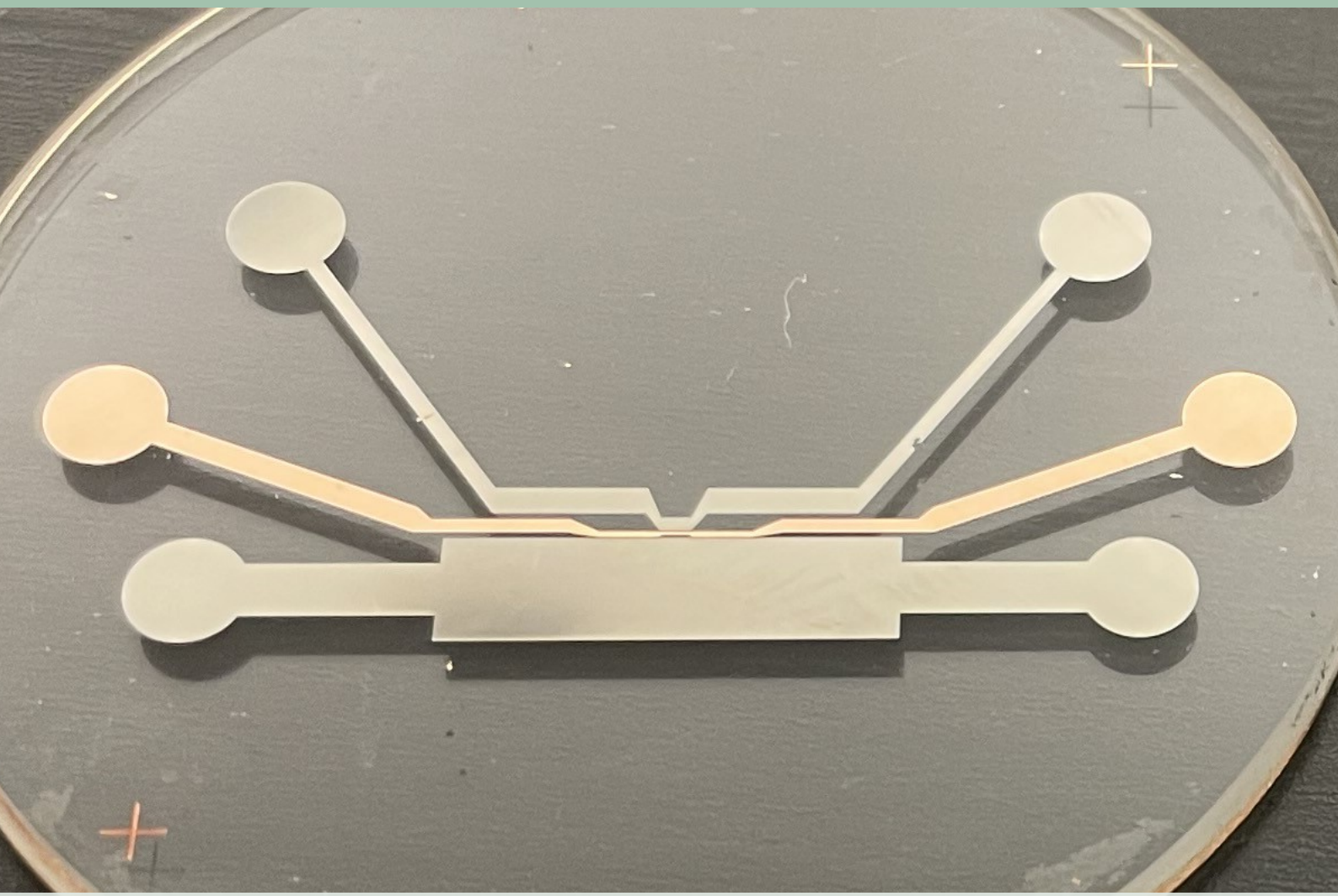
CAMBRIDGE **CARES**

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



Biannual Research Report

October 2020 - March 2021

CAMBRIDGE
CARES

CAMBRIDGE CENTRE
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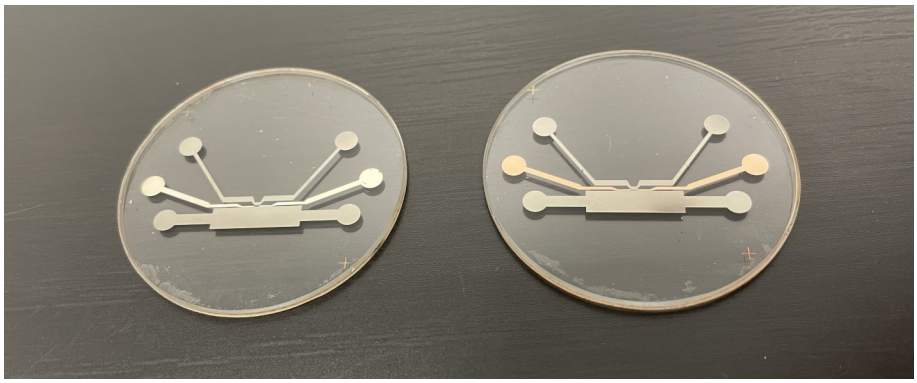

Glass wafers (diameter of 5 cm) coated with silver (left) and copper (right) working microelectrodes, platinum reference electrodes and platinum counter electrodes.

Image by Dr DAI Chencheng, (Research Fellow, IRP 2). *See more on page 39.*

Note on the photographs in this report: Many of the photographs of CARES researchers were taken prior to the pandemic and therefore show researchers unmasked. CARES researchers currently comply fully with local guidance for safe working, including mask wearing.

