have been looking at nickel-iron phosphate and phosphide-carbon composites, coating of functional metal oxides for applications such as niobium-doped titania for transparent conducting oxides, and soot-templated mesoporous titania for catalyst support.

**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 ZONG Yichen (Research Fellow, NUS) has been leading the experimental research on future fuels for low emission energy conversion. The research activities are conducted primarily through the collaboration of NUS and Cambridge researchers. In the past six months, a series of experiments has been performed on both lab-scale burners and a single-cylinder engine. The combustion efficiency and soot emission are two key indicators under investigation. In the experiments, a DMS particle sizer and laser-induced incandescence are used to trace the formation and growth of soot particles in the fuel combustion. Dr ZONG Yichen is also involved in the internal collaboration between IRP4 and IRP JPS on coastline and shipping emission monitoring and the external collaboration with Environmental Engineering, NUS on single-particle chemical composition using SP-AMS. Some of the results have been published in *Fuel* and another manuscript is under review in *Combustion and Flame*.

TAN Yong Ren (PhD student, CAM) is currently studying the soot formation synergic effect of C3 oxygenated hydrocarbons. The oxygenated hydrocarbons chosen in the study are dimethyl carbonate (DMC), dimethoxymethane (DMM) and iso-propanol (i-PrOH) as they have practical value as fuel additives in engines and they have interesting molecular structures to study their synergistic effects. The methodology that TAN Yong Ren is employing to study the fuels is through doping an ethylene flame with the oxygenated hydrocarbons at 5%, 10%, 15% and 20% under a laminar coflow diffusion configuration. He is using colour ratio pyrometry and differential mobility spectroscopy to understand how the oxygenated hydrocarbons affect the soot formation process in a non-premixed system and understand the differences in the synergic effect between them.

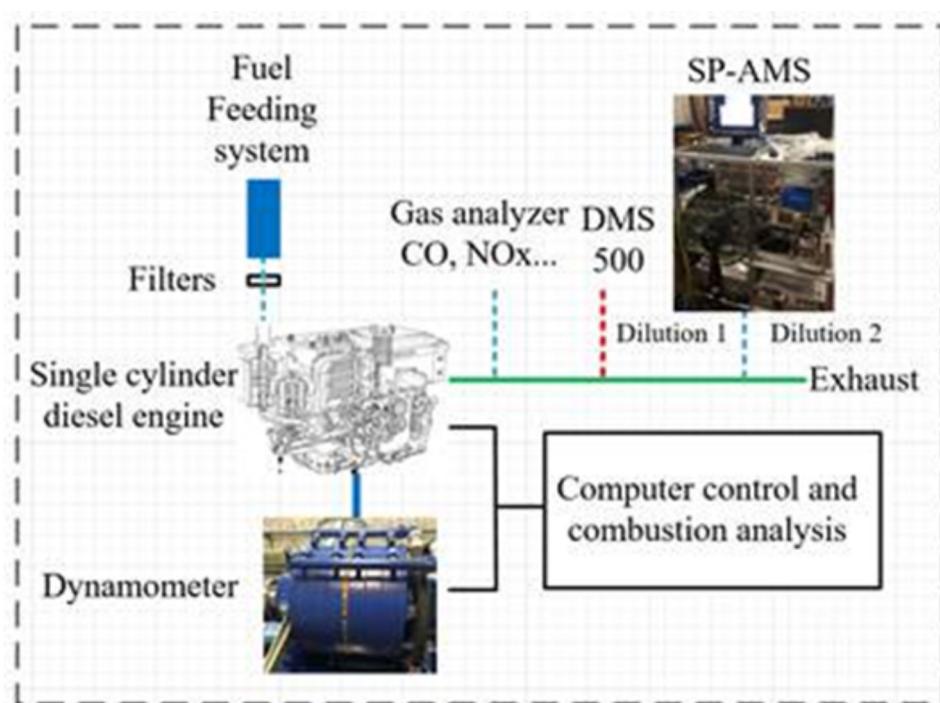


Fig 3.1: Fuel test system on a single cylinder diesel engine.

Dr ZONG Yichen

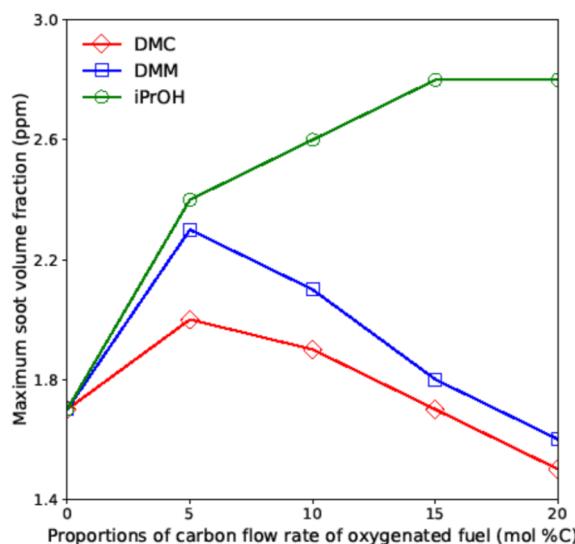


Fig. 3.2: The maximum soot volume fraction for laminar coflow diffusion ethylene flames blended with dimethyl carbonate (DMC), dimethoxymethane (DMM) and iso-propanol (*i*-PrOH) at different proportions of carbon flow rate of oxygenated fuel.

TAN Yong Ren

**Clifford VO Chi Hung (PhD student, NUS)** is writing his thesis on “Metabolism of *Methanococcus maripaludis* S2”. *M. maripaludis* S2 is an archaeon which can convert CO<sub>2</sub> into CH<sub>4</sub>, an interesting microorganism for application in biological carbon capture and utilisation. His main interest is to examine the metabolic processes behind this microorganism. He is currently investigating an enzyme responsible for the production of acetate in *M. maripaludis* S2, a behaviour which has not been reported in the literature. The enzyme was produced in large quantities by a ligation-independent cloning technique in *Escherichia coli*. Its structure was examined via dynamic light scattering and its kinetic activity was investigated via assay.

A collaboration between **Dr Maurin SALAMANCA (Research Fellow, CAM)**, **Dr Sebastian MOSBACH (Senior Research Fellow, CAM)**, **Dr Radomir SLAVCHOV** and other colleagues studying the role of NO<sub>2</sub> and NO in the mechanism of hydrocarbon degradation leading to carbonaceous deposits in engines has been published in *Fuel*.

The results from the colour ratio pyrometry are as shown in Figure 3.2. Increasing iPrOH blending monotonically increases the maximum soot volume fraction (SVF) of the flames. DMC and DMM showed a non-monotonic change in maximum SVF. At a 5% blend, there was an increase in the maximum SVF at different degrees for both fuels. At higher blending ratios of DMM and DMC, the maximum SVF decreases. This is described as the synergistic effect in soot formation. There is a difference in the degree of the synergistic effect of DMM and DMC that can be explained by taking into account the respective fuel decomposition pathways.

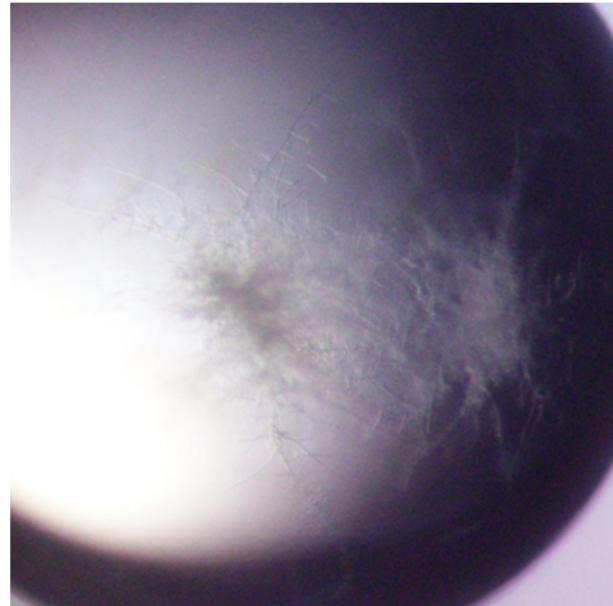


Fig. 3.3: Photo of crystallisation of acetyl coenzyme A synthetase, the enzyme responsible for acetate formation in *Methanococcus maripaludis* S2, as seen under a fluorescent microscope.

Clifford VO Chi Hung

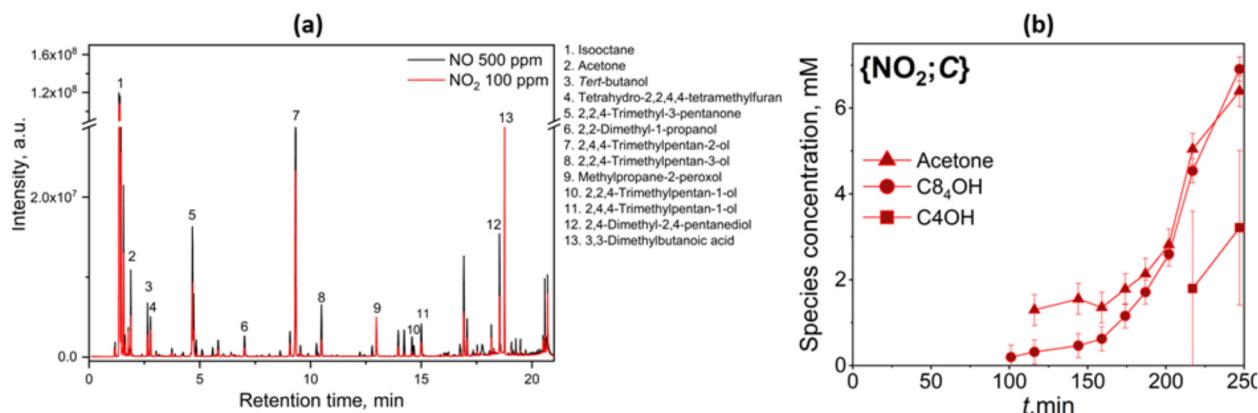


Fig. 3.4: (a) Chromatogram for nitro-oxidation of isoocetane with 500 ppm NO or 100 ppm NO<sub>2</sub>. (b) Evolution of the concentrations of 2,4,4-trimethylpentan-2-ol (C8<sub>4</sub>OH), acetone, and methylpropan-2-ol (C4OH) at 150 °C and increasing NO<sub>2</sub> concentration.

Dr Maurin SALAMANCA

## Update on work package 3.2

### Refinery, fuel and engine of the future — modelling

#### Chemical mechanisms, PAH chemistry, after-treatment

A cross-IRP collaboration with IRP JPS between Dr Sebastian MOSBACH (Senior Research Fellow, CAM), Dr Jethro AKROYD (Senior Research Fellow, CAM) and Dr Feroz FARAZI (Research Fellow, CAM) to apply knowledge-graph technology to the development of chemical models has continued successfully. A mechanism browser tool as a use-case for OntoKin, a semantic representation of chemical kinetic mechanisms within the knowledge graph, has been developed. As an example, the browser tool was applied by a chemist to identify variations in the

rate of a prompt NO<sub>x</sub> formation reaction in the combustion of ammonia as represented by a number of mechanisms in the literature. In addition, autonomous agents were implemented that automatically grow the knowledge graph with quantum calculations of increasingly higher levels for chemical species, thus increasing the quality of available thermodynamic data that feeds into chemical mechanisms. Applying this to an engine pollutant emission use-case is work in progress.

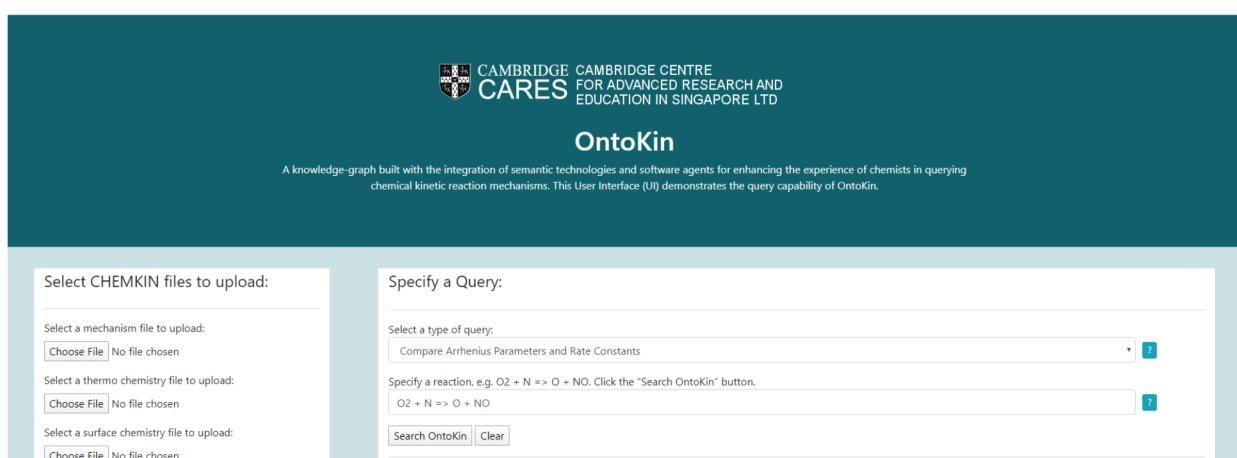


Fig. 3.5: Web user interface for kinetic mechanism knowledge graph with mechanism comparison.

Dr Feroz FARAZI

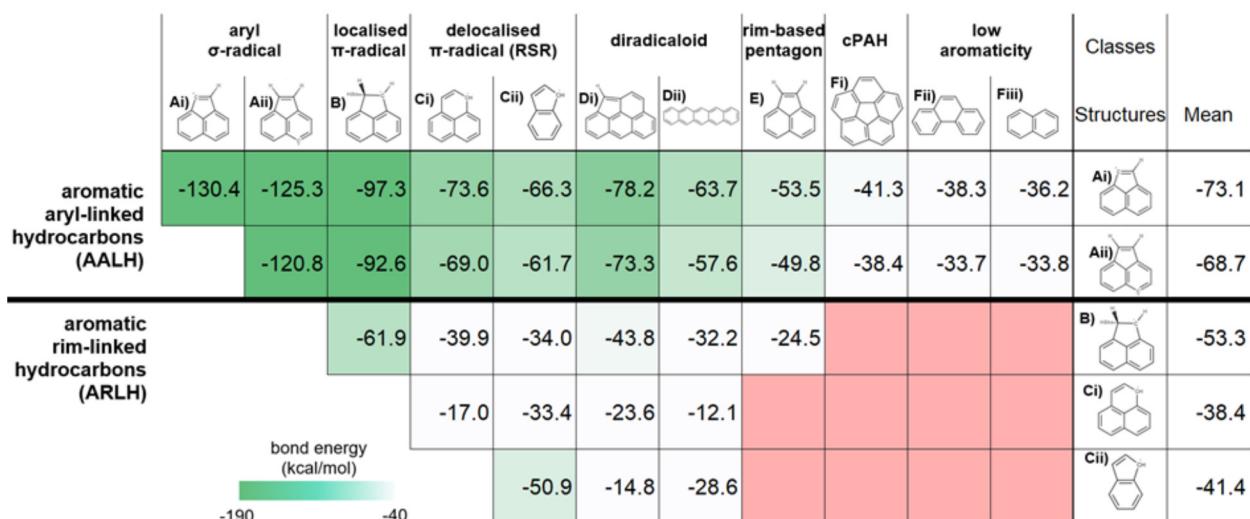


Fig. 3.6: Bond energies between reactive aromatic precursors.

Jacob MARTIN

**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. A systematic exploration, using computational tools, on the reactivity of aromatic soot precursors to find the main species involved in soot formation has now been published in *The Journal of Physical Chemistry C*. This allowed for the matrix of bond energies to be drawn, indicating which species are not likely to fragment.

Two main crosslinks were found; so-called aromatic rim-linked hydrocarbons (ARLH) can be thought of as the rim of a bicycle wheel being welded to another (see Figure 3.7). Aromatic aryl-linked hydrocarbons (AALH) can be thought of as the tyres of the wheel being joined via their edges.

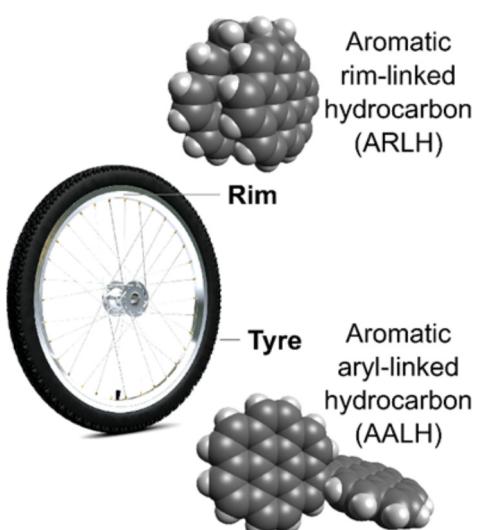


Fig. 3.7: Bicycle tyre analogy for bonding types.

Jacob MARTIN

The reactive sites that lead to the rim-linked species are unique in that they do not decrease in reactivity with size. Figure 3.8 denotes the spin density (blue) showing the electron localisation in  $\pi$ -radicals that is directly proportional to reactivity. Two  $\pi$ -radicals can be observed; those that do not delocalise and those that do. The difference comes about due to the connectivity of the rings and is often related to the presence of non-aromatic pentagonal rings. This presents a new picture of aromatic soot precursors where addition of hydrogen can activate  $\pi$ -radicals within their structure. It was also found that multiple radicals can be activated on a single species, suggesting a mechanism in which the number of radicals on a molecule's structure increases as it grows, until, as Harris and Weiner stated in 1989;

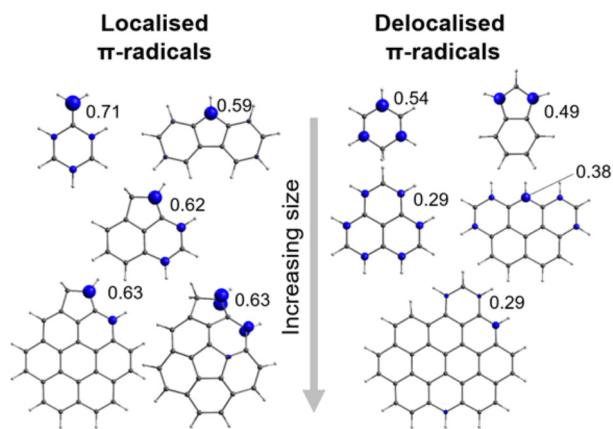
“Once coagulated they will quickly become chemically knit together since a significant fraction of the aromatic species are radicals.”

Further work is being done with **Dr Laura PASCAZIO (Research Fellow, CAM)** looking at pentagonal ring linked species that have been directly imaged in high-resolution Atomic Force Microscopy (AFM). Rim-linked species have also been explored using quantum molecular dynamics revealing stability at flame temperatures. These results are being compiled into a review paper currently. Jacob MARTIN’s thesis (“Investigating the role of curvature on the formation and thermal transformations of soot”) has been submitted and will be examined in April.

**Angiras MENON's (PhD student, CAM)** work focuses on using *ab initio* quantum chemical methods to understand the properties and formation of polycyclic aromatic hydrocarbons (PAHs) and their role in forming carbonaceous nanoparticles in flames. A project on how heptagonal (7-member) rings can be integrated into graphenic PAH structures has been completed by working in conjunction with **Gustavo LEON (PhD student, CAM)**. This work is key to explaining the integration of defects into graphenic structures, which allows the formation of more complex carbon nanostructures such as 3D graphenes. The results show that hydrogen migrations, higher temperatures, and radical character are all important for the formation of seven-member rings. The work has been accepted for publication in *Combustion and Flame*. In other work, the project mentioned above with **Jacob MARTIN (PhD student, CAM)** has focused on the reactivity, electronic structure, and concentration of localised  $\pi$ -radical PAHs. A mechanism for the formation of these localised  $\pi$ -radicals through reactions on rim-based pentagonal rings in PAHs has been constructed by using density functional theory. Kinetic simulations have shown that localised  $\pi$ -radicals are present potentially in significant concentrations at lower temperatures of around 1000 K and remain so until typical flame temperatures of 1500 K. Kinetic Monte Carlo simulations suggest that multiple such localised  $\pi$ -radical sites could exist on a single PAH as well. This work has been accepted for presentation at the 38<sup>th</sup> International Symposium on Combustion. Finally, the rates of bridge forming (cross-linking) reactions between PAHs containing different edge types is underway. This will hopefully shed some insight into which PAHs may preferentially undergo chemical dimerisation.

*Fig. 3.10: Kinetic Monte Carlo simulations performed on reactant PAHs with multiple rim-based pentagonal rings, the key site for localised  $\pi$ -radical formation. The simulations suggest that a significant distribution of reactant PAHs are able to form multiple localised  $\pi$ -radical sites, which could have implications for how they grow and form soot.*

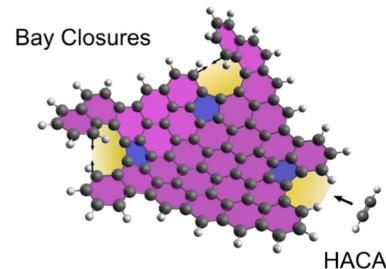
Angiras MENON



*Fig. 3.8: Spin density isosurface (blue) and value of atom with highest Milliken spin density .*

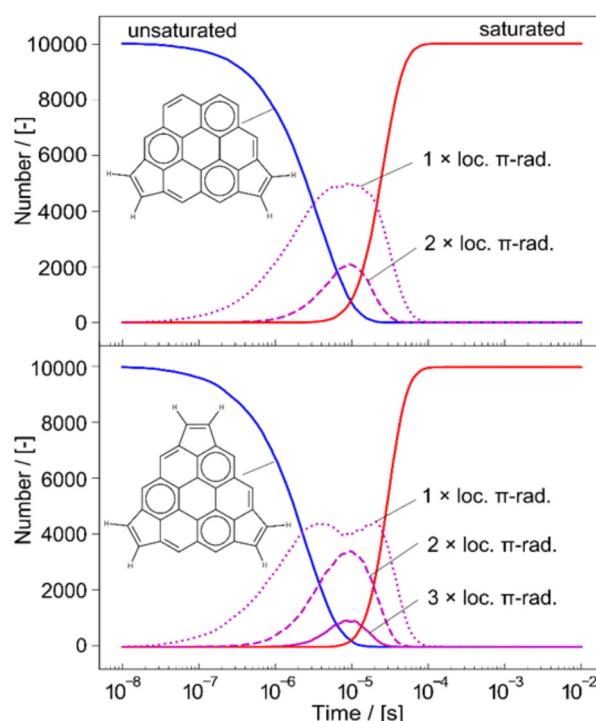
Jacob MARTIN

Rates of 7-member ring formation in PAHs



*Fig. 3.9: Graphical abstract for a paper on seven-member ring formation in PAHs. The sites which can potentially form a seven-member ring are highlighted in yellow.*

Angiras MENON



## Update on work package 3.3

### Better, cheaper, cleaner nanostructures — experimental

#### *Flame synthesis of thin films of mixed metal oxide nanoparticles*

During this reporting period, **Dr SHENG Yuan (Research Fellow, NTU)** has mainly been refining his study of flame-synthesised Ni-Fe phosphate/phosphide-carbon composite films. A deeper understanding of the relationship between synthesis conditions and properties of the resulting films has been gained, especially in terms of how the flame equivalence ratio ( $\varphi$ ) and substrate texture and temperature affect the nature of carbonaceous phases (Figure 3.11). During the study Dr SHENG Yuan designed and commissioned two substrate cooling stages with magnetic and vacuum holding mechanisms to improve the reproducibility of the flame synthesis and deposition technique. The optimised film samples exhibit an oxygen evolution overpotential of  $<350$  mV at  $500$  mA/cm $^2$  in  $1$  M KOH which increases by  $<50$  mV in  $100$  h of continuous electrolysis.

To expand the production capability of the flame synthesis technique, Dr SHENG Yuan is developing a novel burner expected to generate quasi 1-D linear flames that allow continuous production of

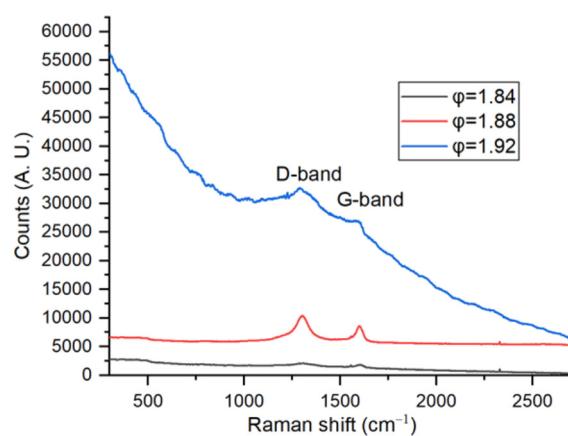


Fig. 3.11: Raman spectra of Ni-Fe phosphate/phosphide-carbon composite films synthesised at different flame equivalence ratios ( $\varphi$ ). The spectra have been shifted vertically for clear presentation.

large films. Computational fluid dynamics studies on the preliminary designs are ongoing. In addition, he has designed a spectroelectrochemical cell for operando FTIR analysis of flame-synthesised materials and electrocatalysts in general. The cell is being manufactured in Singapore. Recently Dr SHENG Yuan has also been active in Work Package 3 of the eCO<sub>2</sub>EP project, helping with the design of CO<sub>2</sub> electrochemical reduction cells (Figure 3.12).

**WU Shuyang's (PhD student, NTU)** main research interest lies in the area of flame synthesised defective TiO<sub>2</sub> for degradation of toxic gaseous pollutants. Over the past six months, his research has mainly focused on the visible-light-driven degradation of volatile organic compounds using vapour-fed flame synthesised blue TiO<sub>2</sub>. In his work, defective blue TiO<sub>2</sub> with a core-shell structure was prepared through the one-step femtosecond stimulated Raman spectroscopy method. The oxygen-deficient flame environment effectively induces the formation of Vo in the TiO<sub>2</sub> nanoparticles. The abundance of defects

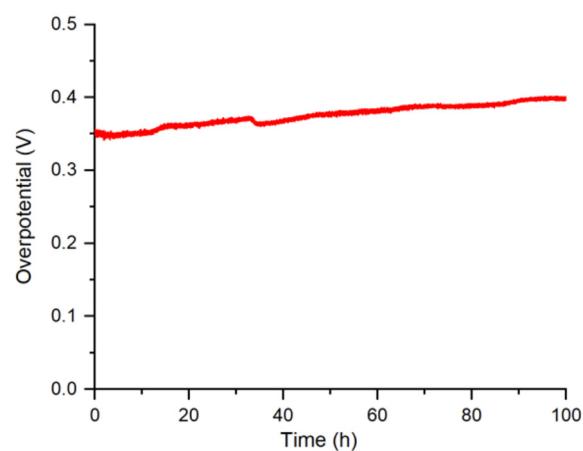


Fig. 3.12: Chronopotentiometric result from a Ni-Fe phosphate/phosphide-carbon composite film sample at an oxygen evolution current density of  $500$  mA/cm $^2$  in  $1$  M KOH.

Dr SHENG Yuan

can be controlled by changing the deposition time. The role of the defects in the photocatalytic reactions was systematically investigated. It is revealed that a moderate content of defects could promote charge separation and enhance the photocatalytic activity of isopropyl alcohol (IPA) degradation. To further investigate the adsorption species and key reaction intermediates for exploring the possible reaction pathway, an *in situ* DRIFTS study was carried out on TiO<sub>2</sub> and P25 for IPA degradation. Since the photo-oxidation reactions take place in sequential steps, the adsorbed IPA is first fully decomposed to acetone. However, the production of acetone only has a slight increase, probably due to the subsequent rapid conversion to intermediate species. The acetone molecule could be attacked by the photo-excited charges and break into a two-carbon species and a single carbon species, which are identified as acetates and formates. The accumulation of the formate and acetate species until steady-state is reached indicates that the rate-limiting step of photo-oxidation of IPA is the mineralisation of formates and acetates to CO<sub>2</sub>. Such a finding provides more insights into the reaction mechanism of IPA photo-oxidation and the correlation of TiO<sub>2</sub> defect level with IPA degradation activity.

In Figure 3.13a, the flame-made samples except for TiO<sub>2</sub>-4 min can completely decompose IPA within 25 min while P25 TiO<sub>2</sub> degrades all IPA in 40 min. Surprisingly, complete mineralisation of acetone to CO<sub>2</sub> was observed on TiO<sub>2</sub>-8 min, TiO<sub>2</sub>-20 min and TiO<sub>2</sub>-35 min in Figure 3.13b. Consistent with the trend of acetone concentration, the CO<sub>2</sub> production on these samples increases slowly in the first 20 min, in which the conversion of IPA to acetone dominates in this stage (Figure 3.13c). Then, the CO<sub>2</sub> production rises rapidly until it reaches the steady state with TiO<sub>2</sub>-20 min showing the highest photocatalytic activity. More photo-induced electrons and holes are generated under the UV-Vis light for flame-made TiO<sub>2</sub> due to its intrinsic electronic structure, which makes the multi-photon oxidation of acetone much easier.

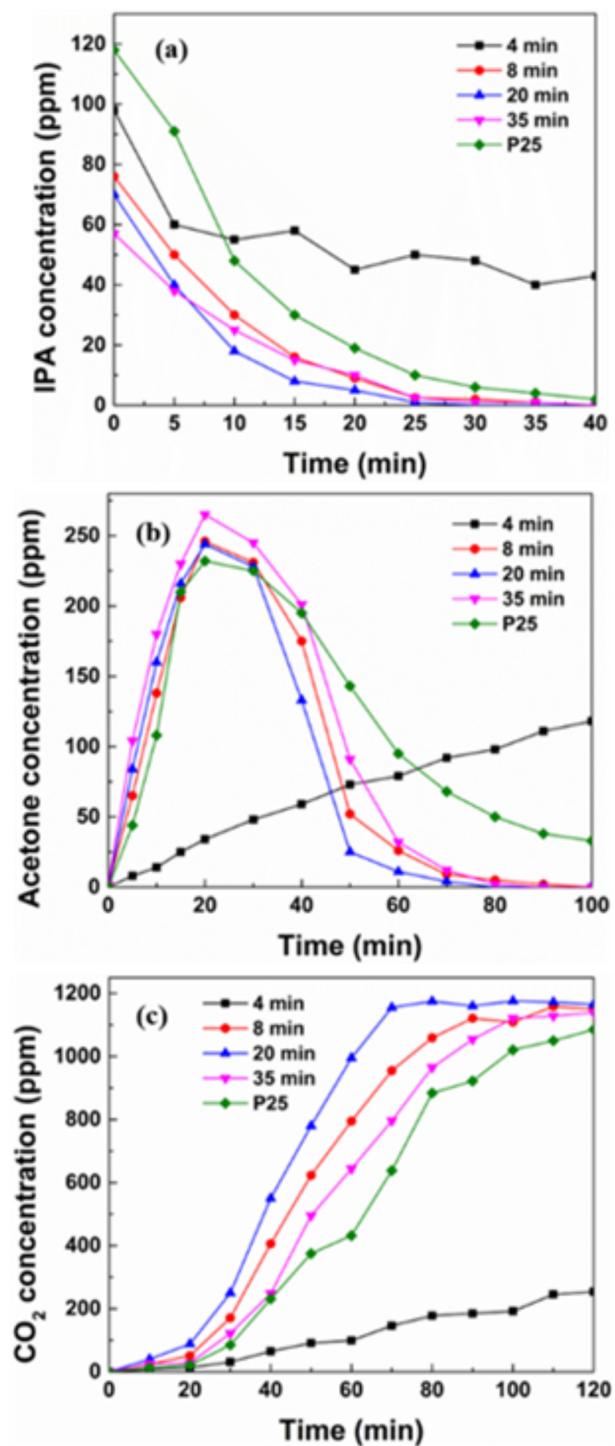


Fig. 3.13: (a) Photocatalytic IPA degradation (b) Acetone production and (c) CO<sub>2</sub> generation over flame-made TiO<sub>2</sub> and P25 TiO<sub>2</sub> (40 mg of TiO<sub>2</sub>, 400 ppm initial IPA concentration, 300 W Xe lamp).

WU Shuyang

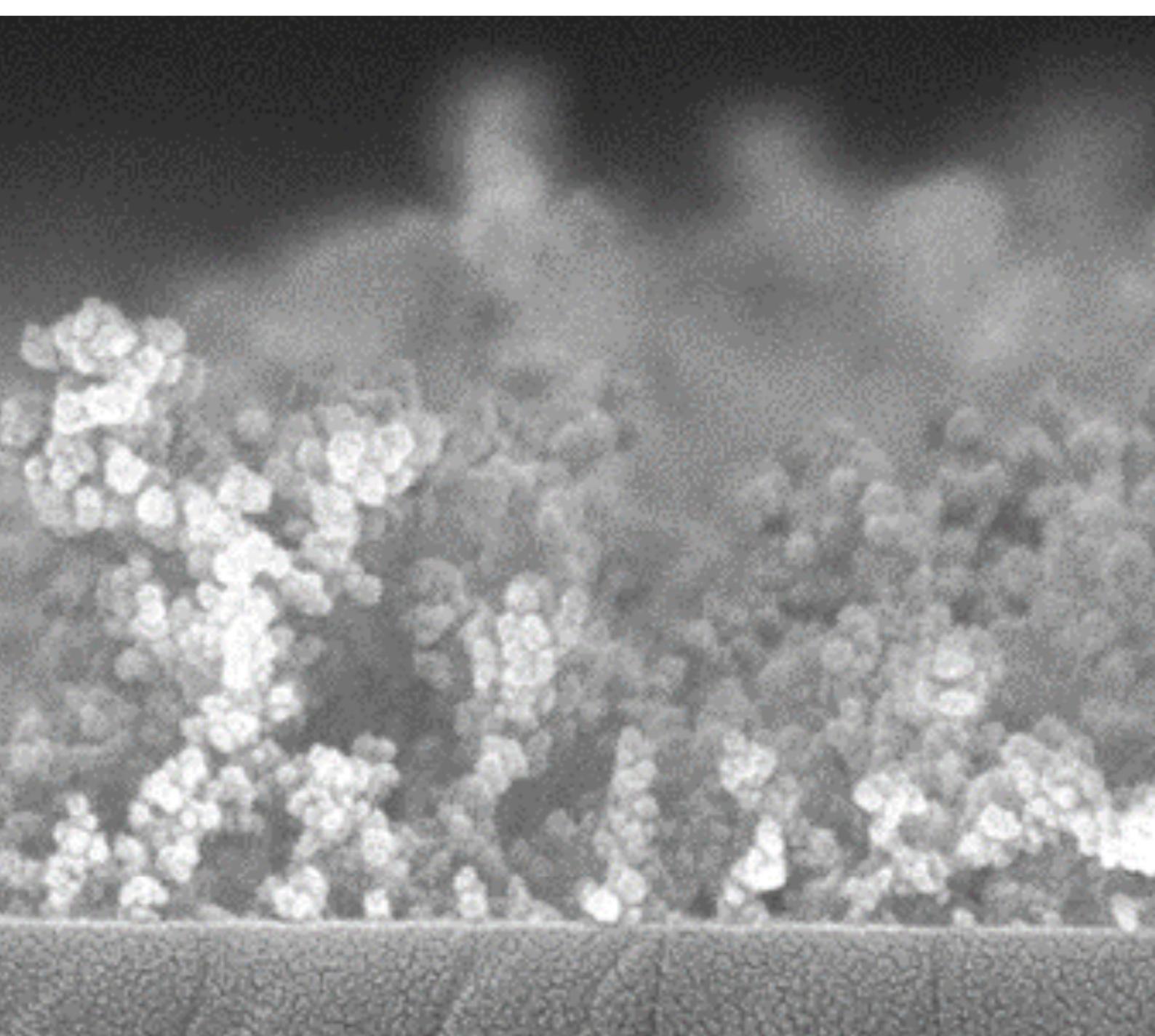
## Update on work package 3.4

### Better, cheaper, cleaner nanostructures — modelling

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

**Manoel MANUPUTTY (PhD student, CAM)** has completed and successfully defended his PhD thesis in November 2019 titled “Morphology and polymorphism of TiO<sub>2</sub> nanoparticles prepared in premixed stagnation flames”. The work contained in the thesis was part of his research in IRP3 in the past four years. Currently, Manoel

MANUPUTTY is exploring the use of premixed stagnation flames for coating of functional metal oxides for applications such as Nb-doped TiO<sub>2</sub> for transparent conducting oxides (TCOs) or soot-templated mesoporous TiO<sub>2</sub> for catalyst support. In the first instance, the question being investigated is how the various flame operating conditions

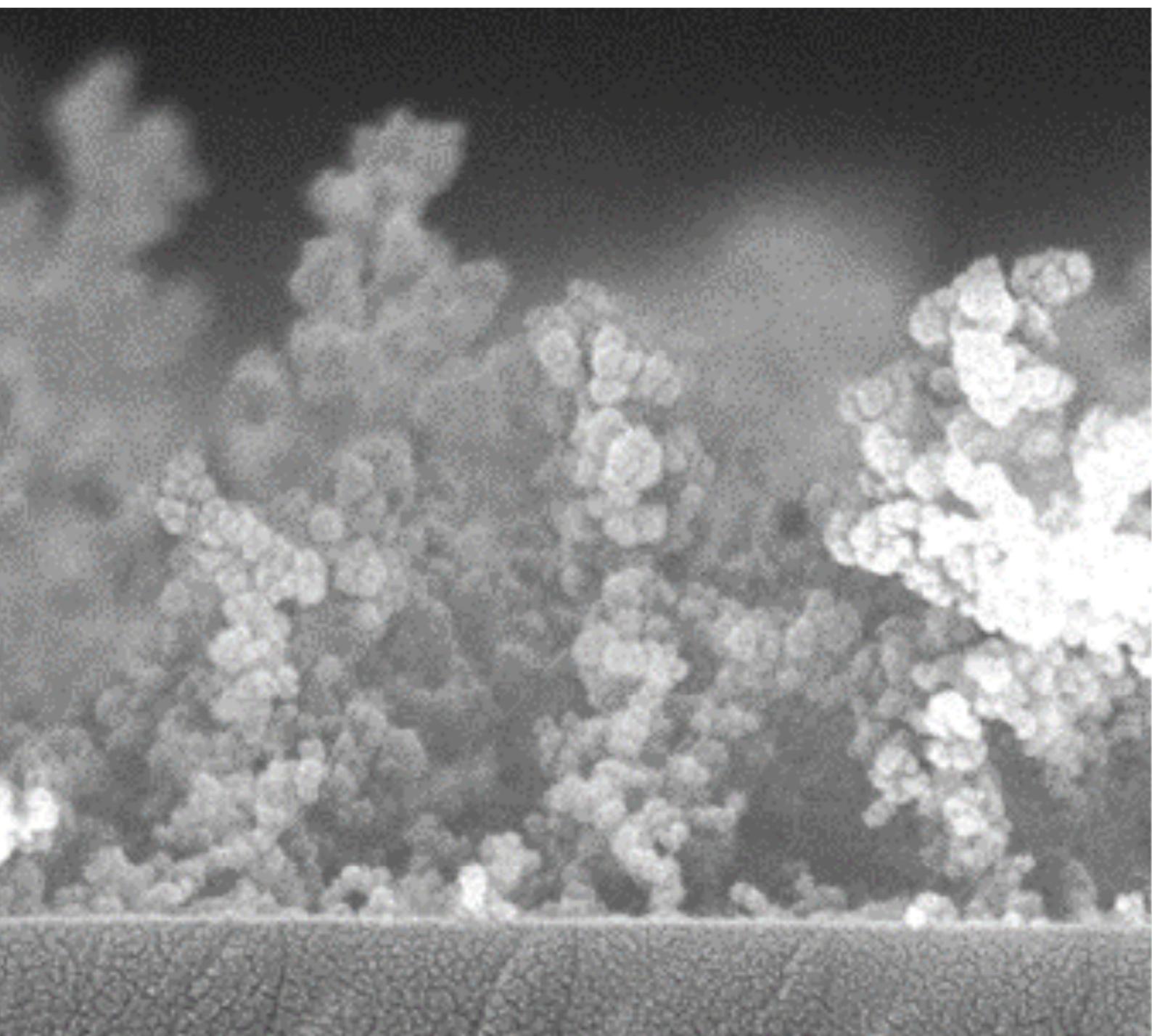


affect the physical and chemical properties of the deposited films. This is done by analysing the flame-prepared films with electron microscopy (such as scanning and transmission electron microscopes) and structural characterisation methods (such as low angle x-ray diffraction). Other than this, Manoel MANUPUTTY is working with **Dr ZONG Yichen (Research Fellow, NUS)** on

developing laser-based diagnostics for combustion experiments including an *in situ* Raman probe designed to study the initial stages of particle formation. The probe has been demonstrated to work well with solid samples but suffers from a weak signal with aerosol samples. Various strategies are currently investigated to increase the signal strength for aerosol samples.

*Figure 3.14: Field-emission scanning electron microscope (FESEM) image of soot-templated mesoporous  $TiO_2$  on a glass substrate synthesised through a two-step flame deposition method.*

Manoel MANUPUTTY



## 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 15.

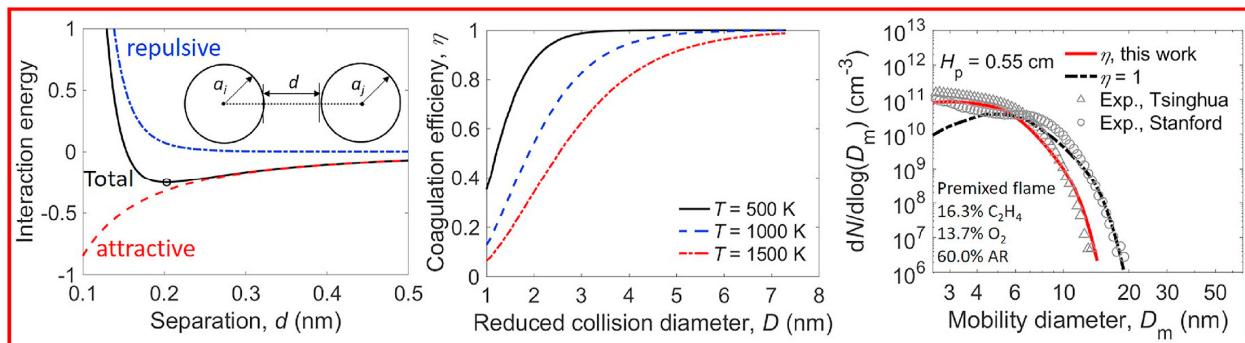
### On the coagulation efficiency of carbonaceous nanoparticles

Dingyu Hou, Diyuan Zong, Casper S. Lindberg, Markus Kraft and Xiaoqing You, *Journal of Aerosol Science*

DOI: 10.1016/j.jaerosci.2019.105478

**Abstract:** In this paper we derived the interaction energy between two spherical nanoparticles from the pair-wise Lennard-Jones attractive and repulsive potentials of the constituent atoms of the two particles, and proposed a coagulation efficiency model based on the average particle kinetic energy and the potential well depth (i.e. the minimum

interaction energy) between two colliding particles. To test the performance of this new coagulation efficiency model, we applied it in detailed population balance modelling of soot particle size distributions (PSDs), and found better agreement with the measured PSDs in a benchmark premixed ethylene flame than that using the unit coagulation efficiency, especially in the range of small particles with mobility diameter less than 5 nm. Moreover, the agreement between the computed and the measured primary particle size distribution (PPSD) was also improved with the new coagulation efficiency model.



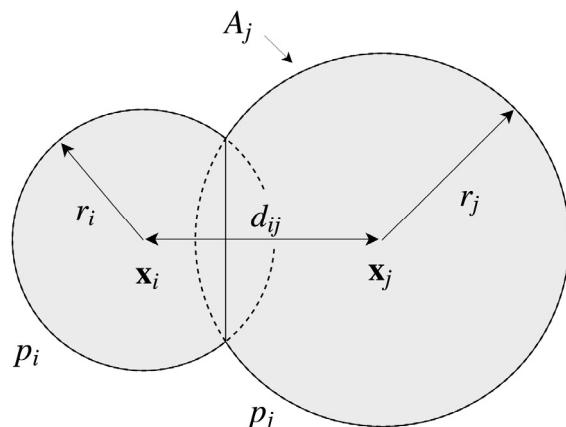
## Numerical simulation and parametric sensitivity study of titanium dioxide particles synthesized in a stagnation flame

Casper S. Lindberg, Manoel Y. Manuputty, Philipp Buerger, Jethro Akroyd and Markus Kraft, *Journal of Aerosol Science*

DOI: 10.1016/j.jaerosci.2019.105451

**Abstract:** A detailed population balance model is used to simulate titanium dioxide nanoparticles synthesised in a stagnation flame from titanium tetraisopropoxide (TTIP) precursor. A two-step simulation methodology is employed to apply the detailed particle model as a post-process to flame profiles obtained from a fully coupled simulation with detailed gas-phase chemistry, flow dynamics and a simple particle model. The detailed particle model tracks the size and coordinates of each primary in an aggregate, and is able to resolve the particle morphology, permitting direct comparison with experimental measurements through simulated TEM-style images. New sintering parameters, informed by molecular dynamics simulations in the literature, are introduced into the model to account for the sintering behaviour of sub-10 nm particles. Simulated primary and aggregate particle size distributions were in excellent agreement with experimental measurements. A parametric sensitivity study found particle morphology to be sensitive to the sintering parameters, demonstrating the need to apply careful consideration to the sintering behaviour of nano-sized particles in modelling studies. The final particle morphology was not found to be sensitive to other model parameters.

Simulated primary and aggregate particle size distributions were in excellent agreement with experimental measurements. A parametric sensitivity study found particle morphology to be sensitive to the sintering parameters, demonstrating the need to apply careful consideration to the sintering behaviour of nano-sized particles in modelling studies. The final particle morphology was not found to be sensitive to other model parameters.



## The role of NO<sub>2</sub> and NO in the mechanism of hydrocarbon degradation leading to carbonaceous deposits in engines

Radomir I. Slavchov, Maurin Salamanca, Danilo Russo, Ibrahim Salama, Sebastian Mosbach, Stuart M. Clarke, Markus Kraft, Alexei A. Lapkin and Sorin V. Filip, *Fuel*

DOI: 10.1016/j.fuel.2020.117218

**Abstract:** A hypothetical mechanism of degradation of the fuel droplet leaking out from the injector nozzle in a direct injection combustion engine has been proposed recently. This involves as a key step a radical chain oxidation initiated by NO<sub>2</sub> and branched by nitric oxide, NO, both produced by the combustion. The degradation causes the formation of injector nozzle carbonaceous deposits. The present work gives an experimental validation of some of the assumptions behind this model. An autoclave is used to oxidize isooctane under conditions relevant to the cylinder

wall near the nozzle (~150 °C, 10 bar, 5% O<sub>2</sub>, 100 ppm of NO<sub>2</sub> by mole and 500 ppm NO in the gas phase), and the degradation products are monitored via gas chromatography-mass spectrometry (GC-MS). The results show no observable fuel degradation in the absence of NO<sub>x</sub>. NO appears to be able to initiate a radical chain by producing NO<sub>2</sub>. Nitric oxide also alters the radical chain by transforming the alkyl peroxy radicals (ROO<sup>·</sup>) to more reactive alkoxy radicals (RO<sup>·</sup>), resulting in a range of different products. In addition, NO tends to terminate the radical chain by neutralizing a fraction of the alkyl peroxy radicals, producing alkyl nitrates as termination products. The existence of a radical chain is supported by demonstrating the antioxidative action of a radical scavenger. The chemical reaction mechanism is investigated, based on the detected products, and the key species involved in the degradation process are identified.

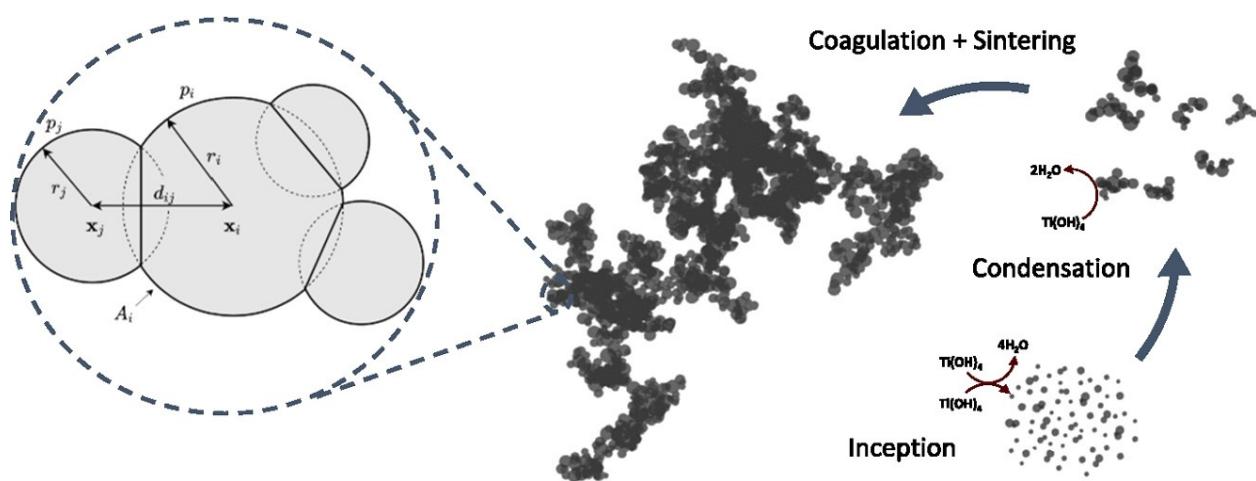
## A detailed particle model for polydisperse aggregate particles

Casper S. Lindberg, Manoel Y. Manuputty, Edward K. Y. Yapp, Jethro Akroyd, Rong Xu and Markus Kraft, *Journal of Computational Physics*

DOI: 10.1016/j.jcp.2019.06.074

**Abstract:** The mathematical description of a new detailed particle model for polydisperse aggregate particles is presented. An aggregate particle is represented as a collection of overlapping spherical primary particles and the model resolves the composition, radius and position coordinates of each individual primary to form a detailed geometrical description of aggregate morphology. Particles transform under inception, coagulation, surface growth, sintering and coalescence processes. The new particle description is used to model the aerosol synthesis of titanium dioxide ( $\text{TiO}_2$ ) aggregates from titanium tetrapi-

sopropoxide (TTIP) precursor.  $\text{TiO}_2$  particles are formed through collision-limited inception and growth reactions of  $\text{Ti(OH)}_4$  from the gas-phase, produced from the thermal decomposition of TTIP. Coupling between the particle population balance and detailed gas-phase chemistry is achieved by operator splitting. A numerical study is performed by simulating a simple batch reactor test case to investigate the convergence behaviour of key functionals with respect to the maximum number of computational particles and splitting time step. Finally, a lab-scale hot wall reactor is simulated to demonstrate the advantages of a detailed geometrical description. Simulated particle size distributions were in reasonable agreement with experimental data. Further evaluation of the model and a parametric sensitivity study are recommended.



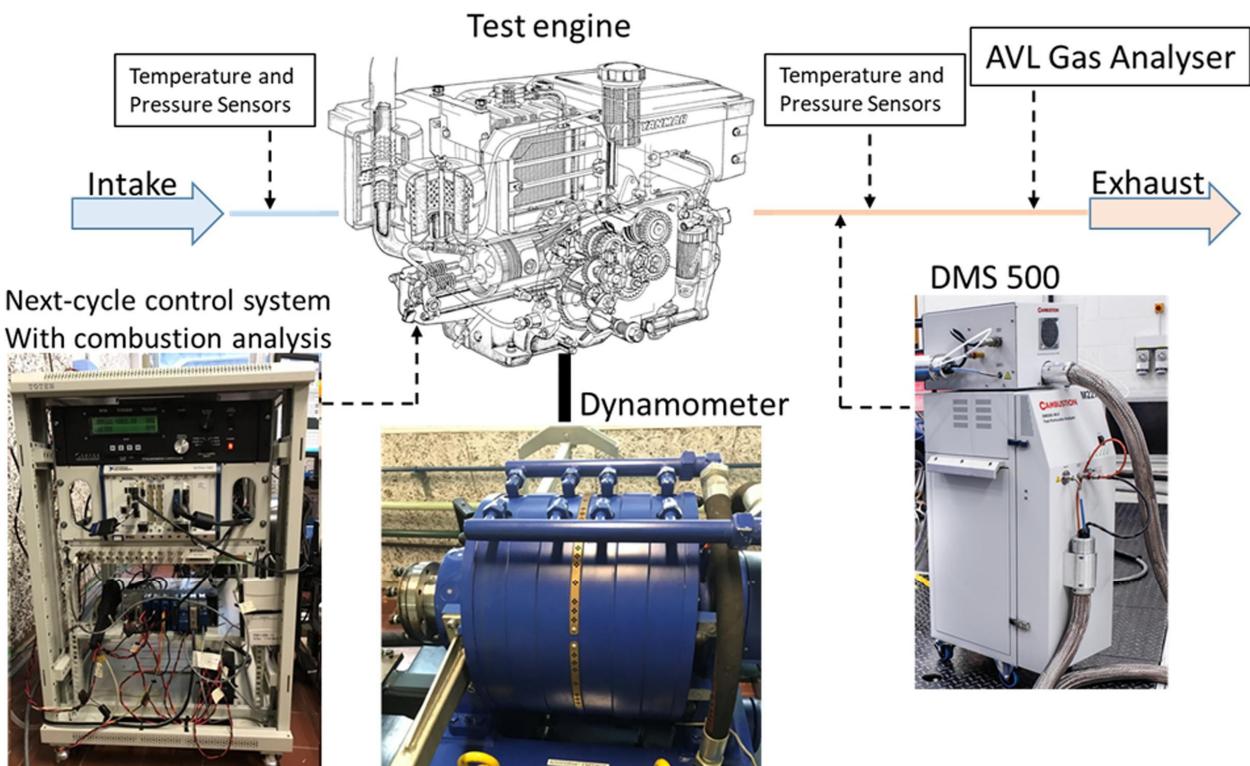
## Experimental study on engine combustion and particle size distributions fueled with Jet A-1

Wenbin Yu, Yichen Zong, Qinjie Lin, Kunlin Tay, Feiyang Zhao, Wenming Yang and Markus Kraft,  
Fuel

DOI: 10.1016/j.fuel.2019.116747

**Abstract:** In this study, a comprehensive investigation of combustion and emission characteristics of Jet A-1 applied in diesel engine was experimentally conducted. Analysis is emphasized on engine performance and soot particle emission both in size and number concentrations when fueled with Jet A-1, compared with traditional diesel fuel. It is concluded that compared with diesel combustion, the combustion phase is obviously retarded when fueled with Jet A-1. The premixed combustion fraction with Jet A-1 is increased and the peak of premixed heat release of Jet A-1 is higher compared with diesel combustion under different injection pressures and dif-

ferent engine loads. Fuel economy with Jet A-1 is significantly improved compared with diesel, which is because of higher low heating value of Jet A-1 as well as more intensive heat release near top dead center (TDC). Jet A-1 and diesel show similar trends in particle size distribution along with the changes of engine loads. Under the low engine load, the particle size distribution is basically dominated by nucleation mode, meanwhile higher concentration of nucleation particles is observed when fueled with Jet A-1 compared to diesel. As the engine load increases, the accumulation particles are increased while the nucleation particles are in turn decreased. When the engine is running under high engine load, the particle size distribution is dominated by accumulation mode. Based on these findings, the potential to improve fuel economy and reduce particulate matter (PM) emissions by using Jet A-1 in a diesel engine was therefore proposed.