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

enquiries@cares.cam.ac.uk
www.cares.cam.ac.uk

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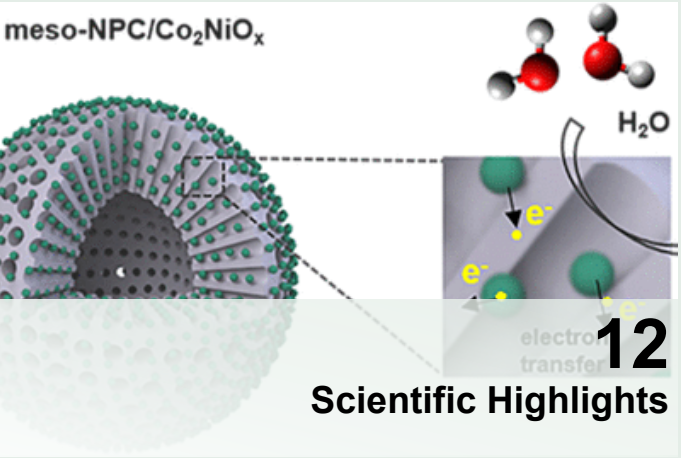

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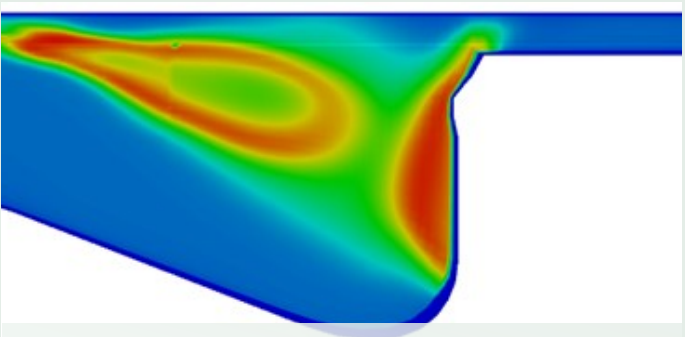

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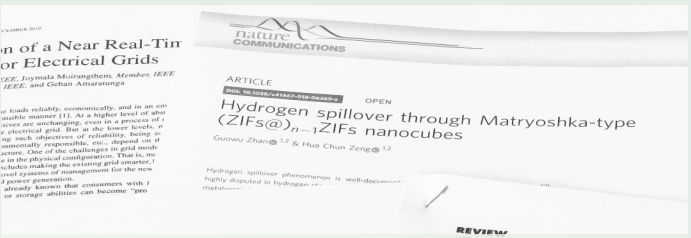

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FOREWORD

I am very pleased to present the 14th Biannual Research Report of the Cambridge Centre for Advanced Research and Education in Singapore (Cambridge CARES). Over the last few months, our office and labs have gradually opened up and the majority of our researchers and staff are now able to work as they did prior to the pandemic. While travel restrictions continue to have an impact on hiring, work is progressing well for our existing projects and several more have commenced since the last report. Two of our smaller projects—"Rapid Industrialization of Next Generation Nanomaterials" (supported by the SMART Innovation Centre) and "An Intelligent Platform for Efficient Energy Management in an Eco-Industrial Park" (a collaboration with E2S2, supported by an Intra-CREATE seed grant) have now been completed.

CLIC

The *Centre for Lifelong Learning and Individualised Cognition* (CLIC) programme commenced in October. We celebrated with an official launch event in February and were honoured to have Prof. Stephen Toope (Vice-Chancellor, University of Cambridge) and Prof. Subra Suresh (President, NTU) give opening speeches, along with several other dignitaries. CLIC is off to a good start and you can read their research update on page 87.

CREATE COLLABORATIONS

Our newest Intra-CREATE project, *Consumer Energy Usage Data in Smart City Development* (CEUS), started in October and has already made good progress. CEUS is hosted by CARES and aims to develop a data-driven platform that allows consumers to analyse their energy usage information and make better-informed decisions. The research update is on page 116.

CARES has also joined the third research phase of the Cooling Singapore programme, which is hosted by the Singapore-ETH Centre and started late last year.

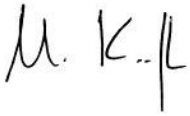
INDUSTRY COLLABORATIONS

The last few months have also brought about new collaborations with industry. CARES now has three projects with the Pharma Innovation Programme Singapore, along with several new and existing industry-funded PhD projects under the Cambridge-CARES Studentship Scheme.

CAMBRIDGE ALTERNATIVE FINANCE COLLABORATION NETWORK

CARES is now the proud host of the Cambridge Alternative Finance Collaboration Network (CAFCN) in the Asia-Pacific region. This initiative was set up by the University of Cambridge Judge Business School and aims to help local policy makers, regulators and industry navigate the digital transformation of global financial systems. I am glad that CARES can be involved in this work and I am looking forward to seeing how it progresses.

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
March 2021

ABOUT US

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

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

The first programme administered by CARES is the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T). The C4T programme is a world-leading partnership between Cambridge and Singapore, set up to tackle the environmentally relevant and complex problem of assessing and reducing the carbon footprint of the integrated petro-chemical plants on Singapore's Jurong Island. It brings together researchers from chemical engineering, biotechnology, chemistry, biochemistry, information engineering, electrical engineering, materials science and metallurgy.

The motivation for the C4T project is to integrate materials design and selection (i.e. for adsorbents and catalysts) with advances in process design to achieve improved selectivity and conversion. Such improvements will provide a reduced carbon footprint and energy demand for both established and new processes. Lowering the cost of CO_2 capture, and technologies and strategies for waste heat utilisation are also underlying drivers in the research. Our six collaborative Interdisciplinary Research Programmes (IRPs) combine state-of-the-art experimental analysis with advanced modelling research from Cambridge and Singapore. Whilst each IRP has clearly defined milestones and deliverables, denoted as work packages (WPs), there is significant interaction between the IRPs.