*Schematic diagrams of experimental setup.*

## Other activities and achievements

**PhD student Casper LINDBERG** submitted his thesis, titled “Detailed population balance modelling of titanium dioxide nanoparticle synthesis”.

**PhD student Clifford VO Chi Hung** presented “Acetate switch in *Methanococcus maripaludis* S2” at the 26<sup>th</sup> *Regional Symposium of Chemical Engineering*, Kuala Lumpur, Malaysia, 30 October – 1 November 2019. He also presented “Behaviours of the methanogen *Methanococcus maripaludis* under diazotrophy growth” at the 3<sup>rd</sup> *International Conference on Functional Materials and Chemical Engineering*, Bangkok, Thailand, 15-17 November 2019, where he received the award for best oral presenter.

**PhD student Angiras MENON** was scheduled to attend the *Johnson Matthey Academic Conference* at the University of Warwick from 31 March – 1 April 2020 to give a talk on “Multiscale Modelling of Soot Formation” before it was cancelled due to the ongoing COVID-19 pandemic.

**PhD student Astrid BOJE** gave a presentation titled “Detailed population balance modelling using a hybrid particle model” at the AIChE conference in Orlando, US 12 November 2019.

**PhD student Jacob MARTIN** gave an invited talk titled “Why is biochar/charcoal unable to thermally transform into graphite?” at the 4<sup>th</sup> E2S2-CREATE Biochar Workshop, Singapore, 17-18 January 2020. C4T Co-Is Prof. Wang Chi-Hwa (IRP3) and Asst. Prof. Wang Xiaoman (IRP1) also presented talks.

**Jacob MARTIN**’s paper “Reactivity of polycyclic aromatic hydrocarbon soot precursors: implications of localized  $\pi$ -radicals on rim-based pentagonal rings” has now been published in *The Journal of Physical Chemistry C* and was picked as the October paper of the month in the department by Chemical Engineering and Biotechnology at the University of Cambridge.

IRP3 and Cambridge-based colleagues from the **Computational Modelling Group** had a record six submissions of papers accepted for presentation at the 38<sup>th</sup> *International Symposium on Combustion*, due to be held in Adelaide, Australia in January 2021.



Clifford VO Chi Hung giving his presentation at the 3<sup>rd</sup> International Conference on Functional Materials and Chemical Engineering, Bangkok.



Jacob MARTIN, ninth from right, with the other speakers and attendees of the 4<sup>th</sup> E2S2-CREATE Biochar Workshop, Singapore.



# IRP4

## BETTER, CLEANER HEAT USAGE

**B**etter, 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 of Organic Rankine Cycles and the associated turbomachinery, high-efficiency heat exchangers, and estimates and measurements of pollutant dispersion from ships and its reception in port and urban areas.

The contributions below describe the work done under the various tasks of this IRP. All the work is proceeding to plan and research results are already being produced for publications and disseminated in good international conferences.

**Professor Epaminondas Mastorakos, PI**  
**University of Cambridge**

## Update on work package 4.1

### Engine combustion — best fuel, best operating condition

Shrey TRIVEDI (Research Associate, CAM) has been performing simulations on a marine-engine-like test configuration using the CFD code CONVERGE. This configuration involves a constant-volume combustor capable of producing pressure, temperature and swirl comparable to real marine engines, after which the fuel is injected at the periphery of the combustor which evaporates and then autoignites. Figure 4.1a shows the cross section of such a configuration. The pressurised and heated air enters from the intake on the left and after a desired level of pressure, temperature and swirl is achieved within the chamber, heavy fuel such as diesel is injected (Figure 4.1b). The bright colours in Figure 4.1b represent the droplet radius, and the flame emanates out of the spray as shown by the dull red colour in the background.

A good agreement with experiments is achieved based on the results for autoignition delay and penetration depth of the spray. A good qualitative agreement based on scalar fields such as temperature and mass fraction of OH is also observed. CONVERGE is found to be very capable of providing good results for this project. The next steps include integrating CONVERGE with the Conditional Moment Closure, a ub-grid turbulent combustion model that takes micro-mixing into account, which is important for quantities such as NOx and soot emissions. Once this is complete, the simulations will be performed on a real marine engine setup. Another direction of this work that will be explored in parallel is to apply the Incompletely Stirred Reactor Network (ISRN) model which can provide reasonable predictions at a smaller computational cost.

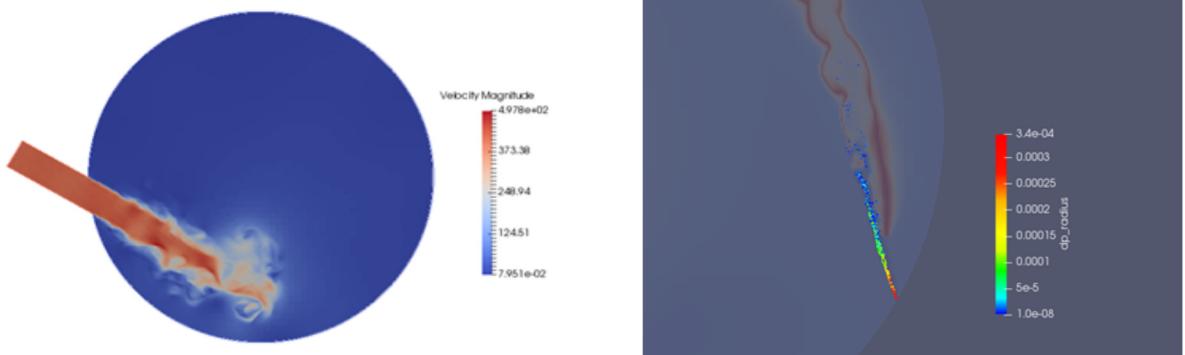


Fig. 4.1: (a) Air at high temperature and pressure entering from the inlet into the combustion chamber. The colourmap shows the velocity magnitude. (b) Spray from the periphery of the combustor autoigniting and leading to a lifted-off flame. Bright colours represent the droplet radius whereas the dull red colour shows flame emanating out of the spray.

Shrey TRIVEDI

## Update on work package 4.2

### Closed power cycles — selection and analysis

**Zheng LIU (Research Associate, NTU)** has been working on the enhancing the performance of an asymmetric twin scroll turbocharger turbine through secondary flow injection. As shown in Figure 4.2, the novel system employs a secondary flow injection device that is integrated with a twin-entry turbine housing.

Based on the Computational Fluid Dynamics (CFD) analysis, Figures 4.3a and 4.3b show the comparison of the Mach numbers within the rotor passages between the baseline and the novel system. A rise in flow velocity was observed at 0.5-1 stream-wise location, and the velocity is

higher near the downstream blade's suction surface (SS) than the pressure surface (PS). The velocity difference between the PS and SS also leads to the pressure difference, thereby producing positive torque with respect to the axis. Under the effects of flow injection, as shown in Figure 4.3b, much higher flow velocity is developed closer to the downstream SS, resulting in a greater pressure difference between the SS and PS compared with the baseline. As a consequence, the flow injection can facilitate the turbine for higher torque production.

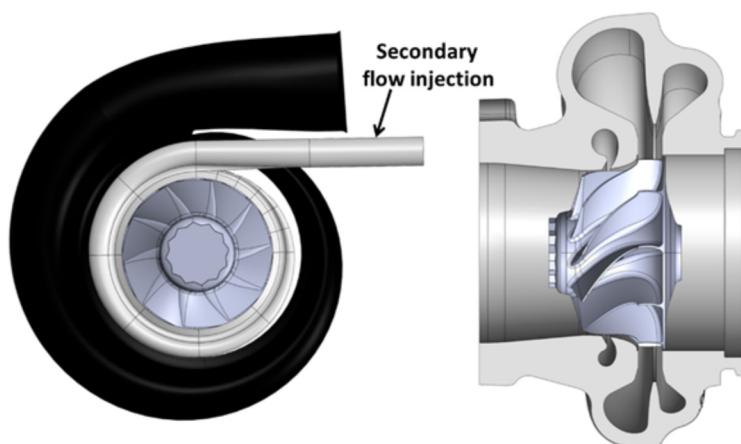


Fig. 4.2: Demonstration of the secondary flow injection system.

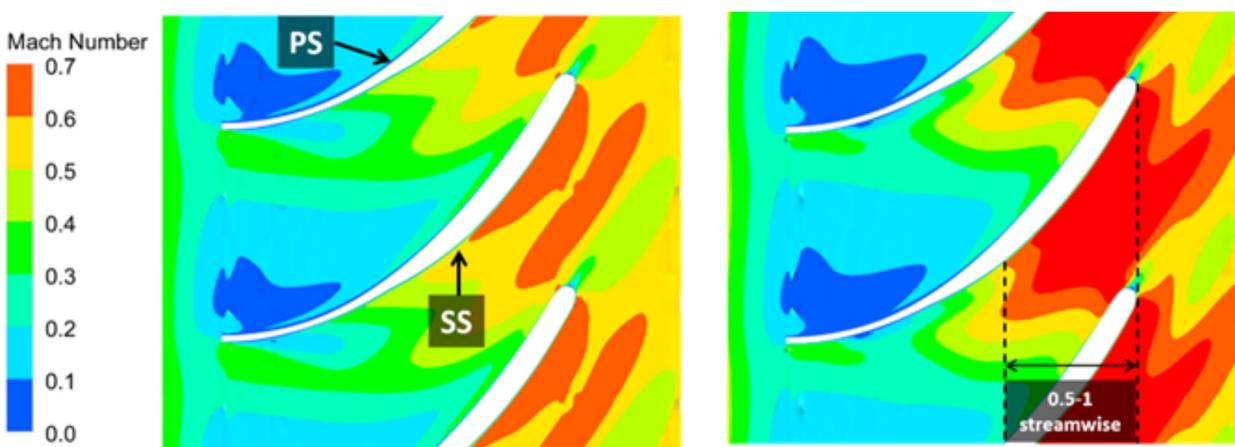


Fig. 4.3: Mach number contours along the turbine blades of (a) baseline, (b) with secondary flow injections.

Figure 4.4 compares the blade loading performance of the novel system with the baseline. As revealed from the flow field analysis, the blade loading is significantly improved downstream to the location where the flow is injected. A greater pressure difference between the PS and SS is the main reason that leads to performance improvement. The injected flow has more impacts on the blade loading at the 90% span (closer to the shroud), where the largest difference compared with the baseline is observed. As it moves to the middle (50%) span, the effect becomes less obvious. However, higher upstream pressure is produced due to flow injection, implying the engine's back-pressure could be increased.

The secondary flow injection system was therefore optimised for a higher power generation during an engine cycle. The optimisation algorithm was based on a Kriging surrogate model integrated with the global search method. The optimisation process was converged at 185 iterations with the maximum improvement of cycle-averaged power by 38.7% compared with the baseline design.

This research finds that the secondary flow injection system can be regarded as a novel turbo-compounding technique, where the turbine torque (actual power) can be increased by introducing additional flow resources. The increased turbine torque will lead to a higher Break mean effective pressure produced by the engine, which is very useful when transient operating conditions are demanded by automobiles, such as during the acceleration and hill-climbing situations. In addition, the injection is helpful when a higher low-end-torque is needed when the conventional turbine cannot supply sufficient energy to meet the desired boost pressure. However, this will be at the expense of additional energy cost, i.e. a lower turbine efficiency.

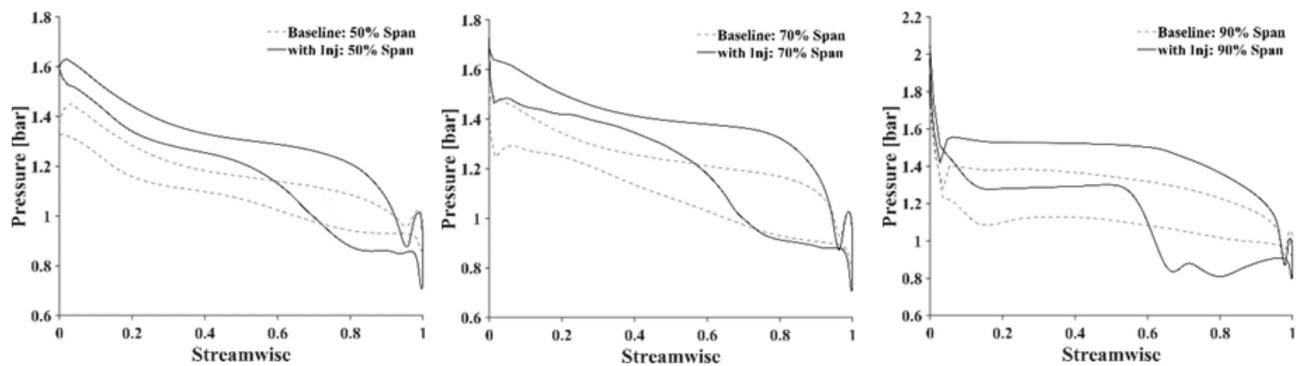


Fig. 4.4: Porous representation of the fin domain in the heat exchanger.

Zheng LIU

## Update on work package 4.3

### High-efficiency heat exchanger

Dr Matthew LAW Lee Liong (Research Fellow, NUS) has been working on three dimensional numerical simulations of the finned oblique tube heat exchangers to study their thermohydraulic performance. Two tube sizes (Oblique 1 and Oblique 2) are considered in the simulations, where Oblique 1 is designed with similar tube surface area and Oblique 2 has similar cross sectional area, compared to their circular counterpart. The objectives of the present work are to investigate the heat transfer and pressure drop performances of the finned oblique tube heat exchanger and compare the results against the conventional finned circular tube heat exchanger. On the air-side, the finned oblique tube heat exchanger offers better heat transfer for both oblique tube sizes with lower pressure drop due to smaller wake regions behind the tubes. On the water-side, although Oblique 1 has very undesirable pressure drop penalty because of its relatively smaller tube cross sectional area, the pressure drop penalty across Oblique 2 is more manageable, given its air-side performance improvements.

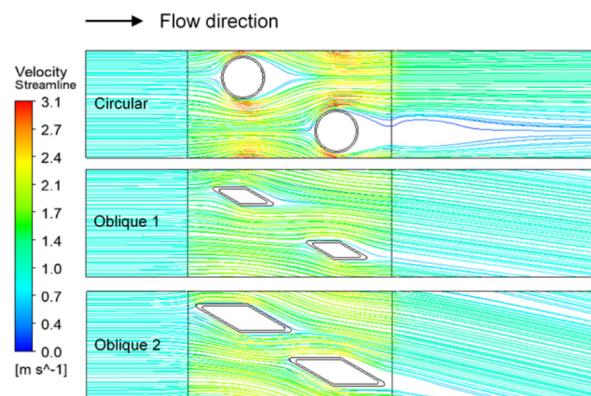


Fig. 4.5: Air flow profiles across different tube geometries at inlet velocity of 0.9 m/s.

Dr Matthew LAW Lee Liong

## Update on work package 4.4

### Process system model for the J-Park Simulator

This part of IRP4 deals with experimental and simulation research of shipping pollution and supplements the air quality simulations and their interface to JPS. In particular:

#### Effects of micromixing in the near-field evolution of a chemically-reactive plume behind a ship

In air pollution modelling, sources are typically treated as a point and then estimates of their dispersion follow the Gaussian plume theory. This is the basis of ADMS, EPISODE and most such codes in air quality modelling. However, a ship's plume may be affected by the ship's structure and hence should not always be treated as a point emission. In addition, there is fast chemistry going on in the near-field of the release, which is

typically neglected in AQM codes, but which is important for aerosol formation. Here, Savvas GKANTONAS (PhD student, CAM, and CARES intern) has applied computational fluid dynamics to simulate the aerodynamics of a 274m-long oil tanker and the dispersion of its exhaust plume, given a realistic operating scenario around Singapore's port (Figure 4.6). The focus is on the evolution of gas-phase pollutants within the exhaust plume and the effects of micromixing, which are expected to affect the near-field level of pollution behind the ship. In this direction, the Conditional Moment Closure (CMC) method will be consequently applied together with a detailed chemical mechanism for gaseous-phase photochemical reactions. The final goal is to compare pollutant predictions with ones typically obtained with modern atmospheric disper-

sion methods that rely only on mean concentrations and simplifying assumptions for the ship plume shape. Preliminary results (Figure 4.7) show that depending on the relative wind speed and direction, and the load of the engine (which

affects the velocity of the exhaust at the stack), the plume may be captured in the downdraft hence creating a very different initial mixing field compared to the assumptions behind Gaussian plume theory.

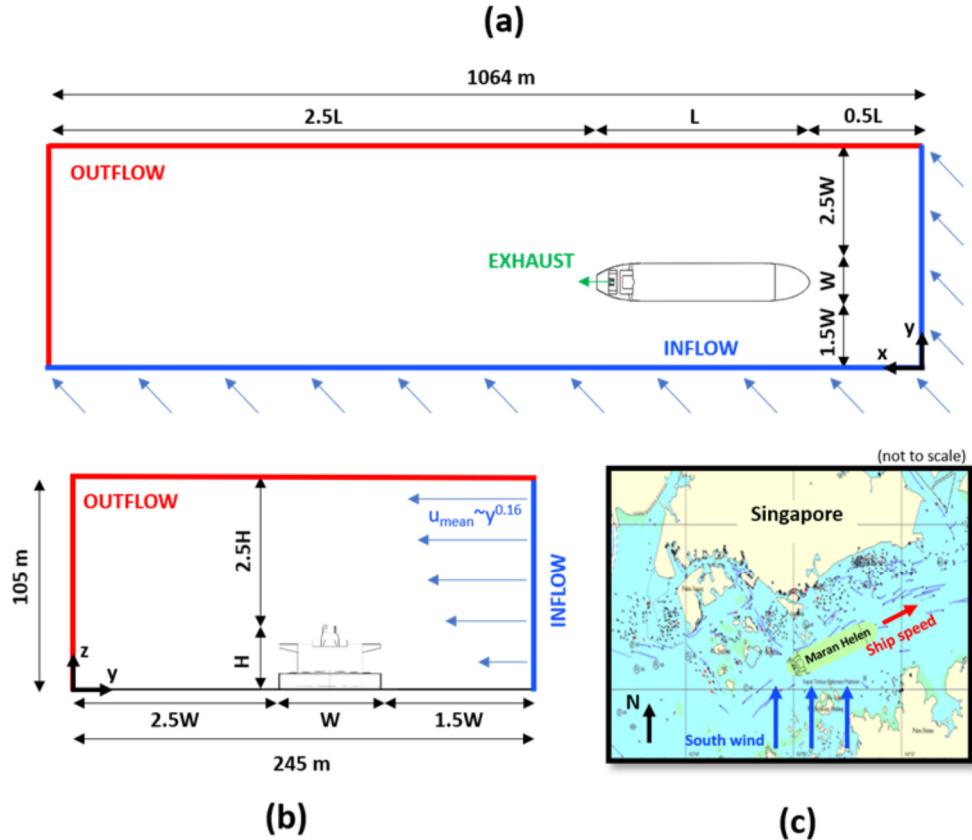


Fig. 4.6: (a) Vessel location and relative speed with overlaid typical ship traffic. (b) Top view of computational domain. (c) Front view of computational domain with indicated wind profile.

Savvas GKANTONAS

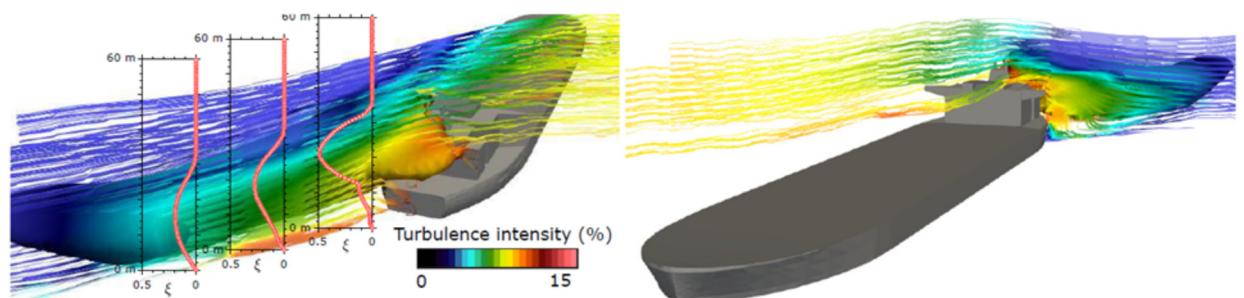


Fig. 4.7: Predicted ship airwake as streamlines in vertical planes aligned with the oncoming wind. Superimposed iso-surface of a mean passive scalar,  $\xi=0.05$ , injected from the exhaust stack.

Savvas GKANTONAS

### Standardising Unmanned Aerial Vehicle use for Emission Monitoring

A drone with 5 kg payload capacity, emission measurement sensors and sampling probes have been bought, tested and assembled to create a UAV suitable for remote measurements of NO<sub>x</sub>, SO<sub>x</sub> and particulate emissions. It is aimed that this will be deployed in port areas and behind ships to measure their plume. **Dr Molly HAUGEN (Research Fellow, CAM)** has completed a training course about unmanned air vehicle (UAV) safety to ensure safe and legal flying. Together with **Mr Savvas GKANTONAS (PhD student, CAM, and CARES intern)**, she has been working on a chamber design to house the instru-

ments while sampling maritime emissions, as well as making the UAV plume- and sea-protected during measurement campaigns. An ensemble of components has been designed and manufactured (Figures 4.8 – 4.9). Further work includes CFD study of the whole drone and probe assembly (Figure 4.10) to assess the effective sampling volume, lab-based testing and field measurements (Figure 4.11).



Fig. 4.8: Drone CAD and mounting equipment sketch for supporting a plate where all emission monitoring systems will be attached. Red line on the left shows the position of a wire rope supporting the drone's landing gear. The red circle on the right shows an in-house clamp where the wire rope will be attached.

*Savvas GKANTONAS*



Fig. 4.9: (Left) Detail of the attachment of the systems' mounting plate onto the drone's landing gear. (Right) Manufactured mounting clamps out of aluminum.

*Savvas GKANTONAS*

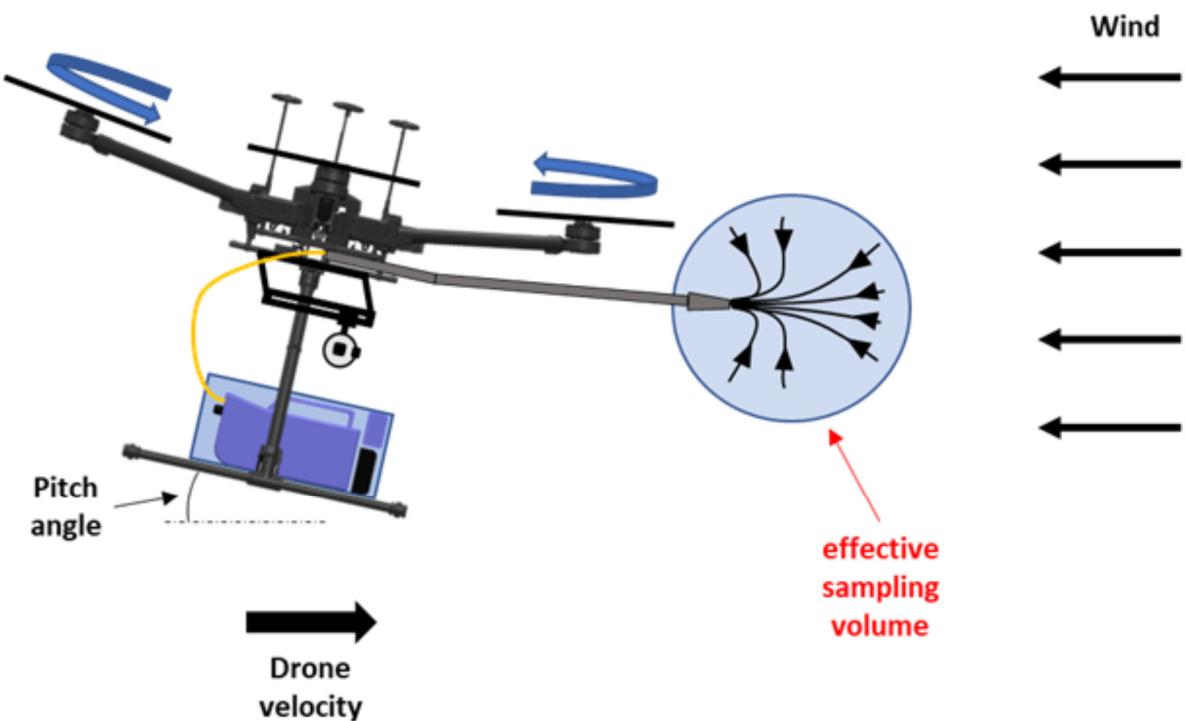


Fig. 4.10: Sketch of the drone and the focal point of the CFD study.

Savvas GKANTONAS



Fig. 4.11: (Left) Smoke visualisation of the drone's downdraft, which helps select the best location for the sampling probe. (Right) Dr Molly HAUGEN with the deployed drone (no sensors attached).

Dr Molly HAUGEN

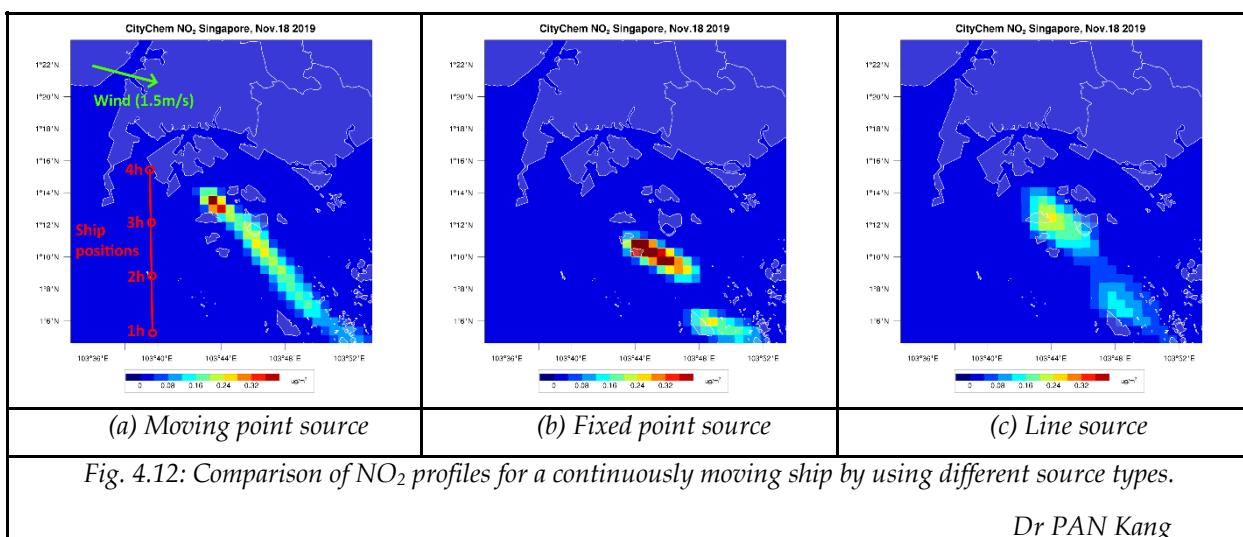
## Development of moving emission source for pollution dispersion modelling

Numerical modelling of the dispersion of emissions generated by ships is important for evaluating the impact of the maritime activities on human health and air quality in coastal area. In the dispersion simulation, the common model used for ships is to assume the shipping emission is continuously generated from a (or multiple) fixed point source(s) along the ship transportation route. Another common assumption is to use a line source that generates the emission continuously along entire ship route during the simulation. However, both assumptions are not realistic for a moving ship as its location keeps changed and emissions are generated at one certain point only for a very short time.

To better simulate the emission generation and dispersion from a moving ship, **Dr PAN Kang (Research Fellow, CARES)** has developed a moving point source model in the open-source emission dispersion code, EPISODE-CityChem. In the

moving point source model, the location for a ship can be updated at different simulation time steps based on the defined moving speed, direction and path. In each time step, the shipping emission is assumed to be generated in the same location for the entire time step, and then the ship location is calculated and updated for next time step to generate new emission plumes. In the model, the ship moving parameters including the ship speed and direction are constant within each simulation hour and can only be updated hourly.

The new moving point source model has been preliminarily tested to simulate the shipping emissions generation and dispersion. As shown in Figure 4.12, the simulated results indicated a much more realistic emission dispersion profile by using the moving point source, compared to a fixed point source and a line source. The new developed moving point source model will be applied to the J-Park simulator to evaluate the shipping emission effects on the coastal cities, such as Singapore and Hong Kong.



## Other activities and achievements

PhD student Savvas GKANTONAS and PI Prof. Epaminondas MASTORAKOS submitted the extended abstract “Effects of micromixing in the near-field evolution of a chemically-reactive plume behind a ship”, in preparation for *13th International ERCOFTAC Symposium on Engineering, Turbulence, Modelling and Measurements (ETMM13)*, Rhodes, Greece, 2020. A poster presentation was prepared for the *Coordinating Research Council on Real-world Emissions* in San Diego, US, postponed from March to August 2020.



# 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 has completed its recruitment. One Research Fellow, Dr Abhiruchi Gadgil Suresh, joined the group in October 2019. IRP BB has been working steadily through this period, including re-planning due to COVID-19.

IRP BB finished creating a curated document aiming at giving IRP members a comprehensive guideline for commercialisation mechanisms and education available in Singapore and on-line, and including funding options for technologies developed within C4T. This was shared with colleagues across parts of CREATE to check for completeness and they requested that we make it available to all CREATE entities, which we have now done. We will edit it biannually to include any new funding options or resources available for commercialisation in Singapore context.

**Professor Steve Evans, PI**  
**University of Cambridge**

## Update on work package BB.1

### Business model innovation potentials

As part of WP1, we continue research on evaluating alternative business models for adopting sustainable innovations and technologies. Our first paper with application to the solar energy market focuses on the interaction of consumer's choice, firms' business model adoption, pricing decision, as well as the operations and maintenance service strategy in light of government's subsidy policies. Based on our model and analytical results, we conduct in-depth numerical investigation on the attractiveness of different business models under various scenarios. In subsequent research, we aim to study the long-term effects of business model innovation for sustainability in the context of remanufacturing. Through these and our other related research, we will develop managerial insights and recommendations to support the development of business model to increase adoption of sustainable innovations.

In collaboration with IRP2, we have started investigating production scheduling problems that can take advantage of on-site generation of renewable energy (when available) to support local electrochemical manufacturing. One of the underlying issues is the uncertainty and intermittency regarding on-site generation of renewable energy, e.g., solar energy. Thus, the challenge lies in how to design a mechanism to maximise the utilisation of renewable energy and minimise the inventory risk across multiple periods. We formulated it as a dynamic programming problem under joint centralised manufacturing and decentralised manufacturing that is supplied by on-site generation solar energy. We will look into its extension to more complex scenarios such as multiple products and stochastic demand across multiple periods.



## Update on work package BB.2

### Policy formulation, customer and industry perceptions

As a part of WP2, we have gone through an iterative process to create a survey document to understand the attitudes and willingness of organisations towards adoption of clean technology. Sustainability officials and higher management in organisations would answer pertinent questions in this survey. We are hoping that we are able to recruit at least 200+ officials to get statistically significant results. It is about to be implemented in the Singapore context across the industrial and non-industrial sectors and we will start getting preliminary results soon. The survey results and analysis will give critical insights about the correlations among drivers of implementing clean technology, actual implementation of clean technology and the attitudes of different organisations. For analysis, every survey question has been assigned a weighting component related to its significance and the 20 questions in the survey are divided into question blocks, each signifying one aspect related to clean technology attitudes and implementation. We will do hypotheses testing and study any correlations emerging from the data and will draw pertinent insights. The sectors we are targeting are big and small industries, public sector, NGOs and financial sector. The results of this survey will pave way to thorough interviews in the field, leading to understanding of sector specific problems and opportunities (WP4).

As part of WP2, we are extending our scope of analyses from Singapore to other countries, including China and the United States, for comparison. Our purpose is to analyse the innovation capability and output of chemical companies and the relevant policy effects beyond Singapore. We have initially compiled a list of 7,000+ target companies (industry coverage: pharmaceuticals, biotechnology, oil and gas, utilities and chemicals) in the world including more than 1,000 companies listed in the United States and more than 3,000 companies listed in China. In addition, we have identified the companies' CUSIP ID to collect the relevant data to measure each entity's financial performance (such as total asset, net income, total revenue, EBIT, EBITDA, current liabilities and

current asset). We have also obtained their research and development expenses as a measure of their R&D input. Lastly, we have extracted all the patents associated with low-carbon technologies from China National Intellectual Property Administration (CNIPA) and United States Patent and Trademark Office (USPTO). These low-carbon technology patents can be defined as patents that belong to technological classes in the International Patent Classification (IPC) Green Inventory. The IPC Green Inventory was developed by the IPC Committee of Experts to facilitate search for patent information related to Environmentally Sound Technologies (ESTs), as defined by the United Nations Framework Convention on Climate Change (UNFCCC). We are in the process of matching each IPC associated with low-carbon technology patents (our treatment group) to an IPC not associated with low-carbon technology patents (our control group) based on the nearest neighbourhood principle for analysis in the next stage of our research.

As part of WP2 and our related Emerging Opportunities Fund project, we have done work on analysing internal carbon pricing in companies. Internal carbon pricing is one of the mechanisms employed by manufacturing and service organisations to reduce their carbon emissions. Under this mechanism, an internal carbon tax is imposed by a firm on its own business units. An internal carbon price internalises the external cost of carbon and incentivises the business units to invest in low carbon alternatives. Companies use internal carbon price to protect themselves from future carbon regulations, protect reputation among the stakeholders (customers, investors, NGOs) and to transition towards a low carbon economy. The firm invests in efficiency improvement projects, buys renewable energy certificates, carbon offsets and involves in other carbon reduction projects to achieve their emission targets. Many organisations such as Microsoft, Disney, Infosys and Shell report in their carbon disclosure projects (CDP) that they used internal carbon price to achieve their carbon emission targets.

We study the problem of how a company should price its carbon across different business units. A game theoretic model with Cournot competition in each of the multiple business units is used to analyse the problem. Our preliminary findings are as follows. A uniform internal carbon price across all business units in the firm achieves the first best solution. However, this might lead to substantial reduction in the activity level or closure of certain business units who face competitors who do not have any carbon pricing within their firms. These

business units might in fact be very competitive if a uniform carbon-pricing regime is adopted across the entire economy/country. Therefore, even though a uniform carbon pricing might be a best strategy for the short term, this might erode long-term competitiveness. We analyse other forms of carbon pricing in this research and show that while short-term profits might be lower with this strategy, this in fact might work better in the long term, if an economy-wide carbon tax is eventually imposed across all companies.



## Update on work package BB.3

### Future roadmap for industrial decarbonisation, including international comparisons

WP3 continues to work closely with the technology IRPs to develop their commercialisation pathways through business model innovation support. We have used various tools to analyse IRP 1 technologies and will extend these across technologies emerging from IRPs 2, 3, 4 and JPS in the next period. The novelty of some of the emerging technologies can be challenging to existing industry structures, emphasising the importance of choosing better business models to unlock the value in the technology. WP3 has also been collecting national and global-sectoral decarbonisation roadmaps in preparation for analysing what works and what doesn't

in roadmapping for industrial decarbonisation. IRP BB has been working separately with the UK government on their roadmap.

## Other activities and achievements

**PhD student K. R. Preethi and PI Prof. S. VISWANATHAN** (2020) submitted a paper, "Carbon Pricing Strategies for Multi-Unit Firms," to the *POMS Annual Conference*, Minneapolis, USA. The conference was due to be held in April 2020 but has been cancelled, so the authors intend to submit and present the paper at the *INFORMS Conference* in Washington DC in November 2020, and simultaneously submit it to a journal in the latter half of the year.

A publication that **Prof. Steve EVANS** is an author on is included in the Top 50 Earth and Planetary Sciences Articles in *Nature Communications* 2019: Jia, L., Evans, S. & Linden, S.v.d. Motivating actions to mitigate plastic pollution. *Nat Commun* 10, 4582 (2019). <https://doi.org/10.1038/s41467-019-12666-9>

**PI Prof. Kenneth G. HUANG** has been elected to the Editorial Review Board of the *Journal of International Business Studies* (the top journal in international business and management) starting 1<sup>st</sup> January 2020.



# 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<sub>2</sub> 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 leveraging the potential of Semantic Web technologies, developing new functionalities to demonstrate its multi-domain and hierarchical capabilities, and to augment its degree of autonomy and intelligence. This includes designing and developing the OntoKin system to allow any user to upload chemical mechanisms to the OntoKin knowledge graph, and to query the knowledge graph to retrieve and compare species and reaction data. We have also extended the OntoKin system to demonstrate through examples how the concept of a Semantic Web based knowledge graph can be used to integrate combustion modelling into cross-disciplinary applications and in particular how inconsistency issues in chemical mechanisms can be addressed.

Furthermore, we have developed an agent framework called “ElChem” to establish real-time communication via the JPS knowledge graph for a cross-domain use case involving both chemical and electrical domains of a chemical plant. The ElChem framework utilises Description Logics (DL) and SPARQL Inferencing Notation (SPIN) reasoning techniques to investigate the interactions between the two systems. This includes having a rule-based system to ensure seamless operation of the plant. The rules are used to define the normal operating conditions for the plant and are capable of detecting any constraint violations. The preliminary results reveal that significant economic benefits can be achieved by the proposed approach.

Moreover, by taking advantage of JPS’ multi-level design for terminology definition, we have demonstrated the application of ontology matching both at the schema and instance levels between data sources for data consolidation. This work involves introducing domain information as an additional metric for ontology matching to improve the matching accuracy, and developing a novel value matcher to evaluate the similarity between two ontological entities based on their literal value set. Each literal value is not only associated with its closest parent individual, but is also associated with all levels of parent individuals. The preliminary results reveal that the user is now able to query the JPS knowledge graph and retrieve additional attributes that are derived from other data sources.

In addition, we are currently investigating the use of an interactive Natural Language Query (NLQ) interface for the chemistry-related domains in JPS e.g. OntoKin (for chemical kinetic reaction mechanisms), OntoSpecies (for chemical species) and OntoCompChem (for quantum chemistry calculations). This work aims to develop an NLQ that is efficient and accurate in providing answers to chemistry-related questions (especially quantum chemistry calculations) posed by the user in a human-readable format e.g. “Find all the reaction mechanisms having water as a reactant”.

**Professor Markus Kraft, PI**  
**University of Cambridge**

## Update on work package JPS.1

### Big data — sensors and data modelling

Gourab KARMAKAR (Research Engineer, CARES), Laura ONG (Software Developer, CARES) and Leonardus Kevin ADITYA (Project Officer, NTU) have integrated an energy demand side management framework, developed as part of an Intra-CREATE Seed Collaboration project between National University of Singapore (NUS) and CARES, into JPS. The objective of the energy demand side management framework is to reduce the peak to average ratio, consequently reducing the stress on the main grid and hence providing cost savings for customers. The framework is modelled via game theory and optimised by a receding horizon optimisation algorithm, while the energy trading is secured via the use of blockchain technology. The framework also includes a model of solar photovoltaic cells, which takes into consideration real-time temperature and solar irradiance, to estimate the amount of renewable energy generated. Three types of energy consumers (loads) have been considered in this framework: residential, commercial and industrial (represented by electrolyser and fuel cell). The demand flexibilities of the various energy consumers are also reflected in the system modelling.

Gourab KARMAKAR has extended the domain ontology for power systems, OntoPowSys, to describe the relevant technologies, prosumers, electrical and energy components etc. utilised in the framework. Instances of the relevant technologies, prosumers, electrical and energy components etc. have been created and incorporated into JPS knowledge graph. Kevin ADITYA has packaged the models and algorithms as agents that can apply the Semantic Web stack to read and understand information from the knowledge graph and modify its data values and structure. Agents can communicate with each other and exchange information via the knowledge graph and semantic input and output parameters. They use Hypertext Transfer Protocol (HTTP) for calling each other and JavaScript Object Notation (JSON) or Internationalized Resource Identifier (IRI) for exchanging input and output parameters. In this framework, agents query the knowledge graph to retrieve the necessary data e.g. energy demand profiles of the past 24 hours, real-time and hourly forecast of the next 24 hours for temperature and solar irradiance, number of solar photovoltaic cells, and translates these data into a suitable format for the optimisation of the energy management. For example, Kevin AD-

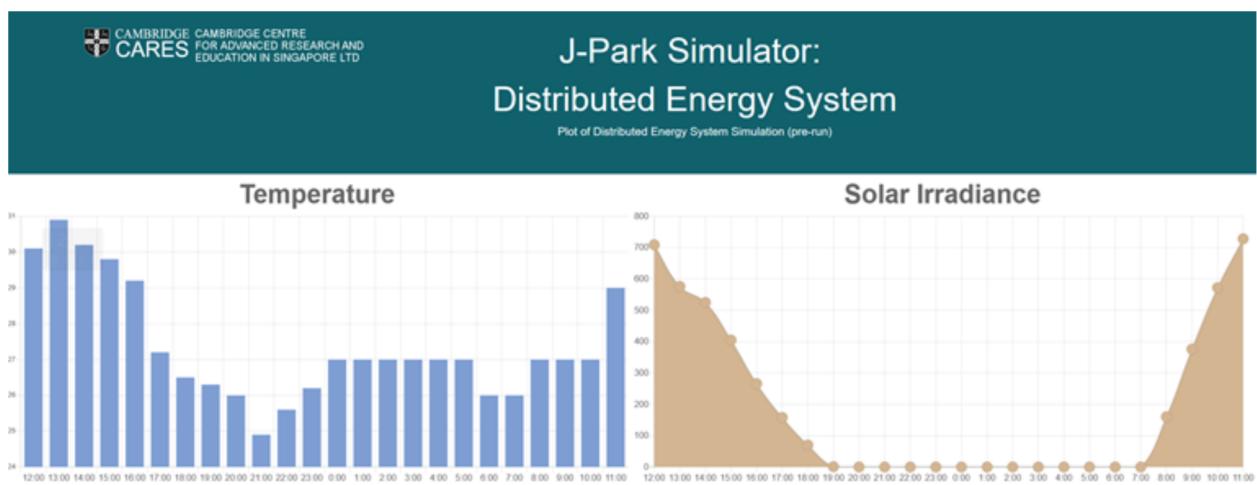


Fig. 6.1: Hourly weather forecast data (temperature and solar irradiance) of the next 24 hours.

ITYA has created an agent to query the knowledge graph for consumption profiles of the individual energy consumers for the past 24 hours. These consumption profiles are subsequently being aggregated into three categories: residential, commercial and industrial. The weather data, aggregated consumption profiles and other necessary data are sent to another agent which acts as a Java wrapper for the optimisation model. Based on the weather forecast data, the optimisation model estimates the level of renewable energy that the solar photovoltaic cells would produce, the optimal energy profiles for the next 24 hours, and thus how much energy is required to be generated and supplied by the main grid in the next 24 hours to satisfy the overall energy demand.

Once the optimal energy profiles are determined, energy trading is materialised based on the Rinkeby Test blockchain framework as Proof of Purchase. Using Javascript and ChartJS, Laura ONG has developed a visualisation for displaying the key variables of this use case: hourly weather forecast data (temperature and solar irradiance) of the next 24 hours, optimised energy profiles of the various energy players, detailed energy profiles for the residential consumers, transaction hashes and receipts for the payment of energy between consumers and producers that are stored on the hyperledger as Proof of Purchase. Upon clicking on the hashes, the user is able to view the transaction information on the Rinkeby Test Network.



Fig. 6.2: Optimised energy profiles of the various energy players based on the weather forecast data.

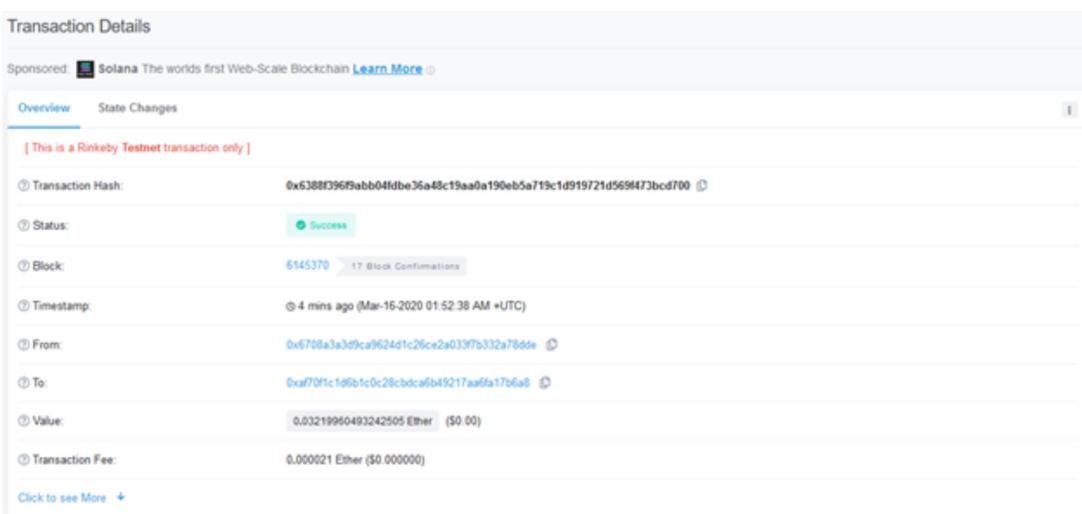


Fig. 6.3: Typical transaction details from a consumer to a producer as shown on Etherscan.IO.

Gourab KARMAKAR, Kevin ADITYA and Laura ONG are also involved in integrating an energy storage technology decision-making tool, developed as part of an Intra-CREATE Seed Collaboration project between National University of Singapore (NUS) and CARES, into JPS by using the existing “parallel world” framework. The objective of the energy storage technology decision-making tool is to develop a system that could recommend appropriate energy storage technology based on a variety of factors such as technological feasibility, maturity, installation cost, etc. Once the energy storage technology is determined, the optimal placement of the energy storage systems for a given grid topology to minimise distribution system losses is determined. An electrical distribution network of Jurong Island has been used to demonstrate the performance of the use case (as shown in Fig. 6.4, Fig. 6.5 and Fig. 6.6).

Whenever the user initiates a new scenario using the existing “parallel world” framework, the first agent connects a renewable energy generator (e.g. photovoltaic generator in this use case) to the electrical grid from the “base world”. The IRI of the modified electrical grid is sent to the second agent, which acts as a Java wrapper for the Gen-

eral Algebraic Modelling System (GAMS) model. The second agent will also query and retrieve a list of IRIs for the potential energy storage technologies from the JPS knowledge graph. Utilising the IRIs of the modified electrical grid and potential energy storage technologies, the second agent retrieves the necessary data e.g. the photovoltaic generator’s characteristics and translates these data into a suitable format for the GAMS model that will recommend the most appropriate energy storage technology (e.g. Vanadium Redox Battery, in this use case). With the chosen energy storage technology, another agent will determine the type of sensitivity analysis to be performed in order to establish the optimal placement of the energy storage systems. Once the type of sensitivity analysis is determined, the corresponding agents will be called to perform loss sensitivity calculations. The Web Ontology Language (OWL) files of the new energy storage systems (e.g. Vanadium Redox Batteries, in this use case) are also created. Another agent will then connect these newly created OWL files to the modified electrical grid based on the results of the loss sensitivity calculations. Finally, an agent executing an Optimal Power Flow (OPF) simulation is invoked to evaluate the impact of the new energy storage systems on the overall CO<sub>2</sub> emissions of

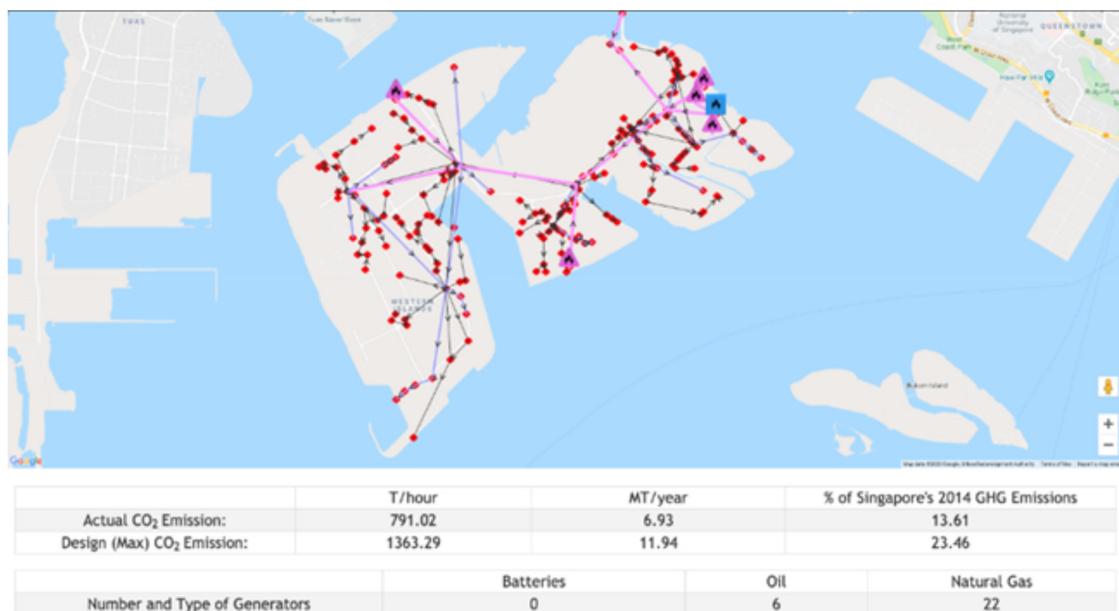


Fig. 6.4: “Base world” displaying the overall CO<sub>2</sub> emissions for the electrical network of Jurong Island in JPS.

the modified electrical grid.

Gourab KARMAKAR has created the agent that determines the optimal placement of the energy storage systems in order to minimise distribution system losses. This involved developing an algorithm based on the system loss sensitivity index with respect to the energy storage systems' parameters. The change in the power system's performance (total power loss) and the energy storage systems' parameters (real power injection) are used to evaluate the loss sensitivity index. Instead of using a single centralised energy stor-

age system for the electrical grid, this algorithm allows multiple energy storage systems to be optimally placed.

Laura ONG has extended an existing visualisation for displaying the electrical network as shown in Figures 6.4, 6.5 and 6.6. Their corresponding estimated CO<sub>2</sub> emissions are indicated in the tables. Upon clicking on the individual red marker, a pop-up window containing the information about the selected component will appear.

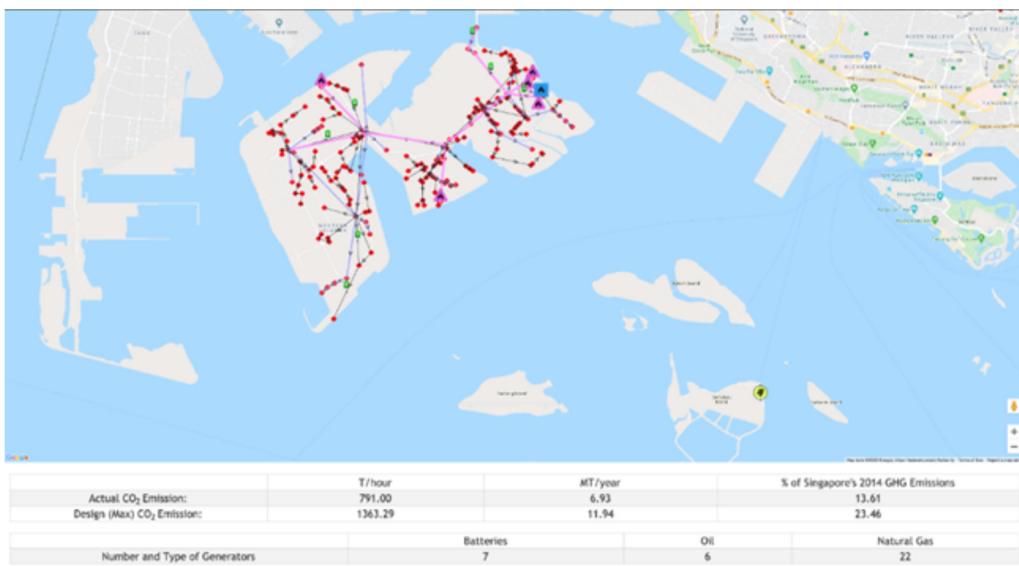


Fig. 6.5: "Scenario 1" displaying the optimal placement of Vanadium Redox Batteries and the overall CO<sub>2</sub> emissions for the modified electrical network of Jurong Island in JPS. The overall energy demands for "Scenario 1" and "Base world" are identical.