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

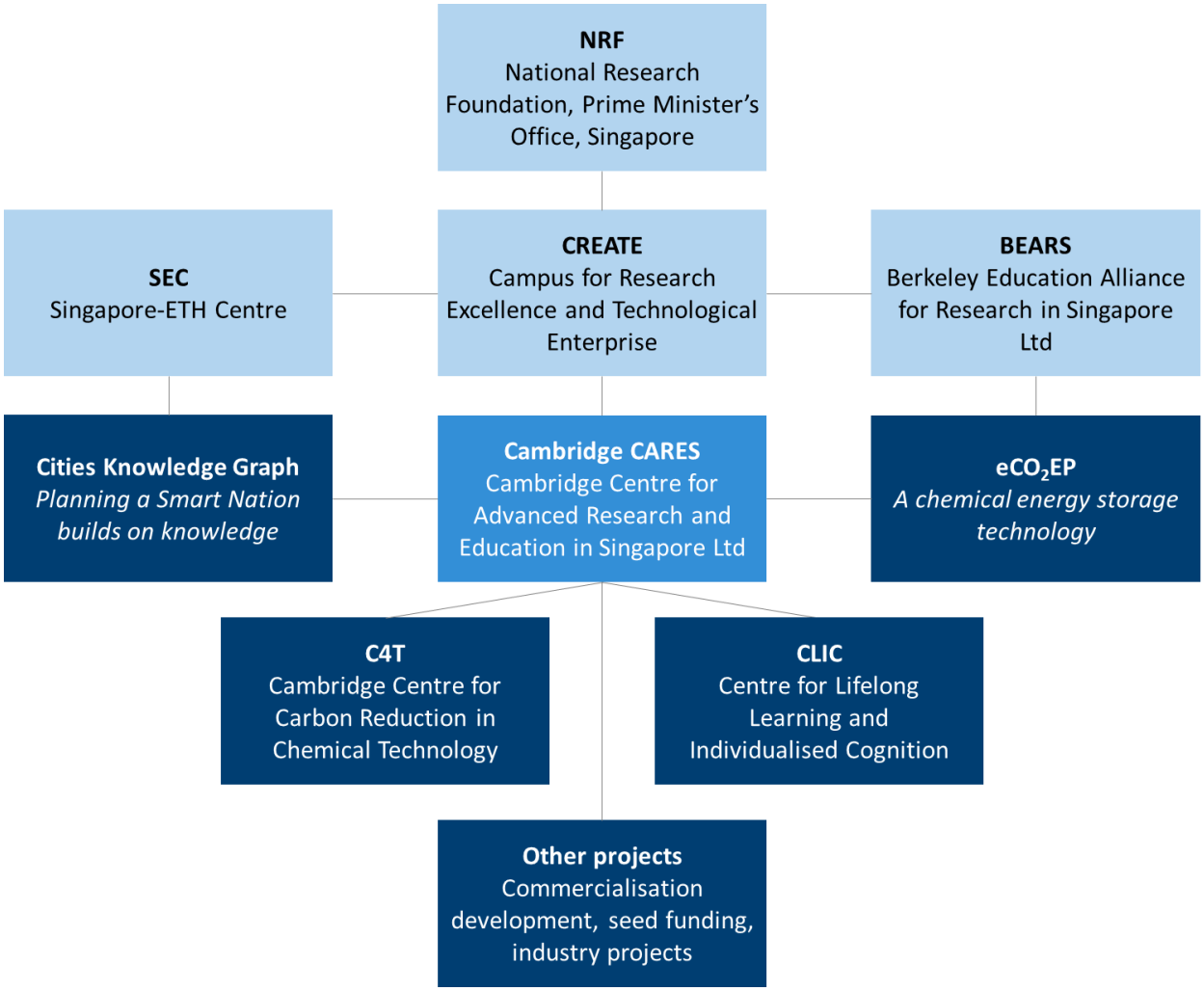
A second large CREATE-funded programme, the Centre for Lifelong Learning and Individualised Cognition (CLIC), began in October 2020. CLIC is a collaboration between University of Cambridge and NTU and focuses on the neuroscience of learning, a new research area for CARES.

CO_2EP, our first large Intra-CREATE grant, is a three-year programme that brings together researchers from the University of Cambridge, the University of California, Berkeley, the National University of Singapore and Nanyang Technological University to develop ways of transforming carbon dioxide emitted as part of the industrial process into compounds that are useful in the chemical industry supply chain. CO_2EP will come to an end in June 2021.

In April 2020, CARES was 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 and spin-offs ongoing. There is one seed-funded, CARES-hosted Intra-CREATE project between University of Cambridge and Nanyang Technological University, and three further projects that involve industry commercial funding. CARES is also now hosting the Asia-Pacific headquarters of the Cambridge Alternative Finance Collaboration Network. 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.



HIGHLIGHTS

OUTSTANDING WORK FROM THE LAST SIX MONTHS OF CAMBRIDGE CARES RESEARCH

FOCUS ON
COMMERCIALISATION

CARES Commercialisation Talks: sharing advice and experience for research commercialisation

Dr Nicholas JOSE, Research Associate

The beginning of 2020 was a moment of optimism for many researchers at CARES. A few of us had quite successful outcomes from our work, and were interested in developing them into commercial ventures. However, the Covid-19 pandemic thrust all of these ambitions into a pit of uncertainty. During the circuit breaker in July 2020, Dr Guo Zhen (Research Fellow at CARES) sent me a brief email asking if we could have a Zoom call about commercialisation. On this call, we reconnected and shared our experiences on the challenges of creating business during the pandemic. We quickly realised that more of these discussions would be extremely helpful – thus, we formed the CARES Commercialisation Talks.

For the first talk we focused on learning about the most common questions CARES members had about commercialisation. Questions ranged from "where do we find funding?" to "how can we partner with industry?" We then had a short intro in what "value" is in a commercial sense, and how to convey this through the "value proposition."

Dr Mikhail Kovalev (Senior Research Fellow, CARES) then talked about his experiences in industry, from A*STAR to Samsung. A major gap in research priorities between university-level research and industrial activities was examined.

Dr Jan Smíšek, Senior Control Engineer at Transcelestial Technologies, spoke with us about some specific differences in work style between academia and startups. The "minimum-viable-product" was introduced as a way to achieve continuous feedback throughout R&D.

Our CARES Director, Professor Markus Kraft, then gave us a wide picture view of his commercialisation journeys, from his time at Kaiserslautern to now. It was an important story of how researchers can choose a variety of paths for commercialisation, filled with valuable tips for research-based entrepreneurs.

May Chen, General Manager of BillionMiles, then spoke with us about how to expand a startup in Singapore through the various funding opportunities available from the government. She gave a detailed overview on what specific concerns we

Dr Nicholas Jose is a Research Associate at the Department of Chemical Engineering and Biotechnology in Cambridge and affiliated with IRP 1. He earned his PhD in Chemical Engineering from the University of Cambridge in 2019. His work focuses on the development of scalable methods for synthesis of high performance nanomaterials.

Nicholas is now based in Cambridge, working for CARES and running his start-up company, Accelerated Materials Ltd. This is an engineering consultancy spin-off of IRP 1 and aims to optimise production of materials at the kilogram scale for commercial applications in antimicrobials, energy storage and catalysis, using machine learning, high-throughput characterisation and novel microreactor technology.

need to address when seeking these funds from an operational point of view.

Dr Magda Barecka, Research Fellow at CARES, gave a highly relevant presentation on the "art and pain of proposals." From her previous experiences in the grant application process, Magda walked people through how to meet the expectations of reviewers by establishing relationships with funding agencies and other PIs.

Dr Massimo Alberti, CEO of Revivo Biosystems, then gave a very inspiring talk on his experiences of starting a company "from scratch" with A*STAR in Singapore. In his words, "It's not a sprint, but an iron man race."

At the end of our series in 2020, Dr Zhen Guo, CARES Research Fellow and founder of Chemical Data Intelligence Ltd (CDI), gave us a roadmap for how to create a business plan, and the important notion of "harvesting" value. After summarising the previous talks, we then explored the next suggestions that CARES members had, which revolved around the Singaporean ecosystem, intellectual property, and inviting other entities in CREATE to join.

These talks weren't just educational, they provided a huge boost to our morale in the midst of the pandemic. Although everything was online, we had found a way to connect on common problems that were extremely specific to our research and position in Singapore. Most importantly, the community we made strengthened the bonds of CARES members, and made our return to the offices and labs even more enjoyable. The second round of talks began in March 2021 and is going strong with fortnightly talks from more CARES members and entrepreneurs.

A screenshot from Dr Jan Smíšek's talk.

FOCUS ON

IMPACT

Feasible pathways to a carbon neutral future

Dr Magda BARECKA, Research Fellow, eCO_2EP

Reduction of carbon dioxide (CO_2) emissions is one of the most urgent and challenging problems of the 21st century. The ambitious goals set by the Intergovernmental Panel on Climate Change (IPCC) have urged many economies to undertake massive investments into the reduction of these emissions. Some emissions-intensive sectors that are fully dependent on the petrochemical feedstocks focus currently on CO_2 emissions reduction by means of underground storage of CO_2. While carbon capture and storage is technically feasible and deployable on large scale, would that be enough to reduce the global carbon footprint of our industries and enable a transition to a carbon neutral future?

Let's have a closer a look at the case of chemical industry and firstly investigate where CO_2 emissions come from. Chemical manufacturing is currently responsible for approximately 15% of CO_2 industrial emissions and massive amounts are generated by unselective conversion of petrochemical feedstocks into chemical products, and also from burning these feedstocks to deliver the thermal energy to run manufacturing processes.

Singapore's Jurong Island.

Could we stop using these chemical products? Current economies are entirely dependent on fossil-fuel derivated chemical products that have penetrated all markets and are indispensable for healthcare, food industries and other sectors. Consequently, this dependence precludes the rapid substitution of the fossil-fuel derived chemicals, so related CO_2 emissions are, at present, inevitable. Capturing CO_2 and storing it underground solves one part of this problem, but does not minimise the extraction of feedstocks required for chemical manufacturing. This is both an environmental concern and a long-term challenge, as the petrochemical feedstocks are non-renewable and will run out one day.

To solve the source of the CO_2 emissions problem, we need to learn to produce from other feedstocks than petrochemical, ideally from the CO_2 which keeps on accumulating in the atmosphere. As running any manufacturing process requires an energy input, using renewable power is a sustainable choice. In this context, electrolysis processes that use electric, green energy power the conversion of CO_2 to useful chemical products are one of the most promising alternative production routes. The main obstacles towards large-scale deployment of electrolysis are related to process economics. Obviously, these new processes are not operating as optimally as their petrochemical equivalents that have been investigated over hundreds of years and use existing facilities and supply chains.

To overcome this limitation, we envision the use of electrolysis as an add-on to the existing chemical production processes to minimise their carbon footprint. In this way, CO_2 emissions could be converted back to a useful chemical at their source (chemical plants). This approach reduces both the emissions of CO_2 and the use of petrochemical feedstocks. By exploring the synergies between the established bulk chemical production processes and CO_2 conversion reactors, we significantly limit the investment and operational costs, making this new technology attractive for the industry. In our recent paper, we present chemical manufactures that can be the early adopters of the electrolysis technology and lead the transformation into a carbon neutral future.

For more information: The paper related to this research, "Economically viable CO_2 electroreduction embedded within ethylene oxide manufacturing" (DOI: 10.1039/D0EE03310C) is published in *Energy & Environmental Science*.

Dr Magda H. Barecka is a chemical engineer interested in process intensification, retrofitting and design. She earned her PhD from TU Dortmund University (Germany) and Lodz University of Technology (Poland) as a joint Diploma.

Magda's current work focuses on the application of novel intensified operations in the field of carbon dioxide conversion. In the eCO_2EP project she is working on electrochemical CO_2 reduction system integration and scale-up, techno-economic analysis and mini-plant optimisation.

Highlighted research outputs from October 2020 - March 2021

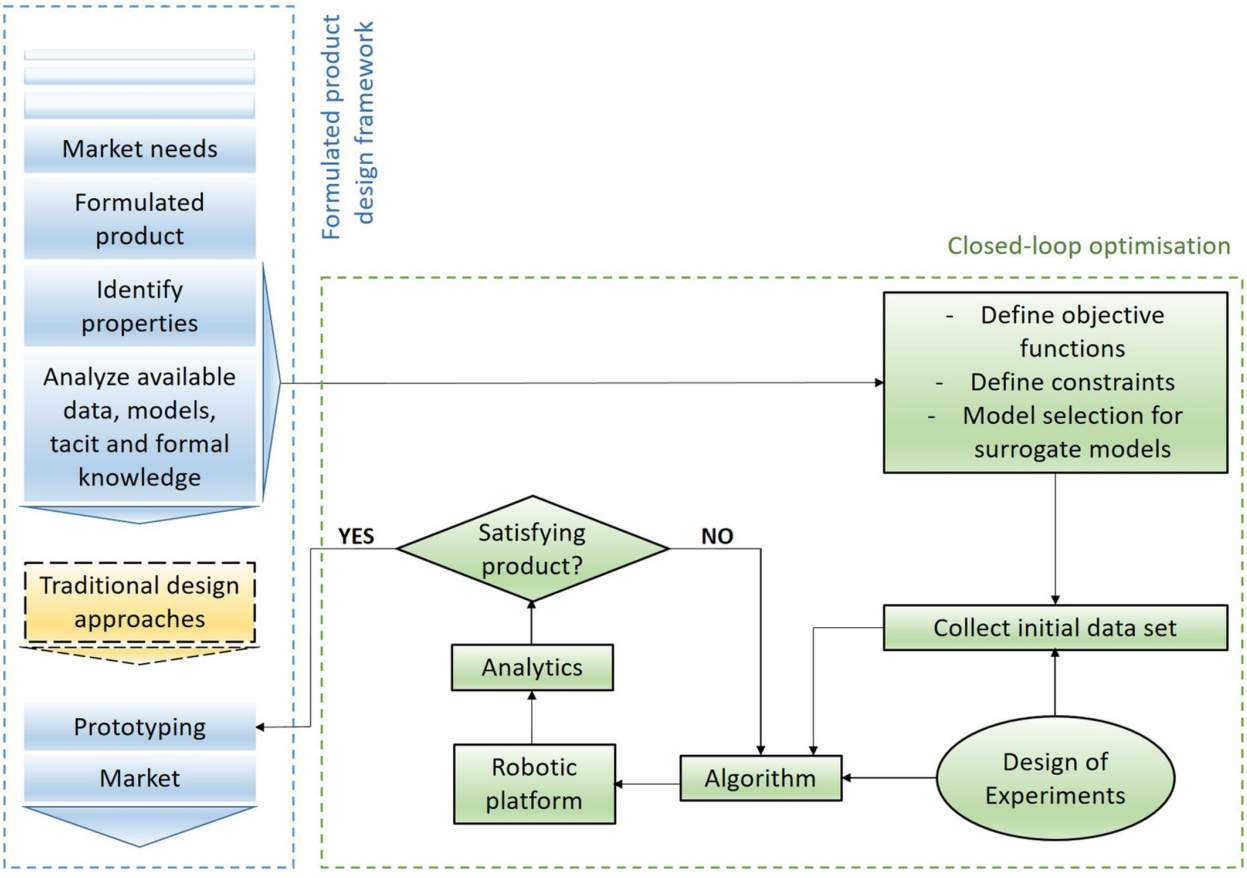
A selection of the top publications from across our programmes.