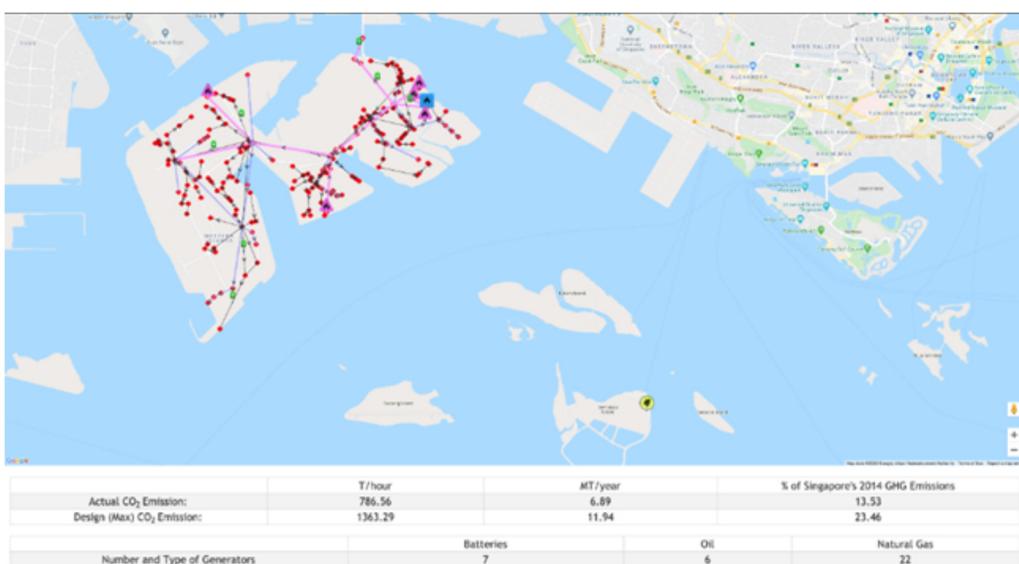


Fig. 6.6: "Scenario 2" displaying the optimal placement of Vanadium Redox Batteries and the overall CO<sub>2</sub> emissions for the modified electrical network of Jurong Island in JPS. The overall energy demand for "Scenario 2" is lower compared to the "Base world".

## Update on work package JPS.2

### Surrogate models and superstructure

We have conducted extensive and successful research in the area of surrogate modelling as exemplified by the number of publications, e.g. "Deep Kernel Learning Approach to Engine Emissions Modelling" (preprint), "LEAPS2: Learning based Evolutionary Assistive Paradigm for Surrogate Selection", "Evaluating Smart Sampling for Constructing Multidimensional Surrogate Models", "Machine Learning Approach for Constructing Surrogates of a Biodiesel Plant Flow Sheet Model" (preprint), "Design of Computer Experiments: A Review", "Parameterisation of a Biodiesel Plant Process Flow Sheet Model", "Design Technologies For Eco-Industrial Parks: From Unit Operations to Processes, Plants and Industrial Networks" and "Outlier Analysis for a Silicon Nanoparticle Population Balance Model".

As JPS progresses on several fronts, it became clear that in order to make use of the full potential of Semantic Web technologies in JPS, it is necessary to do more research on enhancing the current JPS architecture with regard to performance, scalability and scenario analysis ability. This is especially crucial when we want to automate the creation of surrogate models and superstructures. The necessity to develop JPS architecture is even more relevant now than it was in the previous stages as the amount of data and number of data types have increased substantially. We anticipate that as we continue to develop JPS, the existing architecture will become insufficient to meet the new functional needs effectively and efficiently. Consequently, we have identified "architecture development" of JPS as a key research area that needs to be additionally addressed in order to continue developing JPS sustainably.

**Arkadiusz CHADZYNSKI (Senior Software Developer, CARES)** has taken over the responsibility of driving the overall JPS architecture forward. He is also heavily involved with supporting the JPS team concerning questions of software design and non-functional requirements such as performance and scalability. In addition, he has designed and developed an Asynchronous Watching Service (AWS) for JPS in order to deal with the computationally expensive GAMS models that are employed by the agents involved in the carbon tax use case (runtime can be up to 36 hours). The AWS has been designed as an autonomous and reusable component, capable of serving agents operating on different use cases and parallel worlds in multiple threads of execution. The AWS constantly monitors the GAMS modelling system's output directories in different parallel worlds and notifies instances of the agents whenever the results of the GAMS simulations are available for their further processing. In this case, the mentioned agents' instances would not need to wait for the simulation to be completed and hence not be blocked or made unavailable for a long duration. The AWS is also capable of keeping track of which agent it has to forward the response back to. Upon their requests, the AWS informs the agents about its own waiting state immediately, allowing the agents to continue with performing any other functions or accept other requests. The overall design of the AWS is illustrated in Figure 6.7.

Arkadiusz CHADZYNSKI is also involved in preparing a paper, titled “A Parallel World Framework for Scenario Analysis in Knowledge Graphs” which describes the main ideas of the “parallel world” framework, a crucial feature for accomplishing scenario analysis. This work was preceded by a comprehensive research on knowledge graph versioning strategies as well as the use case implementation i.e. codes. An activity diagram for the use case discussed in this paper is shown in Figure 6.8.

Arkadiusz CHADZYNSKI has recently started researching on the use of spatiotemporal Resource Description Framework (RDF) stores that are capable of providing scalable and reliable data stores for semantic geographical data which can be used for modelling the entire city. This work is complementary to other ongoing research involving semantic sensor network ontologies and interpolation methods for virtual sensors. All these research works, in conjunction with the “parallel world” framework, can significantly extend JPS’ capabilities to allow modelling of virtual sensors at the complex level of the entire city for scenario analysis.

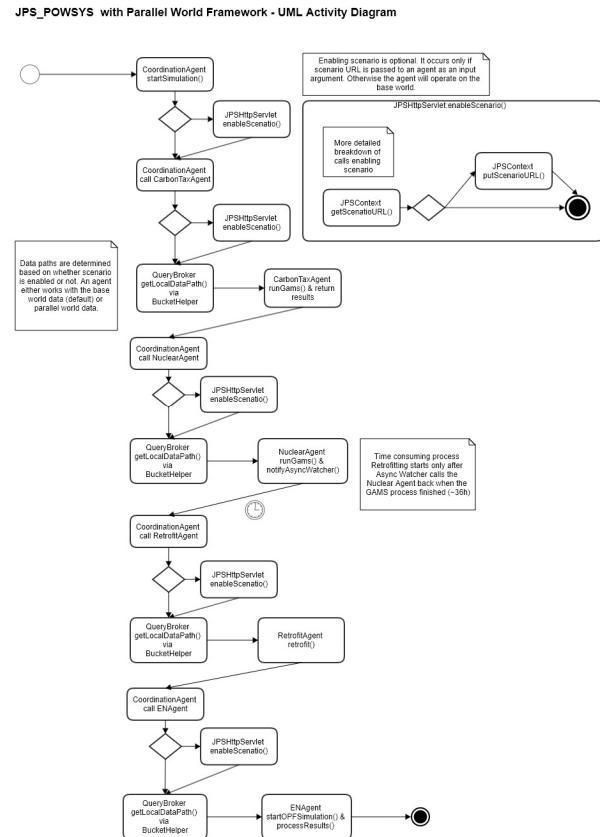


Fig. 6.8: Activity diagram for the use case discussed in the paper, titled “A Parallel World Framework for Scenario Analysis in Knowledge Graphs”.

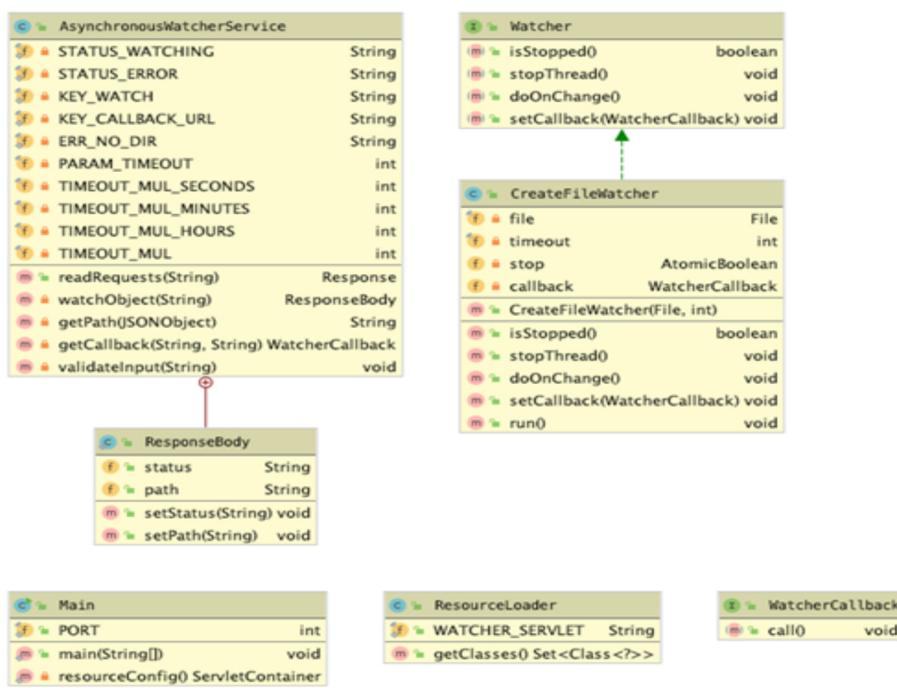


Fig. 6.7: Class diagram for the overall design of the Asynchronous Watching Service (AWS).

## Update on work package JPS.3

### Implementation

Dr Jethro AKROYD (Senior Research Fellow, CAM), Dr Sebastian MOSBACH (Senior Research Fellow, CAM) and Dr Feroz FARAZI (Research Fellow, CAM) have designed and developed the OntoKin system to allow any user to upload chemical mechanisms to the OntoKin knowledge graph, and to query the knowledge graph to retrieve and compare species and reaction data. The system consists of three main components – a User Interface (UI), a business logic layer and the underlying knowledge graph. A web-based UI to demonstrate the OntoKin system is available at the following link: <http://theworldavatar.com/ontokin>.

Dr Jethro AKROYD and Dr Sebastian MOSBACH have contributed to this UI design (as shown in Figure 6.9). Dr Feroz FARAZI has designed and developed the business logic layer that includes a CHEMKIN to OWL conversion agent, an OWL file consistency checking agent, an OWL file uploading component and a query component. The conversion agent can assess the validity of a mechanism in CHEMKIN format, which usually contains a mechanism file and a thermodynamic data file and can optionally contain a surface chemistry file and a transport data file. If the user-provided files represent a complete mechanism, the converter will proceed with the conversion

and reports the success or failure status. Following a successful conversion, the consistency checking agent uses the HermiT Reasoner to determine the consistency of logical axioms provided in the OWL file. If the OWL file passes the consistency check, it is uploaded to the OntoKin knowledge graph using the OWL file uploading component.

The UI allows the user to select from a list of pre-defined queries. The user may additionally constrain the query by specifying a species or reaction. The UI utilises the user's input to create a SPARQL Protocol and RDF Query Language (SPARQL) query that is used to search for relevant results in the knowledge graph. The results are returned to the UI. Figure 6.10 depicts the results of the comparison of thermodynamic data (heat capacity, enthalpy and entropy) for O<sub>2</sub> across a selected set of mechanisms in the knowledge graph.

Dr Feroz FARAZI has iteratively developed the visualisations for species' thermodynamic data (as shown in Figure 6.10) and rate constant (as shown in Figure 6.11) in consultation with Dr Jethro AKROYD and Dr Sebastian MOSBACH. The OntoKin system allows different mechanisms to be queried for using specific reactions and ena-

Fig. 6.9: A screenshot depicting a web-based UI developed for the OntoKin System to allow users to upload mechanisms published in CHEMKIN format to the OntoKin knowledge graph and to query the knowledge graph for species and reaction data.

bles easy comparison of the Arrhenius parameters for the reactions. This is important because different methods can be used to estimate the Arrhenius parameters for a given reaction and the evaluation of the parameters can improve over time. With this feature included in the system, changes in these parameters can be easily identified.

Dr Feroz FARAZI has also extended the OntoKin system to demonstrate through examples how the concept of a Semantic Web based knowledge graph can be used to integrate combustion modelling into cross-disciplinary applications and in particular how inconsistency issues in chemical mechanisms can be addressed. Linked Data, the state-of-the-art approach for producing Semantic Web data, forms the essence of a knowledge graph. Dr Feroz FARAZI and Dr Nenad KRDZAVAC have implemented this in a number of interconnected ontologies, specifically in the context of combustion chemistry. Central to this is "OntoKin", an ontology developed for capturing both the content and the semantics of chemical kinetic reaction mechanisms. OntoKin is used to represent example mechanisms from the literature in a knowledge graph which itself is part of an existing, more general knowledge graph and

ecosystem of autonomous software agents that are acting on it. Figure 6.12 shows an example of how the naming inconsistency issue is being addressed in the context of JPS.

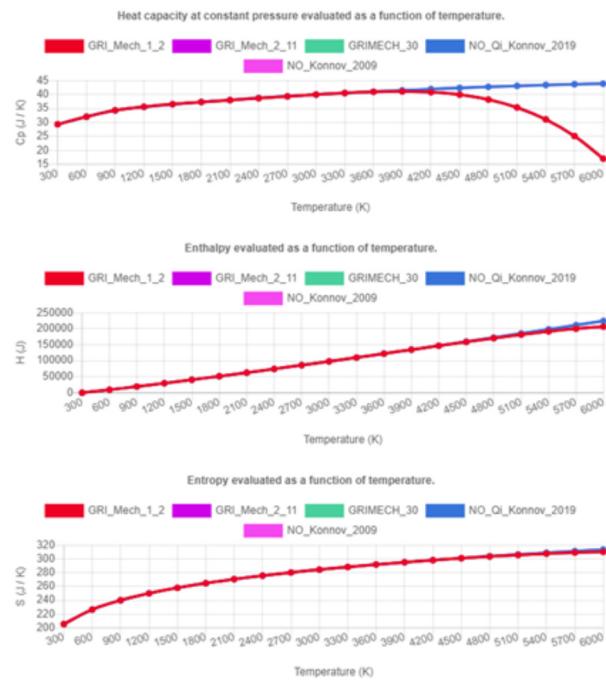


Fig. 6.10: A comparison of thermodynamic data for the species O<sub>2</sub>. Two different trends of heat capacity, enthalpy and entropy are observed across mechanisms at high temperatures.

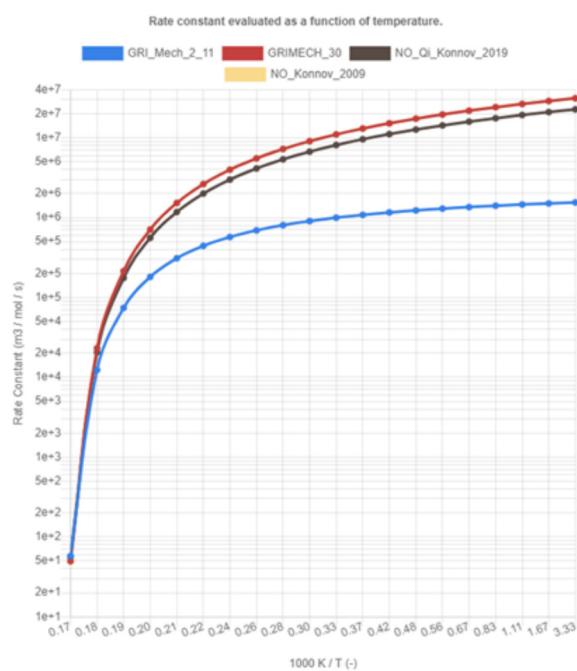


Fig. 6.11: A comparison of rate constants of the reaction O<sub>2</sub> + N  $\Rightarrow$  O + NO across mechanisms.

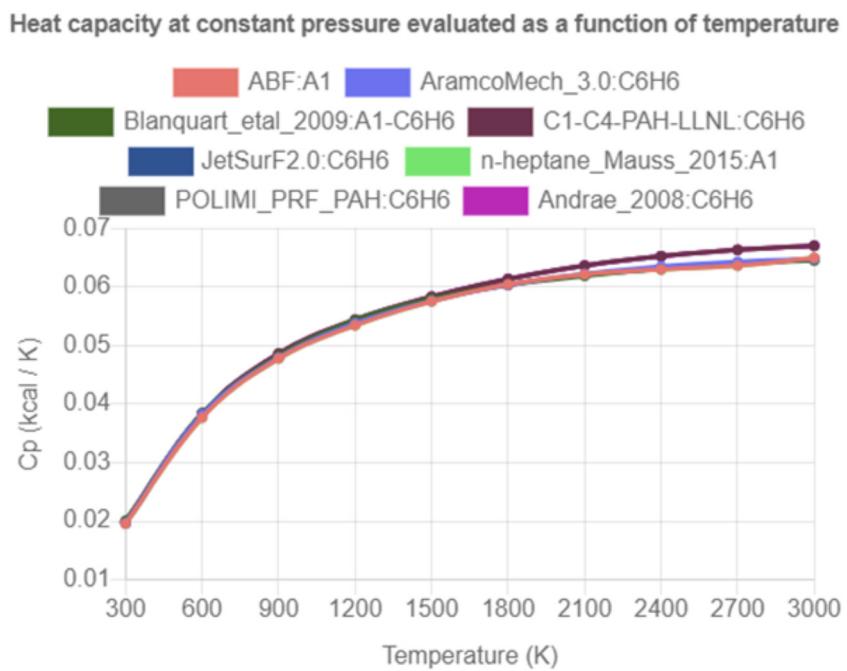


Fig. 6.12: A screenshot depicting the comparison of the heat capacities at constant pressure for benzene appearing in three different names across mechanisms.

In addition, Dr Nenad KRDZAVAC, Dr Jethro AKROYD, Dr Sebastian MOSBACH and Angiras MENON have developed a thermochemistry tool for implementing the modified scalable version of a cross-validation algorithm. This required the optimisation of the data pre-processing phase that determines the error matrices for species and reactions, which produces a list of species to exclude from further processing. The optimised initial data analysis phase verifies whether better estimates of enthalpy of formation can be achieved. Dr Nenad KRDZAVAC has developed the OntoCompChem Upload Service that populates the JPS knowledge graph with quantum calculations of species as part of the implementation of the self-growing knowledge graph project. This development includes the extension of the "Molhub" web service to support parsing of the Self-Consistent Field (SCF) energy and zero-point energy from Gaussian output files, and to store these features in the OntoCompChem knowledge graph which is also part of the JPS knowledge graph. Dr Nenad KRDZAVAC, in collaboration with Angiras MENON, Dr Sebastian MOSBACH, Dr Jethro AKROYD and Dr Feroz FARAZI, have created an algorithm that generates connectivity of chemical elements within a species by using federated SPARQL queries to extract information about species geometry and bonds stored in the JPS knowledge graph.

**Gourab KARMAKAR (Research Engineer, CARES), Aravind DEVANAND (PhD student, NUS)** and Dr Nenad KRDZAVAC are involved in the implementation of rules using SPARQL Inferencing Notation (SPIN) for a cross-domain 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. In this use case, the depropaniser section of a typical natural gas processing plant is considered. The chemical and electrical aspects of the depropaniser section

have been modelled using gPROMS and MATLAB respectively. The real power consumed by the chemical processes is used to couple the chemical and electrical systems. This use case also involved developing an ontology called "OntoTwin", based on existing OntoPowsys and OntoEIP ontologies, using Protégé to describe the relevant electrical and chemical components utilised. In addition, an agent framework called "ElChemo" is developed to establish real-time communication between the two siloed systems via the JPS knowledge graph (as shown in Figure 6.13). The ElChemo framework utilises Description Logics (DL) and SPIN reasoning techniques to investigate the interactions between the two systems. This includes having a rule-based system to ensure seamless operation of the plant. The rules are used to define the normal operating conditions for the plant and are capable of detecting any constraint violations. The preliminary results reveal that significant economic benefits can be achieved by the proposed approach.

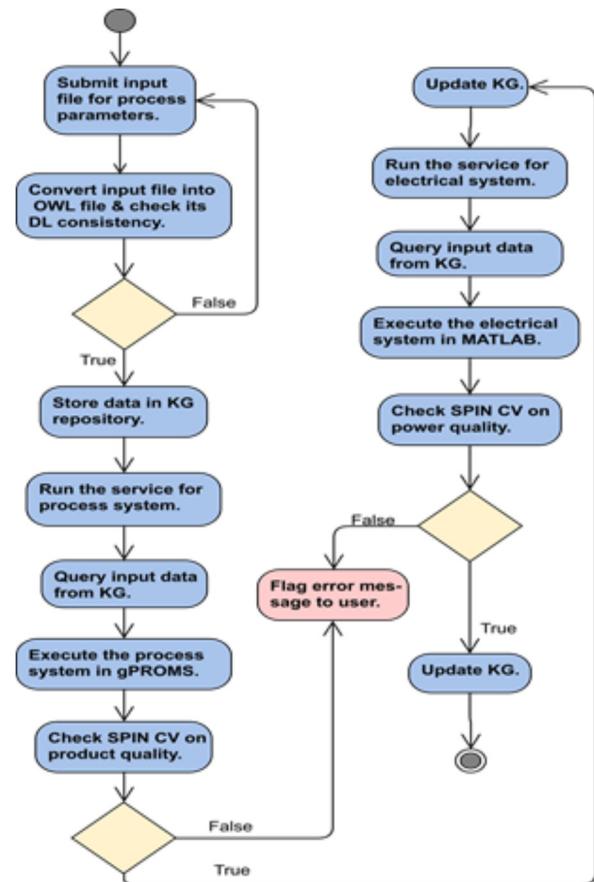
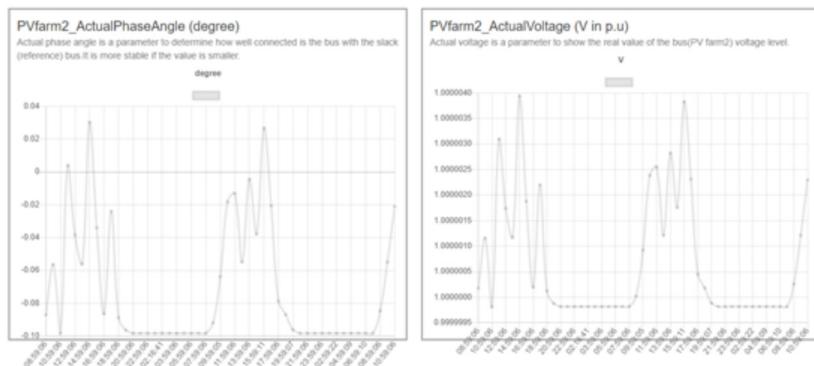


Fig. 6.13: Activity diagram of the ElChemo framework.

**Leonardus Kevin ADITYA (Project Officer, NTU) and Laura ONG (Software Developer, CARES)** have been working on consolidating JPS by restructuring pre-existing projects according to the current architecture. This work involved packaging the pre-existing projects as agents that can apply the Semantic Web stack to read and understand information from the knowledge graph and modify its data values and structure. The agents can now communicate with each other and exchange information via the knowledge graph and semantic input and output parameters. An example of such consolidation work is the composite agent based on the Semakau Island Smart Grid project that explores the scenario of equipping Semakau Island with various types of renewable energy sources. This composite agent consists of a “coordination” agent that manages the calling order between other agents, a “weather” agent which periodically acquires weather data via web scraping and Application Programming Interfaces (APIs) for both real-time and hourly forecast of the next twenty-four hours, and an agent which acts as a Java wrapper for the model to simulate the amount of renewable energy generated by the solar photovoltaic cells given real-time solar irradiance data. The acquired data from the “weather” agent is described with a timestamp and stored in the JPS knowledge graph for further processing by other



Outputs



agents. The agent which acts as a Java wrapper for the simulation model is also responsible for querying the JPS knowledge graph to retrieve the real-time solar irradiance data for the model. The initial simulation model was built using the PowerWorld software and was subsequently parameterised to allow faster and simpler computation. Examples of outputs from the simulation are photovoltaic cells’ actual phase angle and actual voltage. These outputs are also stored in the JPS knowledge graph. Laura ONG has enhanced the visualisation for displaying the key variables of this use case by utilising semantic queries to query the JPS knowledge graph and retrieve the necessary data for further processing (as shown in Figure 6.14). The visualisation is developed using Javascript and ChartJS.

Another example of JPS consolidation work that Kevin ADITYA and Laura ONG have been working on is the composite agent which combines both the chemical process and electrical aspects of a biodiesel plant model. Similar to the above use case, the initial simulation model was built using Apsen Plus software and was subsequently parameterised to allow faster and simpler computation. For this use case, they are creating an agent that based on the user’s input, selects the corresponding simulation model agent to be executed.

Fig. 6.14: Real-time solar irradiance, actual phase angle and actual voltage of the photovoltaic cells model.

## Update on work package JPS.4

### Model analysis and visualisation

**Leonardus Kevin ADITYA** (Project Officer, NTU) has extended the previous work on the carbon tax use case implemented using the “parallel world” framework by creating agents to estimate the overall CO<sub>2</sub> emissions of the electrical grid. This involved developing an agent to query for the CO<sub>2</sub> emission factor of the individual generator, and estimates the individual generator’s CO<sub>2</sub> emission by using their electricity generation levels which are determined by executing an Optimal Power Flow (OPF) simulation. The estimated generators’ CO<sub>2</sub> emissions are stored in the JPS knowledge graph i.e. in the corresponding generator’s OWL file. As a power plant can consist of multiple generators, Kevin ADITYA has also developed another agent to determine the CO<sub>2</sub> emission at the level of individual power plants by querying their corresponding generator’s OWL file and aggregating the individual generator’s CO<sub>2</sub> emission. The aggregated CO<sub>2</sub> emissions are also stored in the JPS knowledge graph i.e. in the corresponding power plant’s OWL file.

**Laura ONG** (Software Developer, CARES) has augmented the visualisation for the carbon tax use case by allowing the user to modify the power load of the buses and displaying the corresponding estimated CO<sub>2</sub> emissions and types of generators in the tables (as shown in Figure 6.15). As this use case is implemented using the “parallel world” framework, agents involved in the same scenario have their access, queries and updates on the knowledge graph delegated to a scenario-specific “sandbox”. In both scenarios, upon clicking on the individual load icon (red point), a pop-up window containing the information about the selected component will appear. The user can modify the value of the input parameters and execute the OPF simulation to determine the corresponding network profile. The corresponding estimated CO<sub>2</sub> emissions are updated automatically to reflect any changes in the electrical network.