C4T IRP 1: Automated robotic platforms in design and development of formulations

Liwei Cao, Danilo Russo and Alexei A. Lapkin, *AIChE Journal*

DOI: 10.1002/aic.17248

Abstract: Product design for formulations is an active and challenging area of research. The new challenges of a fast-paced market, products of increasing complexity, and practical translation of sustainability paradigms require to re-examine the existing theoretical frameworks to include the advantages deriving from the new reality of digitalization of business and research. In this work, we review the existing approaches, clearly stating the role of automation and machine-learning-guided optimization in the broader framework. Moving from this, we review the state of the art of automated hardware and software for formulated product design, and identify the open challenges for future research. Perspectives are given on the emerging fields of automated discovery, scale-up, and multistage optimization, and a unitary picture of the existing connections is provided, in the general context of a completely digital R&D workflow.



Integration of closed-loop robotic platform in the general framework for formulated products design.

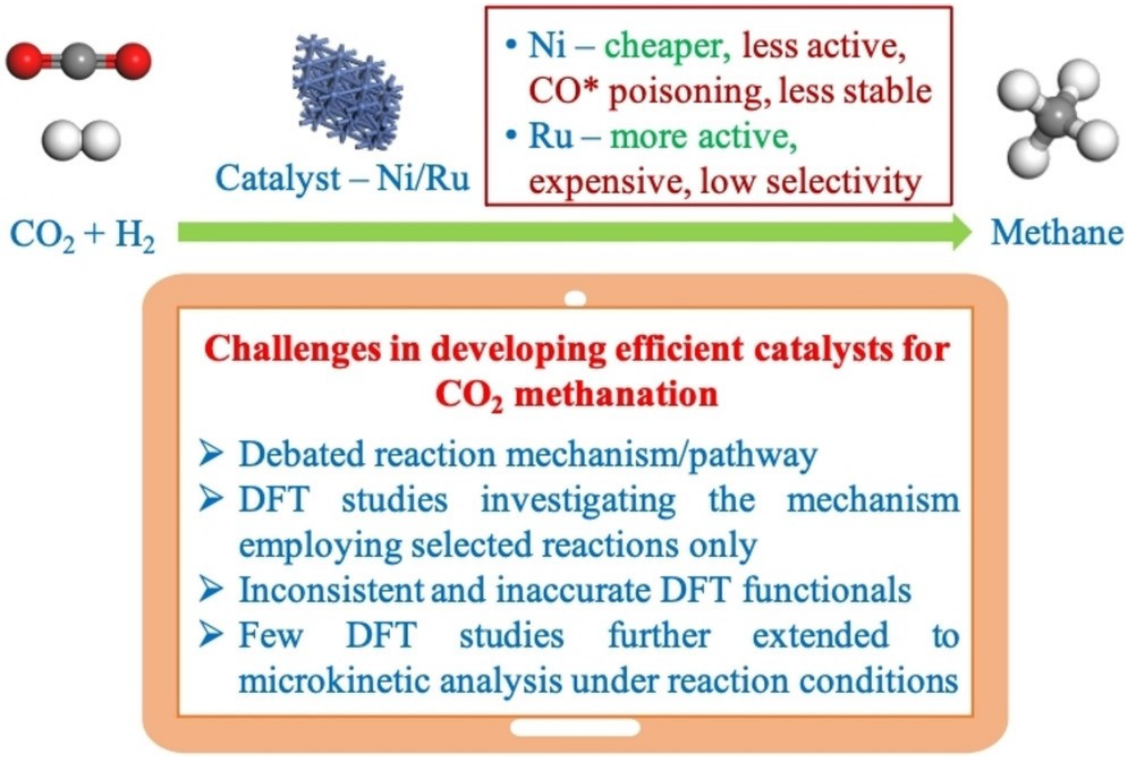
(Figure adapted from Zhang L, Mao H, Liu Q, Gani R. Chemical product design – recent advances and perspectives. Curr Opin Chem Eng. *2020;***27**:22-34.*)*

C4T IRP 1: Investigating CO_2 methanation on Ni and Ru: DFT assisted microkinetic analysis

Ojus Mohan, Shambhawi Shambhawi, Rong Xu, Alexei A. Lapkin and Samir H. Mushrif, *ChemCatChem*

DOI: 10.1002/cctc.202100073

Abstract: A multiscale analysis combining density functional theory (DFT) and microkinetic modeling is performed to resolve the uncertainties in CO_2 methanation reaction mechanism and kinetics on popular Ni and Ru catalysts. The most debated issues are the activation routes of CO_2 and CO (hydrogenation or direct dissociation) and whether the reaction proceeds with or without forming a CO* intermediate. We investigated a comprehensive reaction network of 46 elementary reactions, involving multiple CO_2, CO activation routes and side reactions using a benchmarked DFT functional. Our study shows that the dominant pathway at 550 K and 10 atm includes direct dissociation of CO_2* to CO* on both Ni and Ru surfaces. On Ru, CO* undergoes hydrogenation to form COH* that further dissociates to C*, whereas on Ni, HCO* is formed that gives CH* upon dissociation. The rate determining steps on Ni and Ru are HCO* dissociation to CH* and O* and CH_3* hydrogenation to CH_4, respectively. We further find that selectivity of the reaction on Ni is higher than that on Ru, whereas activity of Ru is higher.