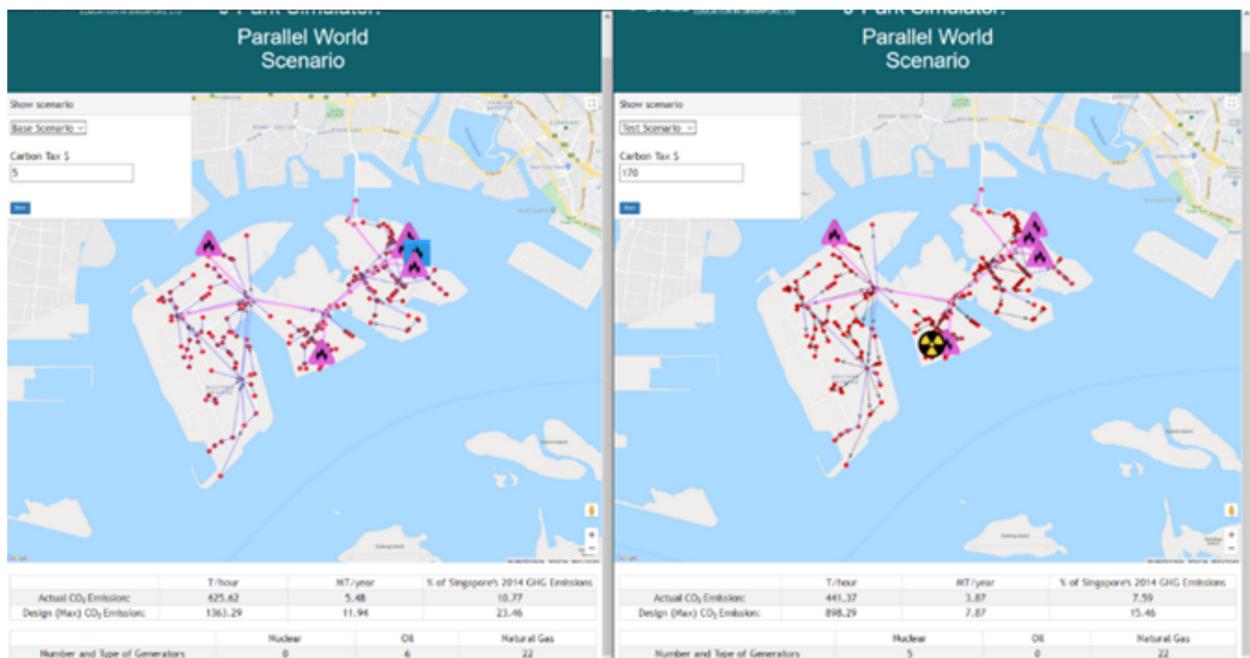


Fig. 6.15: Visualisation of scenario-based analysis. The illustration on the left depicts the “base world” and the illustration on the right depicts the “parallel world” where the electrical network from the “base world” has been modified with retrofitting. Blue square denotes oil generator, pink triangles denote natural gas generators, and radiation symbol denotes small modular nuclear power plant.

**ZHANG ShaoCong (Software Developer, CARES)** has augmented her previous work on ontology matching at terminology/schema level by extending the concept to instance level i.e. data consolidation. For any data-centric system, the quality of data is of utmost importance. Data quality issues often arise due to the creation and maintenance of data by multiple separate parties. Data consolidation aims to enhance the data quality by providing extra information through integrating multiple data sources. However, inconsistencies both at the schema and instance levels between data sources are common and often reduce the data quality of the consolidated dataset. One example of such inconsistencies is instance duplication. ZHANG ShaoCong has investigated the use of her previous work on ontology matching to integrate power plant instances from DBpedia and JPS. Taking advantage of JPS' multi-level design for terminology definition, which results in a deep, heavy weighted structure for the instances, she developed a novel value matcher to evaluate the similarity between two ontological entities based on their literal value set. Each literal value is not only associated with its closest parent individual, but is also associated with all levels of parent individuals. The results from this novel value matcher, in conjunction with a standard string matcher and word matcher, are subjected to a class alignment constraint in order to produce a list of matching instances (e.g. power plant instances in this use case). ZHANG ShaoCong has also implemented a "data linking" agent

which automatically adds an "owl:sameAs" relationship between a pair of identified matching instances. The addition of this relationship is a recommended practice in the linked data community, which will enable a federated query to be executed across different data sources (e.g. DBpedia and JPS in this use case) hence achieving the objective of data consolidation. She has also demonstrated that with this work, the user is now able to query the JPS knowledge graph and retrieve additional attributes (e.g. manufacturing model of the generator unit: <http://dbpedia.org/property/psUnitsManuModel> and the type of cooling source: <http://dbpedia.org/property/thCoolingSource>). This additional information can potentially be used by other agents in JPS to improve the system's modelling accuracy.

**Zhou XiaoChi (PhD student, CAM)** has investigated the use of an interactive Natural Language Query (NLQ) interface for the chemistry-related domains in JPS e.g. OntoKin (for chemical kinetic reaction mechanisms), OntoSpecies (for chemical species) and OntoCompChem (for quantum chemistry calculations). This work aims to develop an NLQ that is efficient and accurate in providing answers to chemistry-related questions (especially quantum chemistry calculations) posed by the user in a human-readable format e.g. "Find all the reaction mechanisms having water as a reactant". Using the user-provided question as an input, the NLQ interprets the question through analysing its structure and in-

<pre> 1 <b>SELECT</b> ?entity 2 <b>WHERE</b> 3   { 4 5     ?entity a "reaction" . 6     ?entity &lt;reactant&gt; "water" . 7 8   } </pre>	<pre> 1 <b>SELECT</b> ?entity 2 <b>WHERE</b> 3   { 4 5     ?entity wdt:P31 wd:Q36534 . 6     ?entity wdt:P186 wd:Q283 . 7 8   } </pre>
	<b>entityLabel</b>
	<b>water-gas shift reaction</b>

Fig. 6.16: SPARQL query constructed based on user-provided question in human-readable format.

tent by using a supervised text embedding model built on top of the Rasa framework, which is an open-source AI framework for constructing contextual assistants. In addition, a Named Entity Recognizer (NER) will identify and label the key words e.g. “reaction”, “water” and “reactant” as “class”, “species”, and “attribute” respectively. Using the interpretations and labels, a draft SPARQL query is constructed from a SPARQL template (as shown on the left in Figure 6.16). The NLQ will query the JPS knowledge graph for terms such as “reaction”, “water”, and “reactant” to retrieve the necessary information for converting them into Uniform Resource Identifiers

(URIs) such as wd:Q36534 and wd:Q283, in order to complete the SPARQL query (as shown on the right in Figure 6.16). Subsequently, the complete SPARQL query is sent to the JPS knowledge graph to retrieve results such as “water-gas shift reaction” which will be returned to the interface. As the JPS knowledge graph is highly cross-domain in nature, language ambiguity can arise e.g. the term “water” exists in both geographic and chemistry domains. Consequently, ZHOU XiaoChi leverages ZHANG ShaoCong’s work on introducing domain information i.e. topic model to analyse the user-provided question for improved accuracy.

## 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 15.

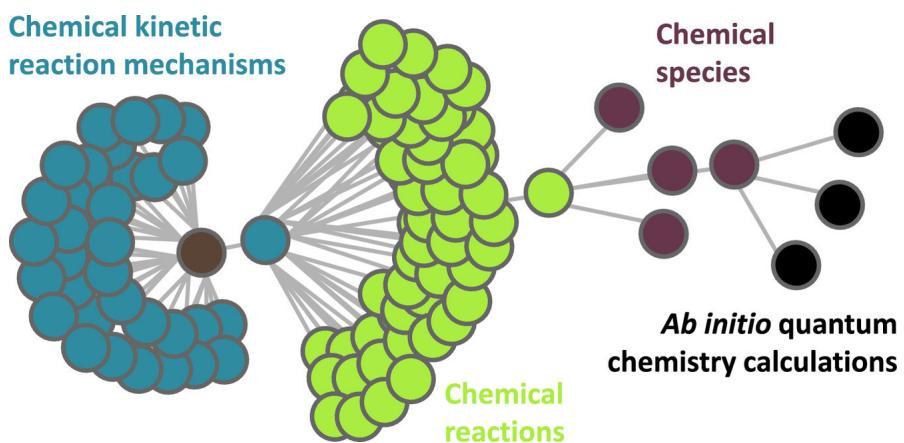
### Linking reaction mechanisms and quantum chemistry: an ontological approach

Feroz Farazi, Nenad B. Krdzavac, Jethro Akroyd, Sebastian Mosbach, Angiras Menon, Daniel Nurkowski and Markus Kraft, *Computers & Chemical Engineering*

DOI: 10.1016/j.compchemeng.2020.106813

Abstract: In this paper, a linked-data framework for connecting species in chemical kinetic reaction mechanisms with quantum calculations is presented. A mechanism can be constructed from thermodynamic, reaction rate, and transport data that has been obtained either experimentally, computationally, or by a combination of both. This process in practice requires multiple sources of data, which raises, *inter alia*, species naming and data inconsistency issues. A linked data-centric knowledge-graph approach is taken in

this work to address these challenges. In order to implement this approach, two existing ontologies, namely OntoKin, for representing chemical kinetic reaction mechanisms, and OntoCompChem, for representing quantum chemistry calculations, are extended. In addition, a new ontology, which we call OntoSpecies, is developed for uniquely representing chemical species. The framework also includes agents to populate and link knowledge-bases created through the instantiation of these ontologies. In addition, the developed knowledge-graph and agents naturally form a part of the J-Park Simulator (JPS) – an Industry 4.0 platform which combines linked data and an eco-system of autonomous agents for cross-domain applications. The functionality of the framework is demonstrated via a use-case based on a hydrogen combustion mechanism.



## Other activities and achievements

**PhD student Aravind DEVANAND** has submitted his thesis, titled “Energy Management Utilising Knowledge Graphs: Case Study of an Eco-Industrial Park.” The thesis was completed in CARES, and encompasses the work of: 1) developing mathematical models for energy management at the energy clustering and enterprise levels of an Eco-Industrial Park, and 2) utilising JPS to handle the associated heterogenous data, and to facilitate communication across different domains and software platforms for cross-domain studies.

**Research Project Manager LIM Mei Qi** prepared and coordinated the presentation of JPS for the CREATE Symposium (December 2019) and the Global Young Scientists Summit (January 2020). In addition to IRP JPS, Mei Qi also managed the Intra-CREATE project: An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park.

**PI Prof. Markus KRAFT** gave an invited talk on “How to Make Use of Cyber-physical Systems and Industry 4.0 in Process Industry, Energy Sector and the Environment” at the *Karlsruhe Institute of Technology Joint Colloquium* in Karlsruhe, Germany, 11 October 2019.

**Prof. Kraft** gave an invited talk on the same topic at the *58<sup>th</sup> Tutzing Symposium: Separation Units 4.0* in Tutzing, Germany, 20-23 October 2019.

**Prof. Kraft** gave a lecture on “Carbon Management” for the *Lee Kuan Yew Senior Fellows in Public Service* programme, Singapore, 13 November 2019.

**Prof. Kraft** gave a plenary talk on “Intelligent Decarbonisation” at *The First International Conference on Energy and AI* in Tianjin, China, 9-11 January 2020.

**Prof. Kraft** has been elected to be a member of the Editorial Board of the new Elsevier Open Access Journal *Energy and AI*.



Prof. Kraft giving his plenary talk at the Conference on Energy and AI; the journal Energy and AI that was launched at the conference.



# eCO<sub>2</sub>EP

## CARBON CAPTURE AND UTILISATION USING A TABLE-TOP CHEMICAL FACTORY

This is CARES' first Intra-CREATE project and is aimed at developing a "table-top chemical factory" that uses electrochemical processes to convert CO<sub>2</sub> into ethylene or to 1-propanol – two molecular products widely used in the chemical industry. Earlier research carried out at CREATE had demonstrated that CO<sub>2</sub> molecules can be transformed into hydrocarbons through the application of electro-catalysis. eCO<sub>2</sub>EP's research studies the viability of scaling CO<sub>2</sub> reduction processes, including techno-economic evaluation of the use of off-peak renewable electricity in areas with excess capacity, with the goal of developing new energy-chemistry solutions for a more sustainable future.

eCO<sub>2</sub>EP Principal Investigators:



*Professor Alexei LAPKIN*  
*University of Cambridge*



*Professor Joel AGER*  
*University of California, Berkeley*

# OVERVIEW



The eCO<sub>2</sub>EP project is currently in its months 24-30. The project is gearing towards demonstration of the combined electrochemical reduction of CO<sub>2</sub> and product separation. At the same time, there is progress in theoretical understanding of the elementary catalytic mechanisms controlling selectivity of the electrochemical reaction. A multi-scale model is being developed to enable optimisation of the eCO<sub>2</sub> reactor towards long-term operation.

**Professor Alexei Lapkin, PI**  
University of Cambridge

**Professor Joel Ager, PI**  
University of California, Berkeley

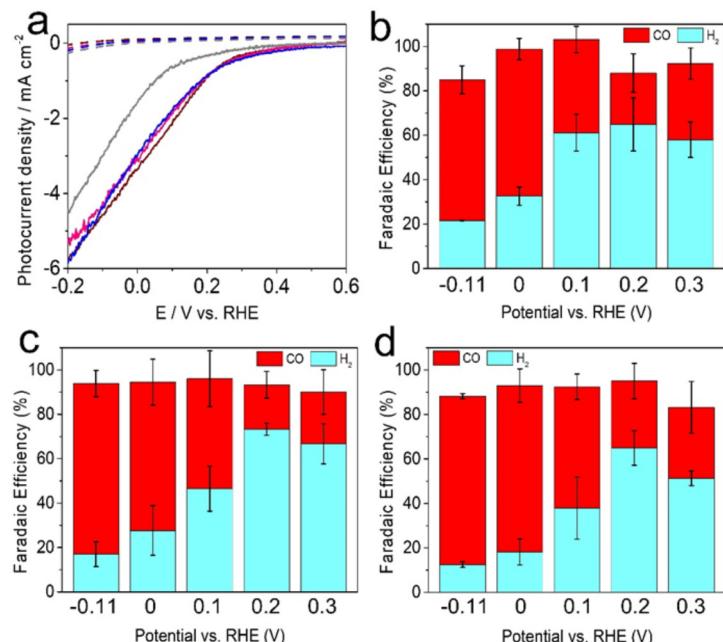
## Update on work package 1

### New catalyst discovery and characterisation

**Dr CHEN Yubo (Research Fellow, NTU)** reports that perovskite oxides based on earth-abundant transition metals have been extensively explored as promising oxygen evolution reaction (OER) catalysts in alkaline media. The electrochemically induced transformation of initially crystalline surface into an amorphous state has been reported for a few highly active perovskite catalysts. However, little knowledge is available to distinguish the contribution of amorphised surface from that of remaining bulk toward the OER. In this work, we utilise the promoting effects of two types of Fe modification, i.e., bulk Fe dopant and free Fe ions absorbed from the electrolyte, on the OER activity of SrCoO<sub>3- $\delta$</sub>  model perovskite to figure out the real active phase. Transition electron microscope and X-ray photoelectron spectroscopy confirmed the surface amorphisation of SrCoO<sub>3- $\delta$</sub>  as well as SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$</sub>  after potential cycling in Fe-free KOH solution. By further cycling in Fe-spiked electrolyte, Fe was incorporated into the amorphised surface of SrCoO<sub>3- $\delta$</sub>  (SrCoO<sub>3- $\delta$</sub>  + Fe<sup>3+</sup>), yielding ~ 6-fold increase in activity. Despite the difference in remaining perovskites, SrCoO<sub>3- $\delta$</sub>  + Fe<sup>3+</sup> and SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$</sub>  exhibited remarkably similar activity. These results reflect that the *in situ* developed surface species are directly responsible for the measured OER

activity. Instead, the remaining bulk of perovskites subjected to reconstruction have little impact on the catalytic performance.

**Dr LIU Guanyu (Research Fellow, NTU)** developed various structural and interfacial engineering strategies to improve the photoresponse and selectivity of III-V semiconductor-based photocathodes for photoelectrochemical reduction of CO<sub>2</sub> with H<sub>2</sub>O toward syngas production. The optimal nanostructured photocathode demonstrates a half-cell conversion efficiency of 0.32% with onset potential of as positive as 0.3 V vs. the reversible hydrogen electrode under 1 sun (100 mW cm<sup>-2</sup>, AM1.5G solar spectrum) irradiation. The highest Faradaic efficiency toward CO production reached around 85% at -0.11 V vs. the reversible hydrogen electrode under illumination. The performance improvement is attributed to the increased light absorption, prolonged minority carrier lifetime and favourable interfacial properties for binding of key reaction intermediates. In addition, a wide range of CO/H<sub>2</sub> ratios are achieved from 1:4 to 6:1, enabling the adjustment of the generated syngas composition. The present findings may provide insight into the development of highly efficient III-V semiconductor-based photoelectrochemical systems for long-term deployment in real-world applications.



*Fig. 7.1: Photoelectrochemical performance of III-V semiconductor-based photocathodes for reduction of CO<sub>2</sub> with H<sub>2</sub>O toward syngas production.*

*Dr LIU Guanyu*

There is a big research gap in the understanding of the mechanistic chemistry going on in the electrochemical cell to achieve faradaic efficiency. To better understand this, real-time analysis of the electrochemical  $\text{CO}_2$  reduction products using PTRTOF MS is the best analytical technique that would provide the time dynamics of eCO<sub>2</sub>EP products. 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 mentioned above, **Dr Divya NAGARAJ (Research Fellow, NUS)** is now capable of demonstrating the eCO<sub>2</sub>EP 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 the reagent ions like  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ . 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.

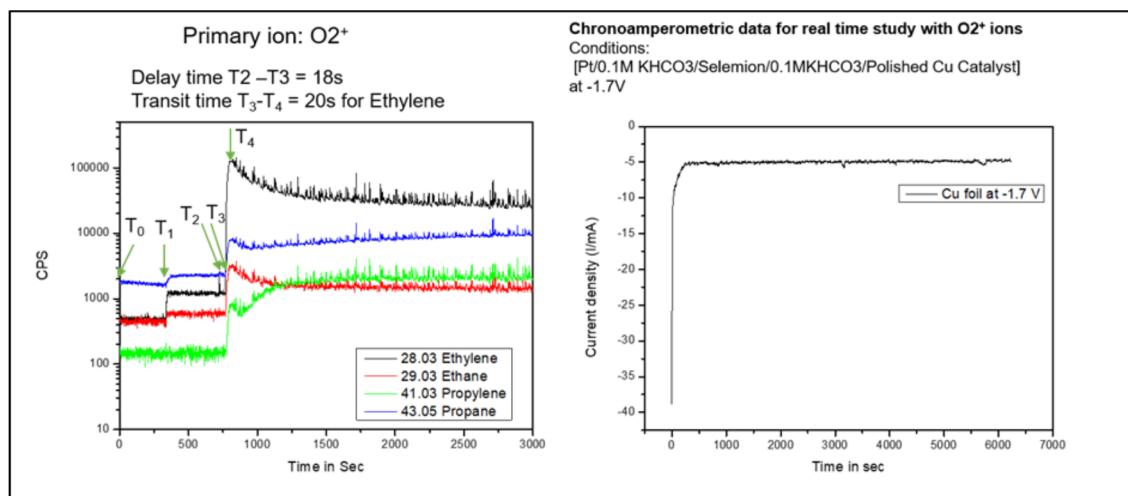


Fig. 7.2: Real-time analysis of electrochemical  $\text{CO}_2$  reduction products to understand the delay time and transit time. (a) Gaseous products profile from PTRTOF MS. b) Chronoamperometric profile obtained for the same reaction.

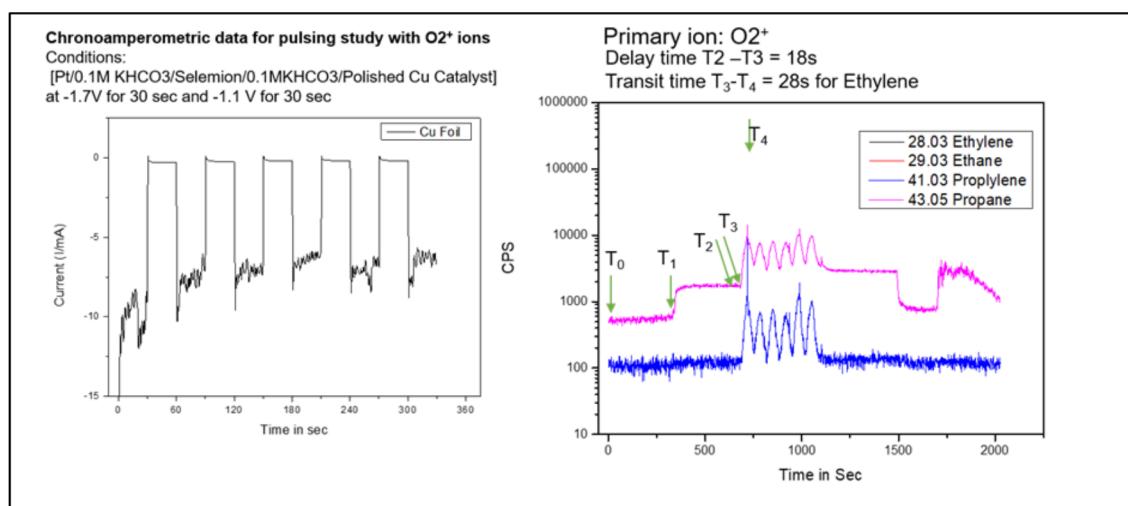


Fig 7.3: Temporal analysis of electrochemical  $\text{CO}_2$  reduction products. (a) Chronoamperometric profile obtained for every 30 sec pulsing between -1.7 V and -1.1 V. b) Gaseous products profile from PTRTOF MS.

Dr Divya NAGARAJ

**Dr REN Hangjuan (Research Fellow, CARES)** joined CARES in January 2020. Her project is to develop a large-scale cathode that can efficiently produce C<sub>2+</sub> chemicals by electrochemical CO<sub>2</sub> reduction. She has developed a Cu-based electrode composed of Cu-based coating, carbon particles and a polytetrafluoroethylene layer. During CO<sub>2</sub> reduction reaction, gas chromatography and high-performance liquid chromatography with high sensitivity were used to detect the gas and liquid products, separately. The present electrode has successfully produced C<sub>2+</sub> products, especially ethylene, and has shown a good stability of 50 minutes at 1.8 V vs. Ag/AgCl (without iR compensation) in 0.1 M KHCO<sub>3</sub>.

Subsequently, the current work is focusing on the improvement of Faradaic efficiency of C<sub>2+</sub> products and stability of cathode under large current and high alkaline in a newly designed flow cell. Besides, this Dr REN Hangjuan wants to use *in situ* techniques and density functional theory calculations to study the chemical science during the CO<sub>2</sub> reduction.

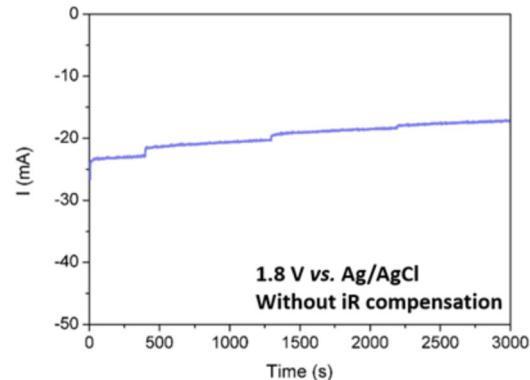
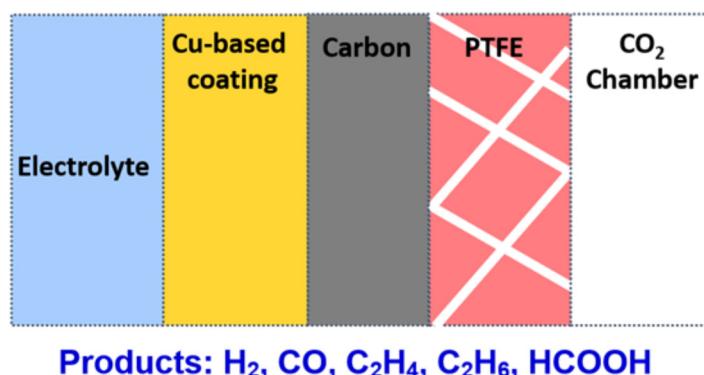


Fig. 7.4: Cu-based cathode and corresponding I-t curve.

Dr REN Hangjuan

## Update on work package 2

### Modelling and data informatics

For an electrochemical reactor, the catalyst is the heart of the reactor which is responsible for producing the desired chemicals or products as it is supplied with corresponding reactants. While the catalyst is responsible for the formation of the products, the cell design is pivotal to ensure that the reactants cover the entire catalyst surface to obtain maximum conversion rate and cell performance. Improper cell design may lead to less coverage of reactants and local hotspots which are detrimental to the catalyst life. In this regard, the design of the gas flow channel becomes an important aspect of cell design. While the literature is rich in various gas-flow channel designs, additional design configurations are needed to be considered for providing optimal surface coverage of the reactants for a large catalyst area (10cm x 10cm).

In this regard, **Dr Kuppa Ashoke RAMAN (Research Fellow, NUS)** and colleagues have tested two different modifications to the gas flow channel. Firstly, a pressure head was added at the inlet of the gas channel to increase the pressure of the supplied reactant mixture. This increase in pressure of the supply gas would drive the reactant mixture to cover the catalyst surface.

The second modification was to provide a conical manifold at the inlet of the gas flow channel. This inlet manifold is arranged with different obstruction so as to distribute the incoming feedgas along various pathways and provide uniform gas distribution into the gas flow channels. Figure 7.6 illustrates the velocity magnitude of the flowfield inside the gas flow channel. A low feed rate of 50 sccm is used in the current simulations. The streamlines show the fluid pathway meandering through the obstacles to pass through the gas flow channels. Currently, we are optimising the configuration of the obstacles to ensure minimal blindspots as the flow stream is converged and transported into the parallel channels, thereby enabling uniform reactant coverage.