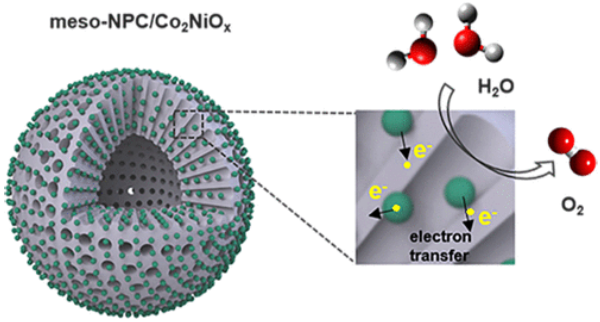
Major challenges in developing more active, stable and selective catalysts for the CO_2 methanation reaction.

C4T IRP 1: Hybrid OER electrocatalyst combining mesoporous hollow spheres of N, P-doped carbon with ultrafine Co_2NiO_x

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

DOI: 10.1021/acsami.0c12305

Abstract: A heterostructure combining mesoporous hollow spheres of N, P-doped carbon (meso-NPC) with ultrafine Co_2NiO_x nanoparticles has been synthesized as a highly active electrocatalyst, named meso-NPC/Co_2NiO_x. The meso-NPC hollow spheres were first fabricated via a novel nanocasting method using mesoporous SiO_2 as the "mold" and the atomic ratio of P in the meso-NPC can be tuned by controlling the amount of one of the filling organics, etidronic acid. Because of the large surface area and abundant surface hydroxyls, the meso-NPC formed strong bonding with the Co_2NiO_x nanoparticles (<2 nm in size) loaded on it. Serving as an OER electrocatalyst, the heterogeneous meso-NPC/Co_2NiO_x shows great working enhancement compared to its single-component counterparts. Through further mechanism study by X-ray photoelectron spectroscopy, a strong effect of electron transfer is found from the Co_2NiO_x to the meso-NPC, which leads to increases in the oxidation state of transition metals (TMs). Most importantly, we also reveal that the increase in the amount of the P dopant in the meso-NPC/Co_2NiO_x system can efficiently facilitate this metal-to-support charge transfer, which also implies that the biphasic interaction between the Co_2NiO_x nanoparticles and the meso-NPC hollow spheres generates active catalytic sites of both TM–N–C and TM–P–C surface species.

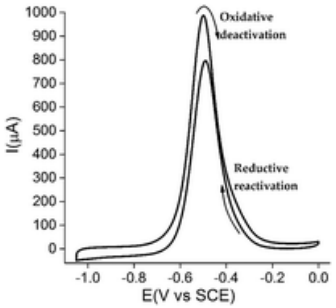


C4T IRP 2: Electrocatalytic dimeric inactivation mechanism by a porphyrinic molecular-type catalyst: integration in a glucose/O_2 fuel cell

Kamal Elouarzaki, Vishvak Kannan, Yian Wang, Adrian C. Fisher and Jong Min Lee, *Catalysis Science & Technology*

DOI: 10.1039/D0CY02443K

We report a chemical inactivation/redox reactivation process (IAP) based on the surface-confined rhodium–porphyrinic catalyst on a multi-walled carbon nanotube surface which presents an excellent and stable electron transfer. We used a chronoamperometric method with mathematical models and digital simulation to investigate the IAP at the catalytic metallic site. We present a mechanistic analysis of the non-catalytic and catalytic responses exhibited by this complex enabling a deep understanding of the thermodynamic and kinetic parameters that govern the IAP. These studies support a mechanism for glucose 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 us to integrate this molecular nanomaterial in a fully molecular fuel cell together with phthalocyanine cobalt at the cathode. The resulting fuel cell reaches 0.3 mW cm^{-2} with a possible regeneration of initial performance.

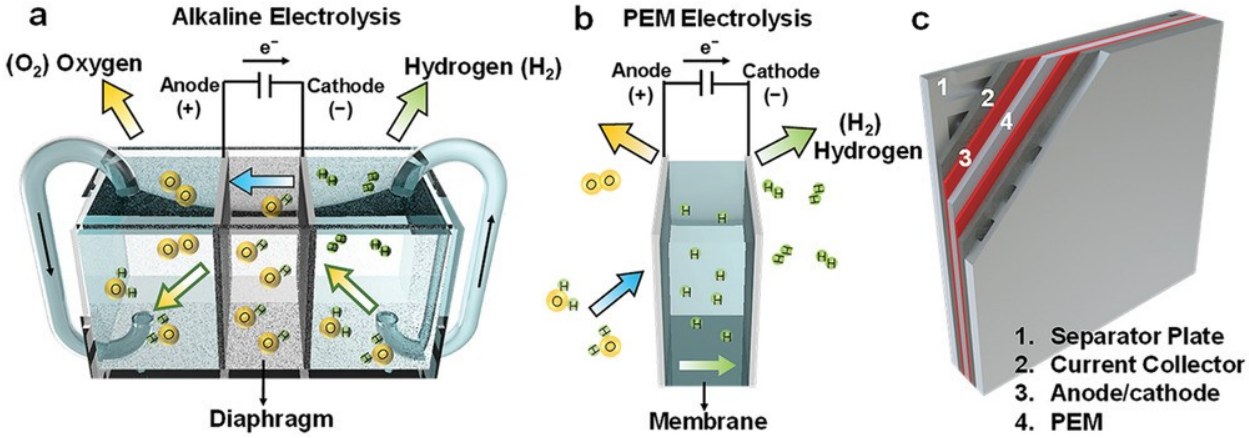


C4T IRP 2 and eCO$_2$EP : Recent development of oxygen evolution electrocatalysts in acidic environment

Li An, Chao Wei, Min Lu, Hanwen Liu, Yubo Chen, Günther G. Scherer, Adrian C. Fisher, Pinxian Xi, Zhichuan J. Xu and Chun-Hua Yan, *Advanced Materials*

DOI: 10.1002/adma.202006328

Abstract: The proton exchange membrane (PEM) water electrolysis is one of the most promising hydrogen production techniques. The oxygen evolution reaction (OER) occurring at the anode dominates the overall efficiency. Developing active and robust electrocatalysts for OER in acid is a longstanding challenge for PEM water electrolyzers. Most catalysts show unsatisfied stability under strong acidic and oxidative conditions. Such a stability challenge also leads to difficulties for a better understanding of mechanisms. This review aims to provide the current progress on understanding of OER mechanisms in acid, analyze the promising strategies to enhance both activity and stability, and summarize the state-of-the-art catalysts for OER in acid. First, the prevailing OER mechanisms are reviewed to establish the physicochemical structure–activity relationships for guiding the design of highly efficient OER electrocatalysts in acid with stable performance. The reported approaches to improve the activity, from macroview to microview, are then discussed. To analyze the problem of instability, the key factors affecting catalyst stability are summarized and the surface reconstruction is discussed. Various noble-metal-based OER catalysts and the current progress of non-noble-metal -based catalysts are reviewed. Finally, the challenges and perspectives for the development of active and robust OER catalysts in acid are discussed.



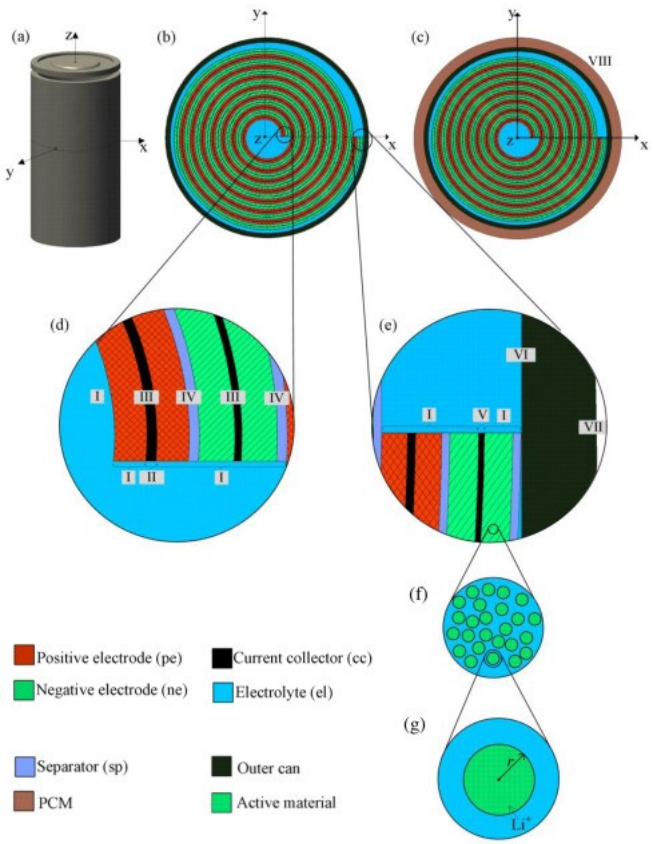
Schematic of the operating principle of the (a) Alkaline water electrolyzer, and b) PEM water electrolyzer. c) Component overview for a typical PEM water electrolyzer.

C4T IRP 2: Monte Carlo assisted sensitivity analysis of a Li-ion battery with a phase change material

Vishvak Kannan, Adrian C. Fisher and Erik Birgersson, *Journal of Energy Storage*

DOI: 10.1016/j.est.2021.102269

Abstract: Safety of Li ion batteries is as important, if not more, as its performance because its usage in contemporary transport applications can otherwise lead to catastrophic scenarios. Owing to the exothermic reactions and complex heat transfer within the Li ion batteries, they are prone to overheating and possible thermal runaway in the absence of adequate thermal management systems. Therefore, to ensure a safe operation it is key to evaluate the uncertainties with respect to a thermal management system along with the uncertainties in the intricate multiphysical phenomena within the system. To achieve this, we conduct Monte Carlo simulations followed by sensitivity analysis to correlate the variability of 14 different factors with the safety of an 18650 Sony cell with a phase change material (PCM) at stressed conditions. These varied factors correspond to the properties of the 18650 battery and the PCM. From the PCM properties, we identify the temperature at which the PCM starts melting to have most influence on the safety of the battery. In addition, we also estimate the probability of the sub -optimal unsafe scenarios occurring by examining the distribution of the maximum temperature within the battery. Finally, we obtain reduced surrogate models with an accuracy of 92% through supervised machine learning algorithms.



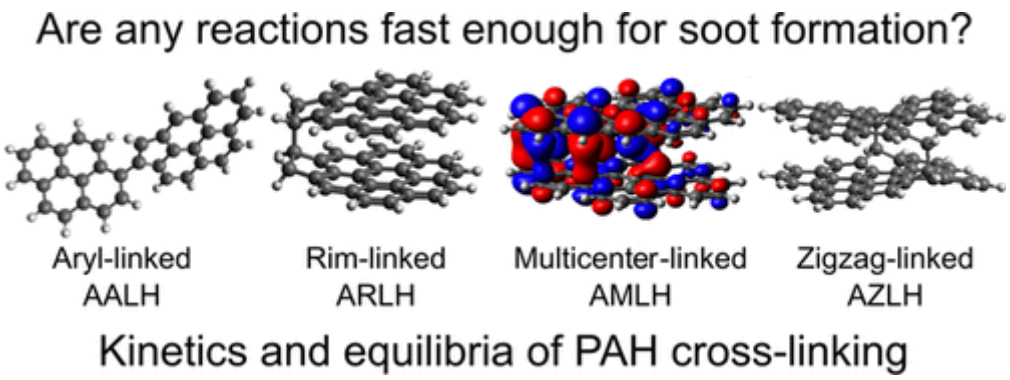
An illustration of (a) The 18650 Li ion battery, (b) 2D cross-section of the 18650 battery without PCM, (c) 2D cross-section of the battery with a PCM layer, (d) Various functional layers in the jelly roll, (e) Outer end of the jelly roll spiral, (f) Agglomerate structure in the negative electrode (a similar structure is considered in the positive electrode as well), and (g) Diffusion of lithium into the active material in the electrodes. The Roman numerals indicate the interfaces between the respective functional layers.

C4T IRP 3: Reactivity of polycyclic aromatic hydrocarbon soot precursors: kinetics and equilibria

Angiras Menon, Jacob W. Martin, Jethro Akroyd and Markus Kraft, *The Journal of Physical Chemistry A*

DOI: 10.1021/acs.jpca.0c07811

Abstract: The thermodynamics and kinetics of cross-linking reactions between PAHs of various reactive edge types that are observed in soot precursors are explored using density functional theory. The forward rate constants confirm that reactions involving aryl σ-radicals are faster than others, but rate constants for reactions between aryl σ-radicals and localized π-radicals can be as large or even larger than for two aryl σ-radicals. However, rates for all cross-linking reactions between small PAHs are likely too slow to explain soot formation. The equilibrium constants show that reactions involving σ and π-radical PAHs are the most favorable at flame temperatures. Equilibrium constants for larger PAHs show that the ability to form bonded-and-stacked structures results in enhanced equilibrium constants for the reaction of two large localized π-radicals compared to those for other edge types. This suggests that combined physical and chemical interactions between larger π-radical PAHs could be important in flame environments.