Water management is one of the key issues in improving the efficiency and performance of a proton exchange membrane fuel cell (PEMFC). As the reactants enter the porous matrix below the flow channel and react with the catalyst, products are formed, diffused through the porous medium and subsequently convected through the gas flow channel. While the gaseous products are usually transported unhindered, the passage of liquid products through the gas diffu-

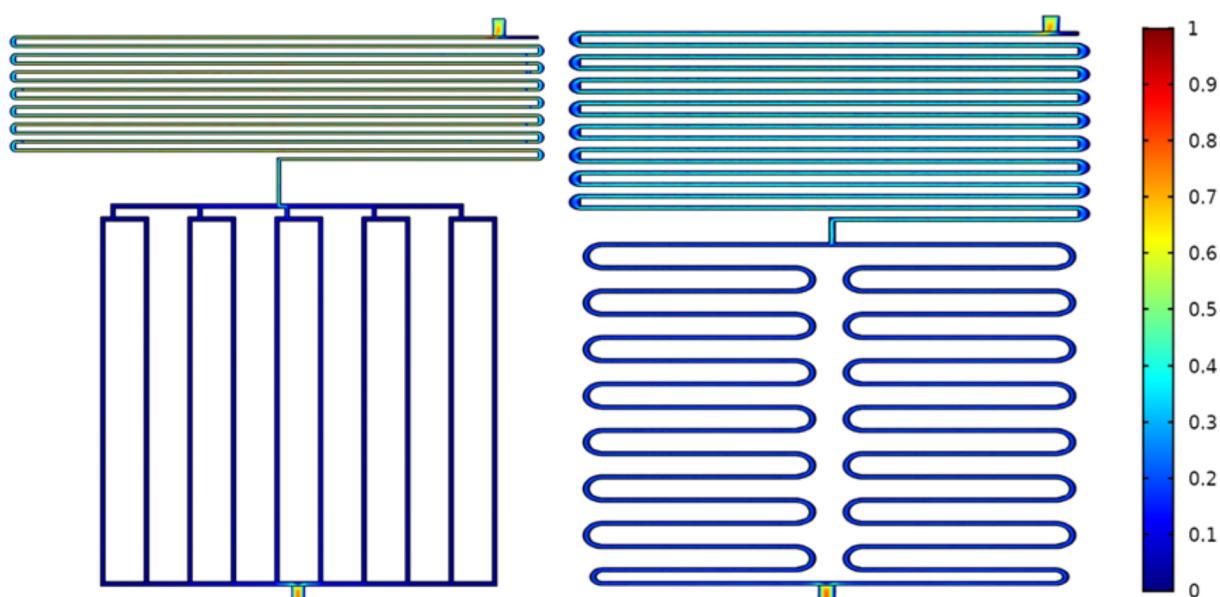


Fig. 7.5: Gas flow channels with a pressure head for branch and double serpentine gas flow channel configurations. The velocity magnitude in the legend is in m/s.

sion layer is resisted by the porous medium. Depending on the structure of the porous matrix, migration and accumulation of liquid products inside the diffusion medium lead to the formation of larger droplets inside the flow channel. These droplets inside the gas flow channel not only hinder the transport of reactant species but could also lead to system shutdown due to flooding. Therefore, a fundamental understanding of the two-phase transport phenomenon inside the porous medium is vital to come up with methods to mitigate the same. Understanding the effect of diverse porous networks on the hydrodynamics of the liquid products and their eventual discharge into the flow channels is important. In this regard, numerical simulations we performed to investigate the dynamics of two-phase flows inside both homogeneous and heterogene-

ous porous matrix. The porous structure is characterised by the pore diameter, distribution and surface wettability. Figure 7.7 displays the liquid flow pattern evolution after emerging from a homogeneous porous matrix of the gas diffusion layer. Some liquid is spread on the catalyst layer while other liquid permeates through the porous diffusion layer and gradually accumulates as a nucleating droplet. Based on the simulation results, we found that the gas velocity, liquid velocity, sphere size and arrangement, and liquid surface tension and viscosity have significant influences on the gas-liquid flow patterns, especially the physics of droplet formation and migration in the gas flow channel. Different from previous literature, homogeneous and heterogeneous porous matrix were designed to improve the liquid distribution in the gas channel.

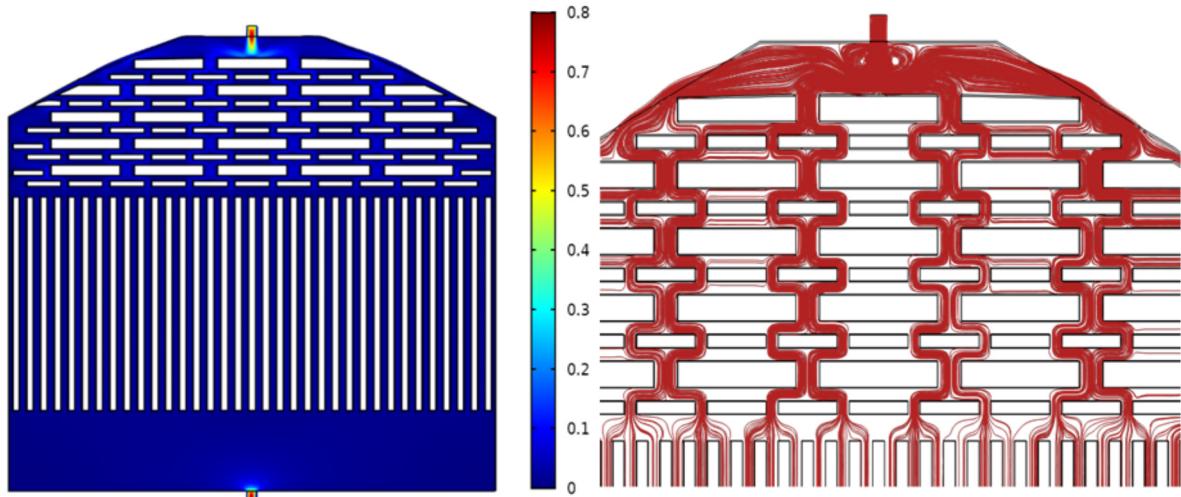


Fig. 7.6: Conical head modification for parallel gas flow channel configuration. The inlet gas is supplied at a low feed rate of 50 sccm. The velocity magnitude in the legend is in m/s. Streamlines show the flow pathway from the conical head into the gas flow channel.

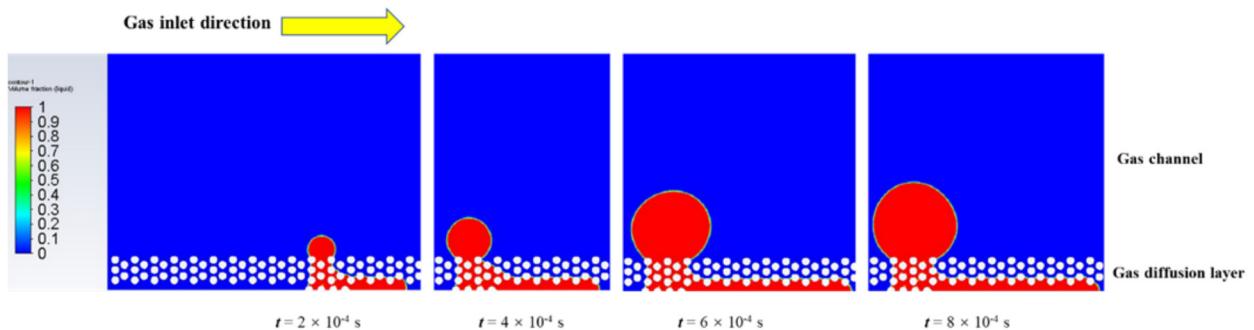


Fig. 7.7: Liquid flow patterns in the gas channel after emerging from the gas diffusion layer.

Dr Kuppa Ashoke RAMAN

**Dr Quang Thang TRINH (Victor) (Senior Research Fellow, NTU)**, under the supervision of **Dr Matthew SHERBURNE (Co-I, BEARS)**, is conducting a study of CO<sub>2</sub> reduction on copper (Cu) catalyst doped with boron (B) using density functional theory (DFT) calculations. It is revealed that the activation of CO<sub>2</sub> forming the intermediate CO on single crystal Cu(111) facet doped with B (called Cu(111)-B) is quite feasible due to the low activation barrier of 69 kJ/mol via the hydrogen-shuttling mechanism facilitated by water molecules. However, the generated CO species bound too strongly on the Cu(111)-B surface with the computed binding energy of -162 kJ/mol, almost the same as the binding energy of CO on Pt(111) surface (a typical case where surface-adsorbed CO molecules act as a poison that covers the active site). Due to the very high affinity of Cu(111)-B with CO, the activation barrier for the CO-CO coupling reaction (dimerisation), which is the key and rate-limiting step towards the formation of ethylene, is also very high at 201 kJ/mol. This extremely high barrier therefore hinders the formation of ethylene during the reduction of CO<sub>2</sub> on Cu(111)-B. Meanwhile, the hydrogenation of surface CO by hydrogen forming the CHO intermediate, which is reported as the key step for the selectivity towards methane formation, is more feasible with the activation barrier of only 61 kJ/mol. These observations give the prediction that single Cu(111)-B might not be the best catalyst for the CO<sub>2</sub>RR to ethylene, and major products will be methane and CO as a strong surface poison. This theoretical prediction is in excellent agreement with experimental data for the CO<sub>2</sub>RR on Cu(111)-B, prepared using the pulsed laser deposition method in Prof. Venky's group at NUS. The total product analysis for the electrochemical CO<sub>2</sub>RR on B doped Cu (111) run at -1.09 V vs RHE shows the main products are H<sub>2</sub>, CO and CH<sub>4</sub> with the Faradaic efficiency of 39%, 16% and 23%, respectively. Dr Quang Thang TRINH is also expanding the investigation for the polycrystalline Cu doped B (called pCu-B catalyst), which might have very different activity in the CO<sub>2</sub>RR. The computed surface energies of different Cu facets doped with B will be used to feed in the Wulff construction model to build the

representative model for pCu-B catalyst, follows by evaluating the key steps for the formation of ethylene on this catalyst and revealing the insight of its activity.

Besides this, Dr Quang Thang TRINH also contributed to several review papers about designing and application of new materials for CO<sub>2</sub> reduction in electrochemical and photocatalytic processes. Those review papers are published on the *Journal of Chemical Technology & Biotechnology*, *Arabian Journal of Chemistry* and *Journal of Alloys and Compounds*.

**Martin (Research Scientist, CARES)** is advancing in his plan to model a gas-diffusion electrodes (GDE) macro-kinetics simulation. He is currently testing the robustness of the model which he has formulated mathematically with Marcus theory using an existing case study. This case is looking at solid oxide fuel cells (SOFC), a process that mimics an electrochemical cell. In his case study, the GDE for SOFC is modelled under open circuit and steady state conditions. The model is formulated in zero-dimension to study the time evolution of the surface species as a function of initial fuel (reactant) concentration, in this case, the concentration of CO gas. Thus, surface diffusion is ignored in this study.

The results of surface coverages as a dependent of reactant concentration are presented in Figures 7.8 and 7.9. It is shown that the metal (nickel) vacancy is populated by CO(Ni), i.e. carbon monoxide on surface nickel with higher concentration of the gas carbon monoxide. From the O<sup>2-</sup> (YSZ) surface coverage (Figure 7.9), a jump in site fraction can be seen at around CO gas partial pressure of 1200-1300 Pa. This jump is evidence of two different regimes in the mechanism, which is, at a sufficient high CO gas partial pressure, the electrochemical reaction to form stable oxygen on a nickel surface, O(Ni), is dominant over reactions that form stable oxygen on zirconia surface, O (YSZ).

Moreover, the i-V curve is generated as a characteristic of the system and as a demonstration that Marcus theory can model the faradaic current as a function of applied potential (voltage) likewise the more general, yet inferior, formulation of Butler-Volmer (Figure 7.9). This i-V curve is a quantity that is usually analysed by electrochemists or electro-chemical-engineers to test the sensitivity of an electrochemical system. Another advantage of using Marcus theory or elementary reaction mechanism over Butler-Volmer general expression in electrochemistry is detailed and accurate grained-level results where the fluxes of intermediate species can be studied under certain physical conditions such as voltage, temperature and more importantly fuel amount.

Additionally, Martin has formulated the mechanism for CO<sub>2</sub>(g) (carbon dioxide gas) reduction into the desired products, i.e. ethylene, 1-propanol and their pre-cursors. This mechanism was presented in the last eCO<sub>2</sub>EP half-yearly review meeting. The next step is to put this mechanism as an input to the built model in order to be able to optimise the table-top GDE.

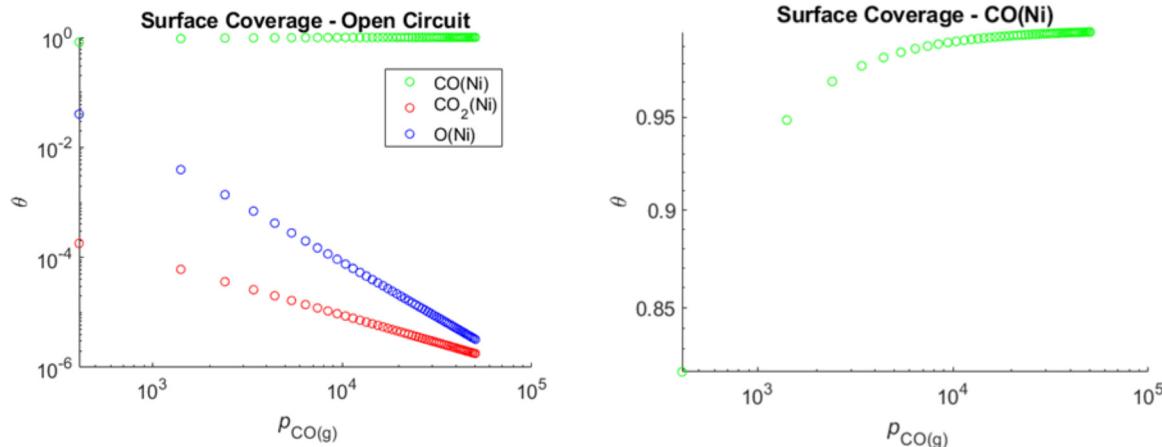


Fig. 7.8: Modelled surface species site fraction as a function of gas carbon monoxide partial pressure (units: Pa) for the nickel surface of SOFC. (Left) y-axis is in logarithmic scale for CO(Ni), CO<sub>2</sub>(Ni) and O(Ni). (Right) y-axis is in normal scale for CO(Ni).

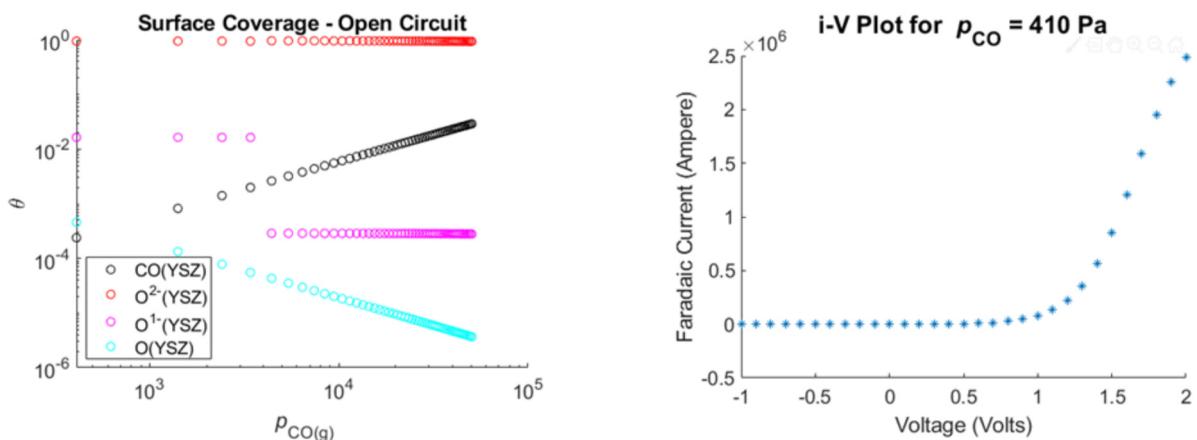


Fig. 7.9. (Left) Modelled surface species site fraction as a function of gas carbon monoxide partial pressure (units: Pa) for the zirconia surface of SOFC. (Right) Voltage vs faradaic current plot for a fixed carbon monoxide fuel concentration.

MARTIN

## Update on work package 3

### Chemical factory on a table

Dr Magda BARECKA (Research Fellow, CARES) joined CARES in October 2019 and is mainly involved in the whole plant design/integration and process optimisation for the table-top factory converting carbon dioxide to ethylene. She has been coordinating the development of the complete process flowsheet, including various separation steps. She has been involved in the coordination of reactor upscale and plant commissioning. Dr Magda BARECKA has also been working on design of liquid products separation and based on shortcut modelling results has shortlisted three of the most promising separation approaches, which will be experimentally tested during upcoming months. Lastly, she has been determining approaches for further industrial implementation of carbon dioxide to ethylene electroconversion technology (Figure 7.10).

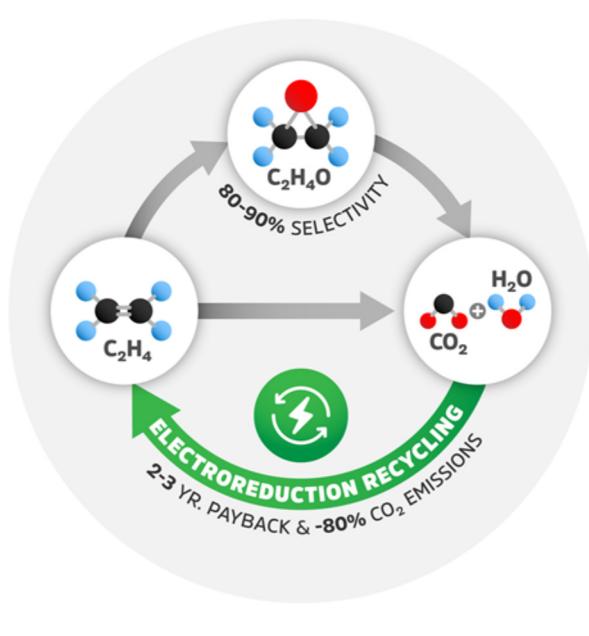


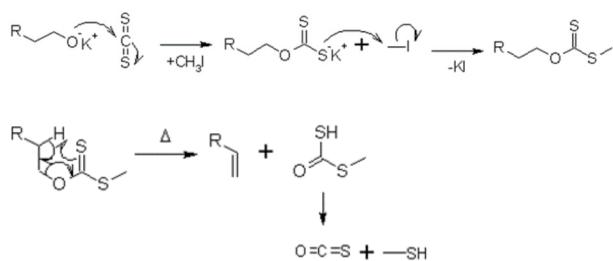
Fig. 7.10: Proposed concept of CO<sub>2</sub> recycling within the ethylene oxide production process. The approach based on integration of CO<sub>2</sub> electroreduction is economically viable and has a potential to reduce up to 80% of CO<sub>2</sub> emissions from ethylene oxide plants.

Dr Magda BARECKA

Dr Alexandre KHUDOROZHKOV (Research Fellow, CARES) reports that target compounds, namely zeolites and metal-organic frameworks (MOFs) with the corresponding pore diameter providing good selectivity towards separation of C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> were synthesised. Characterisation of compounds via different methods (XRD, FTIR, Raman, ICP) was completed. BET surface area of some of these samples was determined as well, providing a very important parameter which should be taken into account in single- and multi-component adsorption experiments. Experimental setup for the breakthrough experiments is under construction. Calibration of single- and multi-component setup was done.

Due to the utilisation of highly alkaline solution in the anode part of the gas-diffusion electrode, methods like pervaporation or membrane separation are not feasible due to the fast degradation of a membrane material. Thus, for the effective liquid phase separation of ethanol and water it was proposed to use one of the following methods:

- adsorption of ethanol on chabazite-type zeolites (CHA), which are highly stable in alkaline solutions, with consequent desorption of C<sub>2</sub>H<sub>5</sub>OH
- Chugaev elimination reaction with the formation of ethanol xanthate in alkaline solution and its consequent degradation forming ethylene:



It is planned to conduct liquid phase separation experiments utilising these methods to evaluate the most effective one. High-performance liquid chromatography will be used as a method of liquid phase analysis.

**Shishir JAIRAM (Research Engineer, CARES)** has been working on large scale design and development of a pilot plant for carbon capture. He has recently worked on the development of the process flow diagrams, design of the reactor and the engineering. His initial task was to develop a suitable flow diagram to help in designing the pilot plant (Figure 7.11); with the process flow diagrams it's easy to recognise the parts as well as the whole system. The other important aspect of the pilot plant development is the design of the reactor. The reactor design included different criteria with the emphasis on the flow field of the gas for the cathode. Shishir JAIRAM has been able to design the reactor based on the discussion and will be going ahead with the fabrication. Using this model, different gas flow rates were considered and used for simulating the same and thus the design was finalised. The different flow

rates along with the suitable material identification by Shishir JAIRAM has helped in tackling different issues; another major issue has been to make sure that the gas diffusion electrode is porous enough and can be placed in the reactor without being displaced. This ensures that the reactant gas is equally distributed across the electrode.

Shishir JAIRAM has also been working on the full assembly of the reactor and is currently looking at the engineering aspects of the pilot plant. He has identified different equipment required for the development of the pilot plant and also has been assembling the reactor. The images below give the idea of the pilot plant development (Figure 7.12) along with the design of the reactor (Figure 7.13).

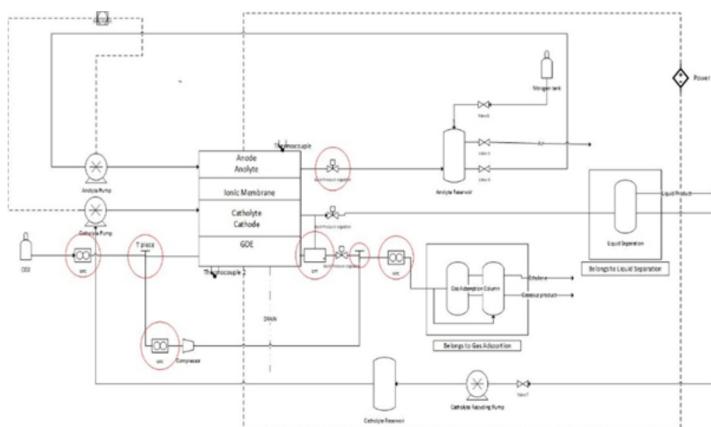


Fig. 7.11: Flow sheet of the plant.



Fig. 7.12: Current assembly facility of the reactor.

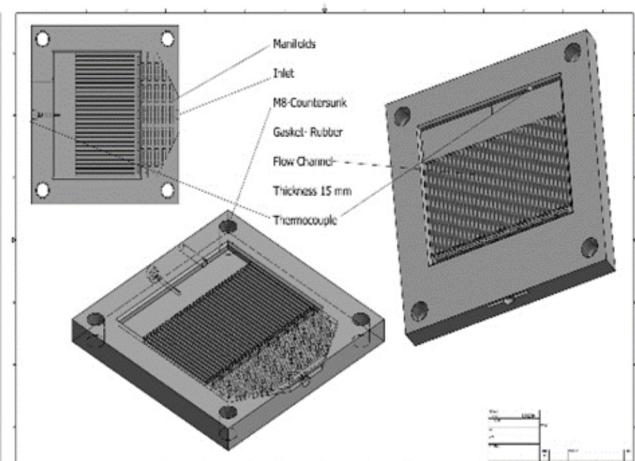
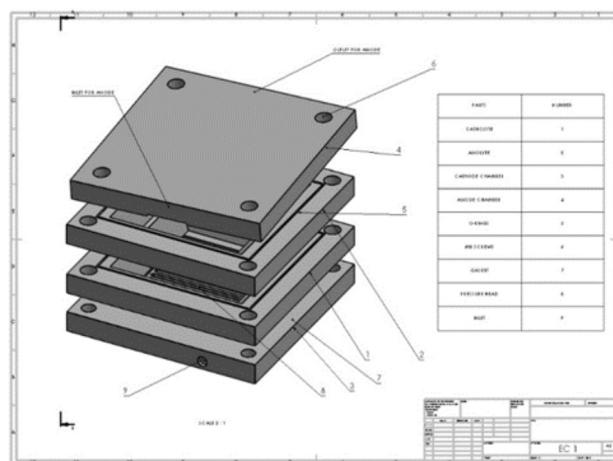


Fig. 7.13: (left) Design of the reactor. (right) Flow channel of the cathode.

## Scientific output

The following are the CREATE-acknowledged publications generated by eCO<sub>2</sub>EP during the reporting period, excluding those already featured in the Scientific Highlights section on page 15.

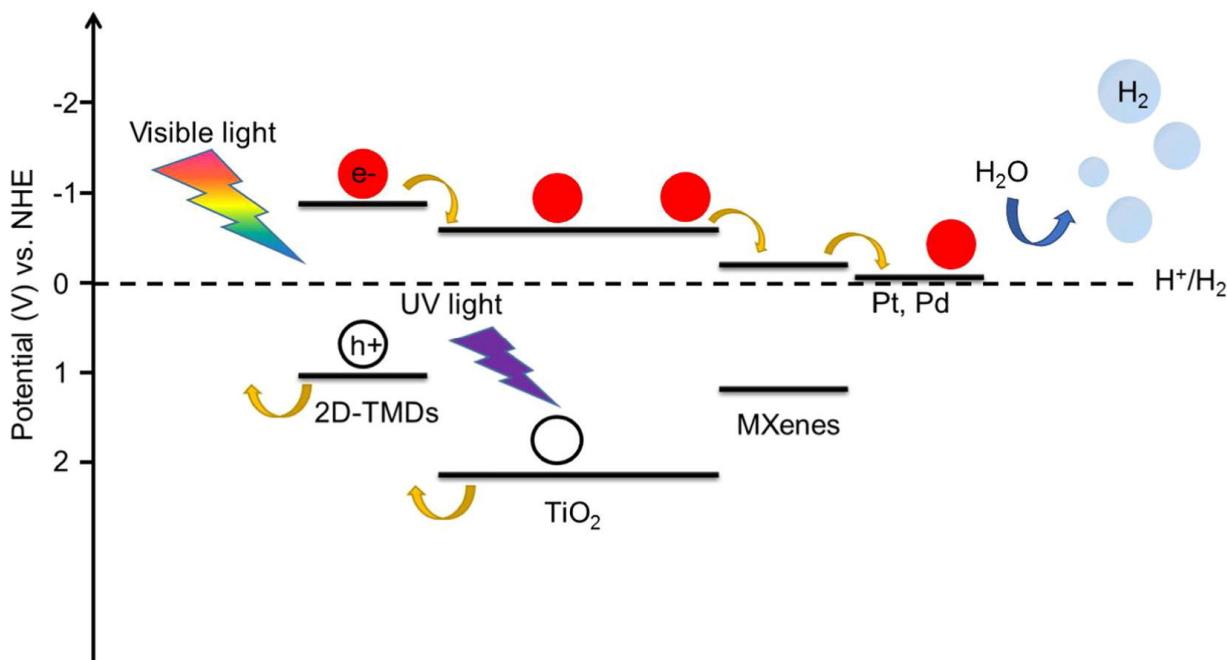
### Recent progress in TiO<sub>2</sub>-based photocatalysts for hydrogen evolution reaction: a review

Ha Huu Do, Dang Le Tri Nguyen, Xuan Cuong Nguyen, Thu-Ha Le, Thang Phan Nguyen, Quang Thang Trinh, Sang Hyun Ahn, Dai-Viet N. Vo, Soo Young Kim and Quyet Van Le, *Arabian Journal of Chemistry*

DOI: 10.1016/j.arabjc.2019.12.012

Abstract: TiO<sub>2</sub> has gained tremendous attention as a cutting-edge material for application in photocatalysis. The performance of TiO<sub>2</sub> as a photocatalyst depends on various parameters including morphology, surface area, and crystallinity. Although TiO<sub>2</sub> has shown good catalytic activity in various catalysis systems, the performance of TiO<sub>2</sub> as a photocatalyst is

generally limited due to its low conductivity and a wide optical bandgap. Numerous different studies have been devoted to overcome these problems, showing significant improvement in photocatalytic performance. In this study, we summarize the recent progress in the utilization of TiO<sub>2</sub> for the photocatalytic hydrogen evolution reaction (HER). Strategies for modulating the properties toward the high photocatalytic activity of TiO<sub>2</sub> for HER including structural engineering, compositional engineering, and doping are highlighted and discussed. The advantages and limitations of each modification approach are reviewed. Finally, the remaining obstacles and perspective for the development of TiO<sub>2</sub> as photocatalysts toward high efficient HER in the near future are also provided.



## Halide perovskite photocatalysis: progress and perspectives

Kim Anh Huynh, Dang Le Tri Nguyen, Van-Huy Nguyen, Dai-Viet N. Vo, Quang Thang Trinh, Thang Phan Nguyen, Soo Young Kim and Quyet Van Le, *Journal of Chemical Technology and Biotechnology*

DOI: 10.1002/jctb.6342

**Abstract:** Organic-inorganic metal halide perovskites (HPs) have emerged as new frontier materials for optoelectronic and energy applications. In addition to various well-known applications, such as solar cells, light-emitting diodes, photodetectors, and resistive switching memories, HPs can be utilized as efficient photocatalysts for numerous electrochemical reactions, including carbon dioxide (CO<sub>2</sub>)

reduction reactions, hydrogen evolution reaction, photosynthesis, and wastewater treatment. However, the use of HPs toward photo-driven catalysis remains a tremendous challenge owing to their poor stability in polar solvents. Nevertheless, huge progress has been made to counter this critical issue for improving the performance of HPs as efficient photocatalysts in a wide range of applications. In this review, we first introduce the structures and properties of HPs. Next, we highlight the recent approaches on the fabrication of HPs, including thin films and nanostructures. Strategies for implementing HPs in catalysis systems and their working mechanisms are thoroughly summarized and discussed. Lastly, the current challenges and prospects of the application of HPs toward photocatalytic reactions are fully addressed.

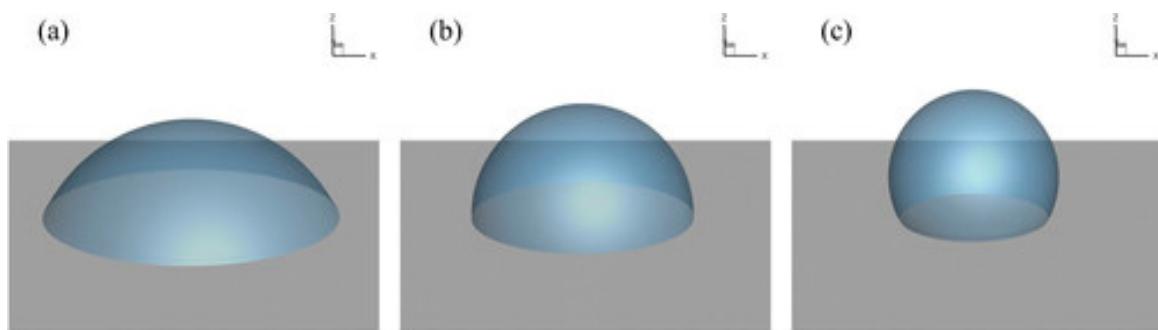
## Electrically induced droplet ejection dynamics under shear flow

K. Ashoke Raman, Erik Birgersson, Yi Sui and Adrian C. Fisher, *Physics of Fluids*

DOI: 10.1063/1.5143757

**Abstract:** Droplet nucleation, condensation, and transport is a ubiquitous phenomenon observed in various industrial applications involving power generation and energy conversion to enhance heat transfer. Recent studies have shown that electrowetting (EW) has emerged as a new tool to enhance pool boiling heat transfer. In these applications involving heat transfer through pool boiling, the interplay between the incoming air and an EW-induced jumping droplet is instrumental in determining the overall heat transfer enhancement. This study

investigates the transport dynamics of EW-induced droplet ejection in shear flow. 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 capture 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 angle of flight, aspect ratio, and surface energy are found to increase with an increase in the applied voltage. Variations in pulse width induce a phase shift in the temporal evolution of the angle of flight and aspect ratio. Due to an increase in drag forces, the droplet traverses a larger streamwise distance at higher gas densities.



Equilibrium interface profiles of a hemispherical water droplet initially placed on surfaces with  $\theta_Y$  = (a) 60°, (b) 90°, and (c) 120°.

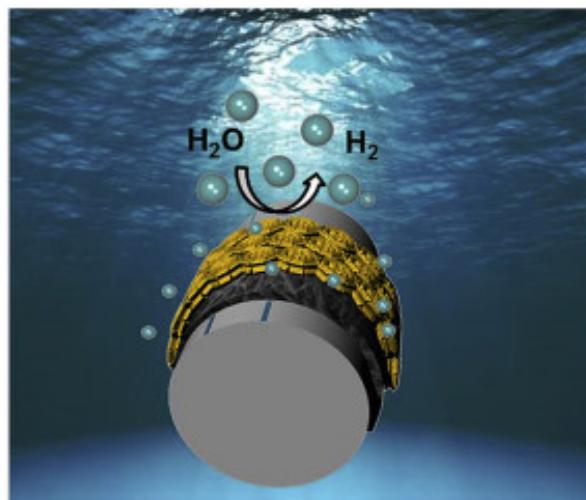
## Hierarchical molybdenum disulfide on carbon nanotube-reduced graphene oxide composite paper as efficient catalysts for hydrogen evolution reaction

Mahider Asmare Tekalgne, Khiem Van Nguyen, Dang Le Tri Nguyen, Van-Huy Nguyen, Thang Phan Nguyen, Dai-Viet N. Vo, Quang Thang Trinh, Amirhossein Hasani, Ha Huu Do, Tae Hyung Lee, Ho Won Jang, Hoang Sinh Le, Quyet Van Le and Soo Young Kim, *Journal of Alloys and Compounds*

DOI: 10.1016/j.jallcom.2020.153897

Abstract: Herein, we report a composite structure composed of vertically grown molybdenum disulfide ( $\text{MoS}_x$ ) nanosheets supported by conductive carbon nanotube-reduced graphene oxide (CNT-rGO) on Vietnamese traditional paper ( $\text{MoS}_x/\text{CNT-rGO}/\text{VTP}$ ) for a high-performance electrochemical hydrogen evolution reaction (HER). In the fabrication, CNT-rGO is first prepared on VTP by roll coating, following which the vertically aligned  $\text{MoS}_2$  nanosheets are synthesized on the surface of CNT-rGO/VTP through a simple hydrothermal reaction. The catalyst exhibits excellent HER electrocatalytic activity including a low onset potential of 190 mV, Tafel slope of 59 mV dec<sup>-1</sup>, and excellent

stability in an acidic electrolyte solution. The excellent catalytic performance can be attributed to the abundant active edges provided by the vertically aligned  $\text{MoS}_x$  nanosheets, as well as the effective electron transport provided by the CNT-rGO conductive substrate. Therefore, our study demonstrates an inexpensive and simple method to facilitate the large-scale application of non-noble catalysts. In addition, the method can be extended to the development of other transition metal dichalcogenide composite structures for electrochemical applications.

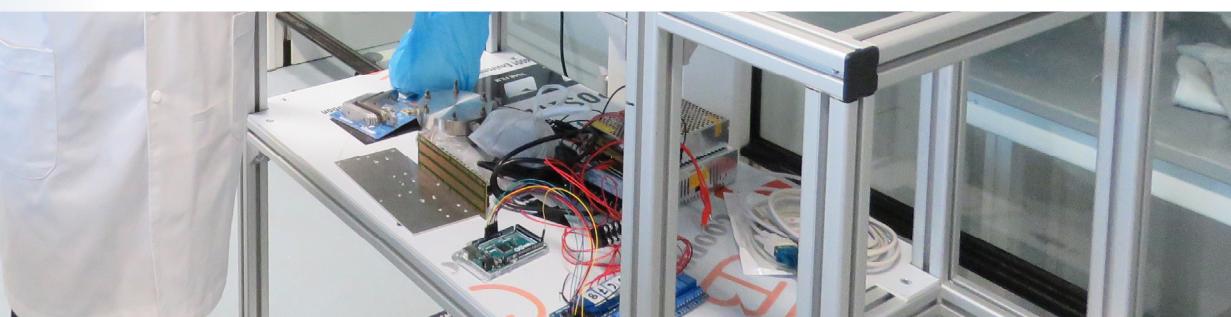


## Other activities and achievements

**Research Fellow Dr Kuppa Ashoke RAMAN** has submitted a conference abstract titled "Role of homogeneous and heterogeneous porous matrix on the liquid transport behaviour inside the gas flow channel of PEMFC" to the 26<sup>th</sup> International Symposium on Chemical Reaction Engineering.



# SMALL PROJECTS



## OTHER CARES-FUNDED PROJECTS

In addition to C4T and eCO<sub>2</sub>EP, CARES hosts a number of other projects. The Cities Knowledge Graph project started 1<sup>st</sup> April 2020 and will eventually be a similar size to eCO<sub>2</sub>EP; it is a collaboration with the Singapore-ETH Centre (SEC).

There are also a number of smaller or shorter projects in CARES. These give our researchers an opportunity to explore new areas, develop technologies for commercialisation or build relationships with new industry partners or public sector collaborators. The smaller projects are also often a good opportunity for interns (such as Aman SINGHAL, pictured above during his time working on the RINGS project) to have a novel experience of research and technology development not easily available during their undergraduate degrees.

The current CARES small projects include: Development of Multi-Step Processes in Pharma (funded by the private-public partnership, Pharmaceutical Innovation Programme Singapore PIPS); RINGS (funded by SMART Innovation Centre); Automated Chemical Routes (funded by BASF); Intelligent Platform for Efficient Energy Management (a collaboration with E2S2 and NUS under the Intra-CREATE seed fund).

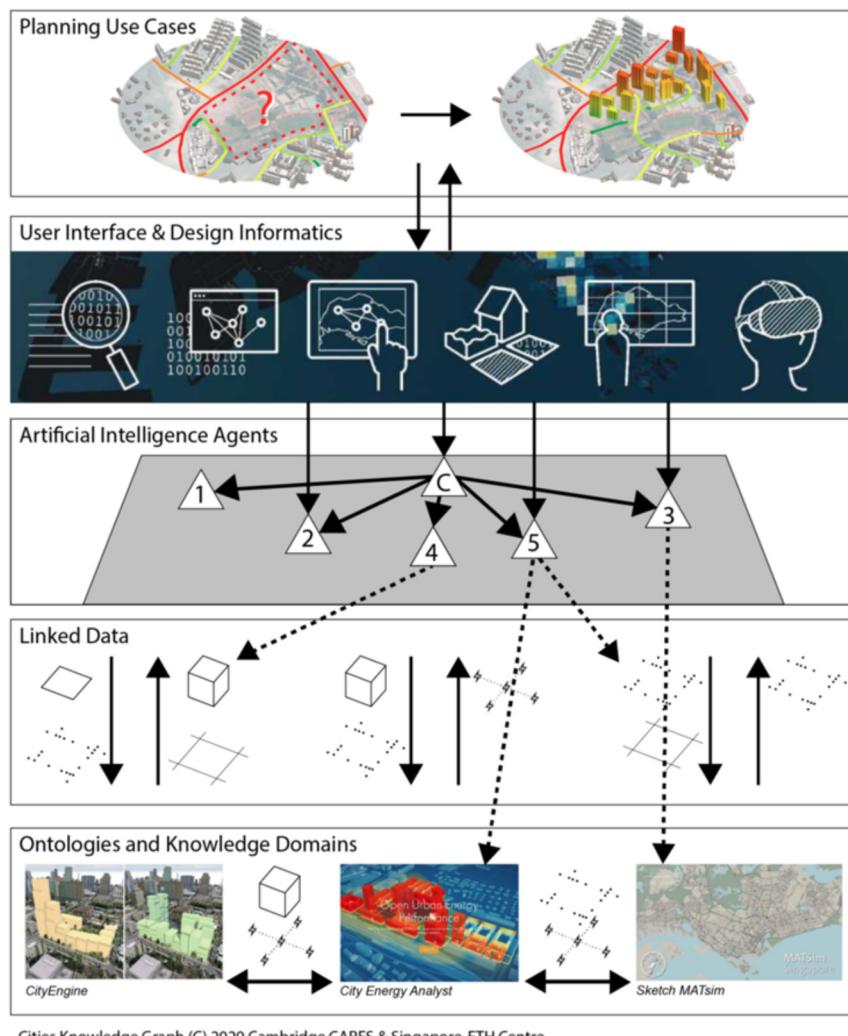
## Cities Knowledge Graph

### Intra-CREATE large grant

Cities-Knowledge Graph (CKG) is an Intra-CREATE collaborative project in the urban systems thematic area. The project brings together expertise from Cambridge CARES, the host institution of the project, and SEC (the Singapore-ETH Centre, established by ETH Zürich - the Swiss Federal Institute of Technology Zürich). The team is led by Principal Investigators from University of Cambridge (Prof. Markus KRAFT) and ETH Zürich (Prof. Stephen CAIRNS). The project commenced on 1 April 2020 and is due to run for three years. The project is in the process of recruiting post-doctoral researchers. Regular team meetings are conducted to ensure that the

team is well-informed and updated about the developments in the project, and to enhance communication between team members, both of which are crucial to foster close collaborations in an inter-disciplinary project.

This research aims to harness rapidly growing and diversifying data streams to improve the planning and design of cities. It will do so by developing an innovative digital platform, known as the Cities Knowledge Graph (CKG), designed to combine data and share knowledge about cities, and to inject new precision and responsiveness to static instruments of planning, such as the city master-plan.



*Fig. 8.1: The Cities Knowledge Graph platform bridges the gap between planning use cases and planning knowledge domains. This project will leverage existing expertise and tools from SEC and CARES.*

## Automated Chemical Routes

### With funding from BASF

Guided by Prof. Alexei LAPKIN (PI, CAM, IRP1), Dr GUO Zhen (Research Fellow, CARES, IRP1) completed this industrial project in December 2019. A final report was prepared and sent to BASF for review. Throughout this project, basic working procedures for automated analysis of chemical routes were established. Several functions were implemented, such as building a reaction network, network refinement, route searching, identification of strategic compounds, searching for similar reactions etc. On the basis of this technique, new chemical routes for the target compounds were proposed. Compared to current synthesis routes in industry, these routes were more sustainable, in terms of feedstocks, solvents and reagent used, and the number of steps. Cur-

rently, these results are under review by BASF.

From January 2020, Dr Guo has transferred to back to IRP1 and commenced work on one of the new C4T Emerging Opportunities Fund projects to continue working on the methods of reaction networks in collaboration with other researchers. The goals are to further improve functionality of this approach.

In addition to the industrial work, a paper was published in *Current Opinion in Chemical Engineering*. In line with the goal of the reaction network approach, the potential of circular chemistry based on renewable feedstocks was discussed in this paper. The concept of circular economy is show in Figure 8.2.

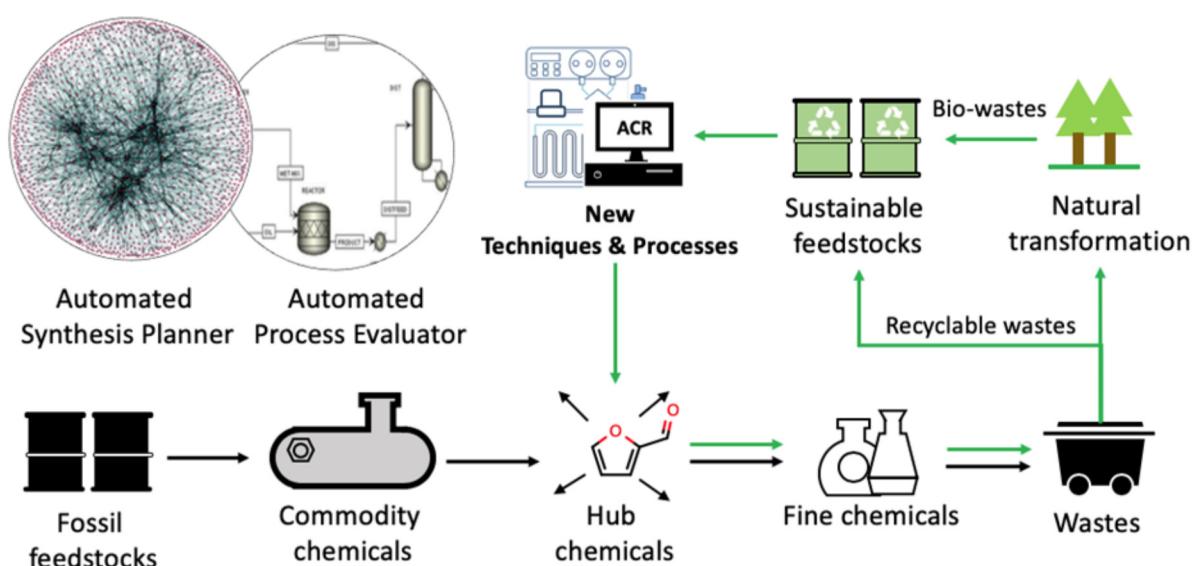


Fig. 8.2: Architecture of the PHIL experiment for DC microgrid.

## Development of Multi-Step Processes in Pharma

### With funding from Pharma Innovation Programme Singapore (PIPS)

For a given active pharmaceutical ingredient (API), the complexity of the multi-step chemical synthesis and the enormous number of possible reagent and reaction condition combinations are significant bottlenecks for rapid large-scale manufacturing. Pharma Innovation Programme Singapore (PIPS) brings together local research organizations and multinational pharmaceutical companies such as GSK, Pfizer, and Merck Sharp & Dohme (MSD), with the goal of improving manufacturing technologies in the pharmaceutical industry. The work conducted by **Dr Simon SUNG (Research Fellow, CARES)** and **Mohammed Jeraal (Research Associate, CARES)** is focused on developing novel automated self-optimising systems that can rapidly identify sustainable and high yielding multi-step chemistry routes to produce APIs. This will be achieved by combining programmable chemical handling equipment, analytical tools and machine learning (ML).

In the laboratory, with greater experience in chemistry, Simon has led the chemical synthesis of the starting materials, the choice of reagents and solvents to use for the case study API, and solvent and reagent physical parameters (descriptors) to incorporate ML directed optimisation. Descriptors describing the size and charge properties the compounds are generated through COSMO-RS computational chemistry software. Mohammed, with previous experience in developing automated self-optimising chemical synthesis reactors, has successfully developed a UI application that has interfaced flow chemistry equipment (Vapourtec), an automated liquid handling robot (Gilson), Agilent and Advion HPLC-MS analyses, and an optimising ML algorithm call the Thompson sampling efficient multi-objective optimisation (TSEMO) (see Figure 8.3). Overall, *without user interference*, the system in its current state is able to repeatedly perform reactions, selecting and controlling the reagents, sol-

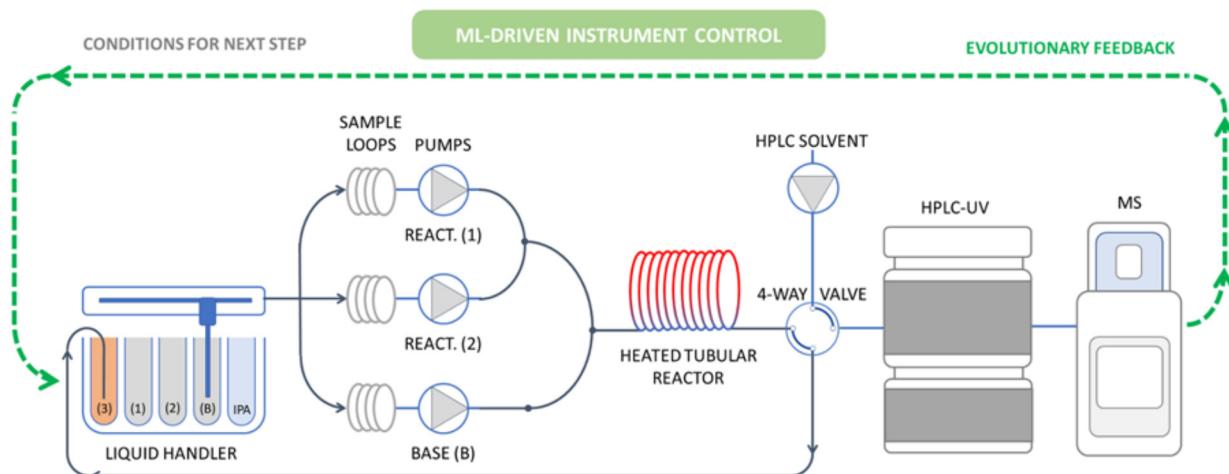


Fig. 8.3: A representative scheme of the reaction system developed. A liquid handler loading two reactants (REACT. (1) and (2)) and a base (BASE (B)) into sample loops of a flow chemistry system. The reacting compounds are then passed through a heater tubular reactor, after which a 4-way sampling valve is automatically triggered to take a reaction sample to a HPLC-UV and MS for analysis. Automated interpretation of the analytical data is then inputted into the ML algorithm, which then generates a set of reaction conditions and reagents to use in the following reaction.

Dr Simon SUNG and Mohammed JERAAL

vents and reaction conditions for the synthesis of a chemical, optimising for multiple simultaneous objectives such as yield, space-time yield, cost, and EcoScore (an in-house developed environmental sustainability and safety parameter).

As well as debugging the existing system, future developments will involve including purification procedures such as liquid-liquid extraction di-

rectly into the flow path, with ML playing a significant role in rapidly identifying suitable solvents and conditions. And finally, the process development of a multi-step preparation route to an API (already chosen in collaboration with Pfizer, GSK and MSD) will be demonstrated using the system.

## An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park

### Intra-CREATE seed grant

The Intra-CREATE Seed Collaboration project “An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park”, a collaboration between National University of Singapore (NUS) and CARES, commenced on 1 March 2019. The project aims to develop a platform for efficient management of energy production and consumption in an Eco-Industrial Park (EIP). During this reporting period, we have packaged various previously developed models and algorithms as agents that can apply the semantic web stack to read and understand information from the knowledge graph and modify its data values

and structure. Agents can communicate with each other and exchange information via the knowledge graph and semantic input and output parameters. They use Hypertext Transfer Protocol (HTTP) for calling each other and JavaScript Object Notation (JSON) or Internationalized Resource Identifier (IRI) for exchanging input and output parameters. We have also materialised the energy trading for the energy demand side management framework using the Rinkeby Test blockchain framework. In addition, we have developed visualisations for displaying the key variables of the use cases.

## Rapid Industrialization of Next Generation Nanomaterials

### With funding from the SMART Innovation Centre

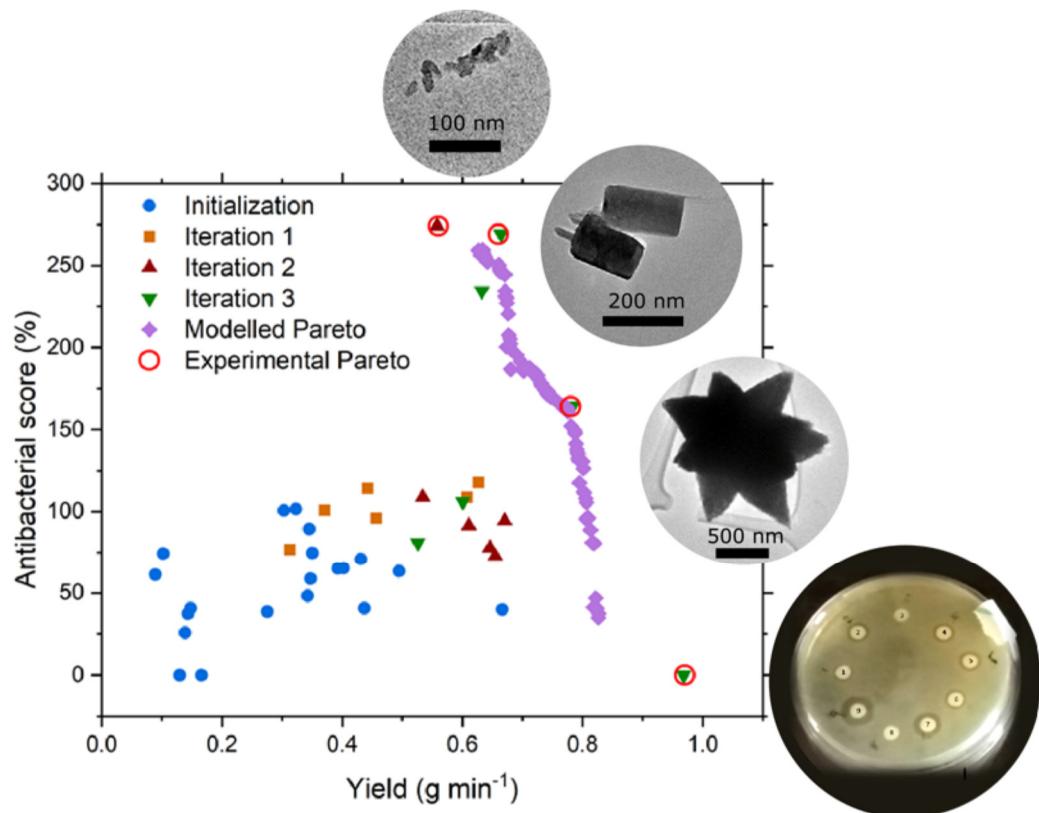
The goal of the RINGs project (Rapid industrialization of next generation nanomaterials) is to develop and commercialise scalable processes for advanced nanomaterial synthesis. In this project, co-funded by the SMART Innovation Centre and led by **Dr Nicholas JOSE (Research Fellow, CARES)**, continuous microreactors, machine learning and automated methods are being combined as a platform for materials development and scale-up. The proof-of-concept project is the rapid development of antibacterial nano-ZnO coatings.

In the first half of this project a broad study of emerging material markets that are ripe for inserting the RINGs technologies was conducted. It was found that healthcare, energy storage and coatings industries are rapidly growing and benefit largely from nanotech. The project is now actively approaching and working with Singaporean research institutions, local SMEs and MNCs

in Singapore to gauge the specific demands of each industry and how we can provide value with our technology. This will lead to the construction of a business model and plan.

Using the machine algorithms developed in Prof. Alexei LAPKIN's group in Cambridge, we were able to rapidly screen process variables to find a trade-off between the antibacterial activity and yield of zinc oxide particles, as seen in the figure below. Characterisation reveals that diverse morphologies are formed along this trade-off curve (or "Pareto Front").

Progress continues on a scale-up rig for the production of kilograms of nanoparticles per day, which has been constructed and automated in the CARES lab. A promising manifold design is currently being evaluated. This will enable rapid scale-up of materials developed at the laboratory scale, from gram to kilogram and ton-scale quantities.



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## ARTICLE

DOI: 10.1038/s41467-018-06269-z

## OPEN

Hydrogen spillover through Matryoshka-type  
(ZIFs@)<sub>n-1</sub>ZIFs nanocubesGuowu Zhan<sup>1,2</sup> & Hua Chun Zeng<sup>1,2</sup>

Hydrogen spillover phenomena  
highly disputed in hydrogen  
metal–support systems

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Energy 150 (2018) 1039–1057

Contents lists available at ScienceDirect

Energy

environmental power dispatch with  
all hydro power

uan<sup>a</sup>, B.Y. Qu<sup>b</sup>, Gehan A.J. Amaralunga<sup>c</sup>

ng Technological University, Singapore  
yuan University of Technology, China

 $H_2O_2$  ProductionSelective Electrochemical  $H_2O_2$   
Two-Electron Oxygen Electro-Yuanyuan Jiang, Pengjuan Ni, Chuanxia Che  
Biao Kong, Adrian Fisher, and Xin Wang\*

Direct electrochemical production of hydrogen peroxide ( $H_2O_2$ )  
two-electron oxygen electrochemistry, for example, the oxygen re  
in fuel cells or water oxidation in water electrolyzers, could provi  
attractive alternative to locally produce this chemical on demand  
efficiency of these processes depends greatly on the choice of the  
various catalysts with different properties.

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/](http://www.cares.cam.ac.uk/publications/)

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