C4T IRP 3: Flame synthesized blue TiO_{2-x} with tunable oxygen vacancies from surface to grain boundary to bulk

Shuyang Wu, Manoel Y. Manuputty, Yuan Sheng, Haojing Wang, Yong Yan, Markus Kraft and Rong Xu, *Small Methods*

DOI: 10.1002/smtd.202000928

Abstract: Fabrication of nonstoichiometric metal oxides containing oxygen vacancies (OVs) has been an effective strategy to modulate their (photo)catalytic or (photo)electrochemical performances which are all affected by charge transfer at the interface and in the bulk. Considerable efforts are still needed to achieve tunability of OVs, as well as their quantitative characterization. Herein, a one-step flame synthesis method is reported for the first time for fast fabrication of blue TiO_{2-x} with controllable defect content and location. Temperature-programmed oxidation (TPO) analysis is applied for the first time and found to be an excellent technique in both differentiating and quantifying OVs at the surface, grain boundary (GB), and bulk of TiO_{2-x}. The results indicate that a moderate level of OVs can greatly enhance the charge transfer. Importantly, the OVs locked at GBs due to the thermal sintering of nanoparticles during the synthesis can facilitate the anchoring and reduction of Pt species.

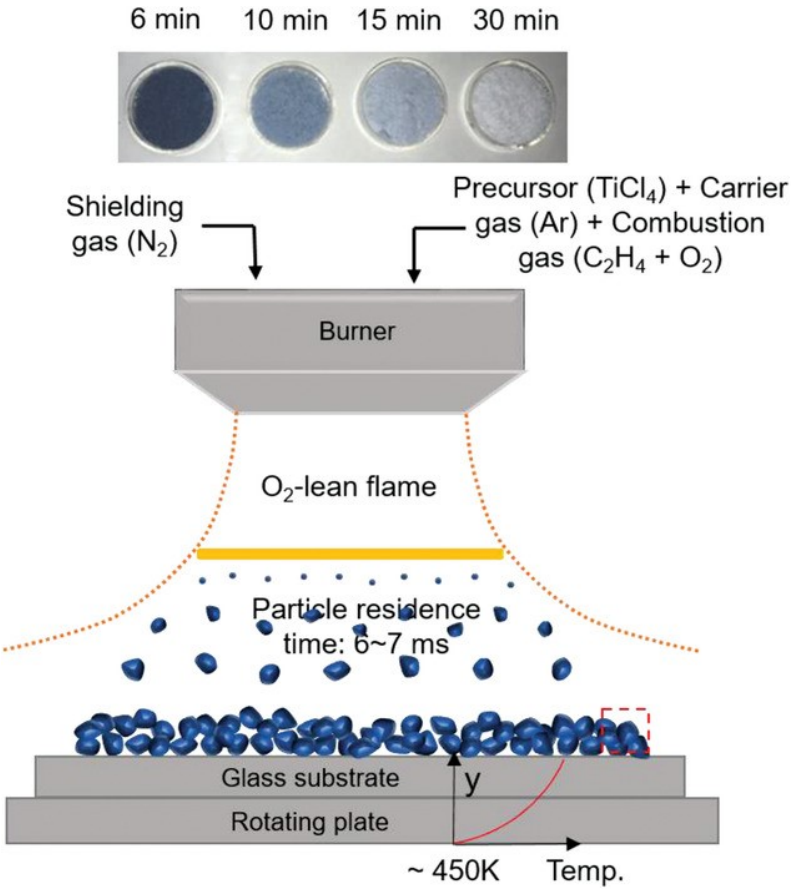


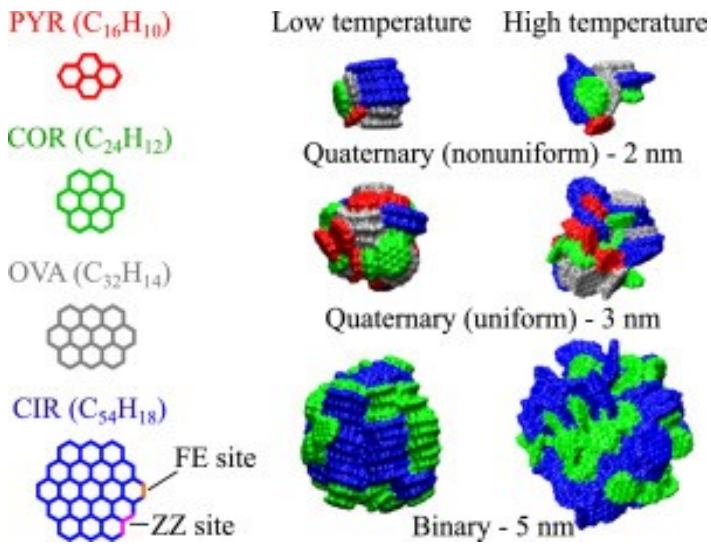
Illustration of FSRS synthesis process of TiO_{2-x} and photo images of samples obtained at various deposition times.

C4T IRP 3: Surface properties of heterogeneous polycyclic aromatic hydrocarbon clusters

Kimberly Bowal, Laura Pascazio, Hongyu Wang, Dongping Chen and Markus Kraft, *Proceedings of the Combustion Institute*

DOI: 10.1016/j.proci.2020.06.123

Abstract: In this paper we investigate the impact of molecular inhomogeneity on the surface properties of soot particles. Using replica exchange molecular dynamics and solvent-excluded surface analysis, we evaluate detailed surface properties directly from particles containing polycyclic aromatic hydrocarbon molecules of different sizes. The temperature-dependent behaviour of surface roughness and number densities of reactive sites are evaluated for particles from 1–5 nm in diameter. The percentage of carbon atoms and zig-zag sites on the particle surface are found to be independent of molecular composition, while molecule heterogeneity influences the accessible hydrogen atoms and free-edge sites. These relationships allow the prediction of surface composition for a given particle diameter. The surface densities of carbon and hydrogen atoms are explained by the morphological changes and molecule size contributions for solid-like and liquid-like configurations. Small molecules contribute significantly to the particle surface properties at low temperatures, regardless of the proportion of molecule sizes, which results in an increased density of accessible carbon atoms for heterogeneous particles. Interestingly, the surface density of edge carbon atoms and free-edge sites can be predicted from the average molecule size alone. The density of hydrogen atoms on the surface follows the average expected values from the constituent molecule sizes, suggesting that for particles containing many different molecule sizes the α parameter corresponding to the HACA mechanism converges to a linear temperature-dependent trend. This quantitative evaluation of the accessibility of reactive sites for heterogeneous particles provides important information for understanding soot particle growth and oxidation.

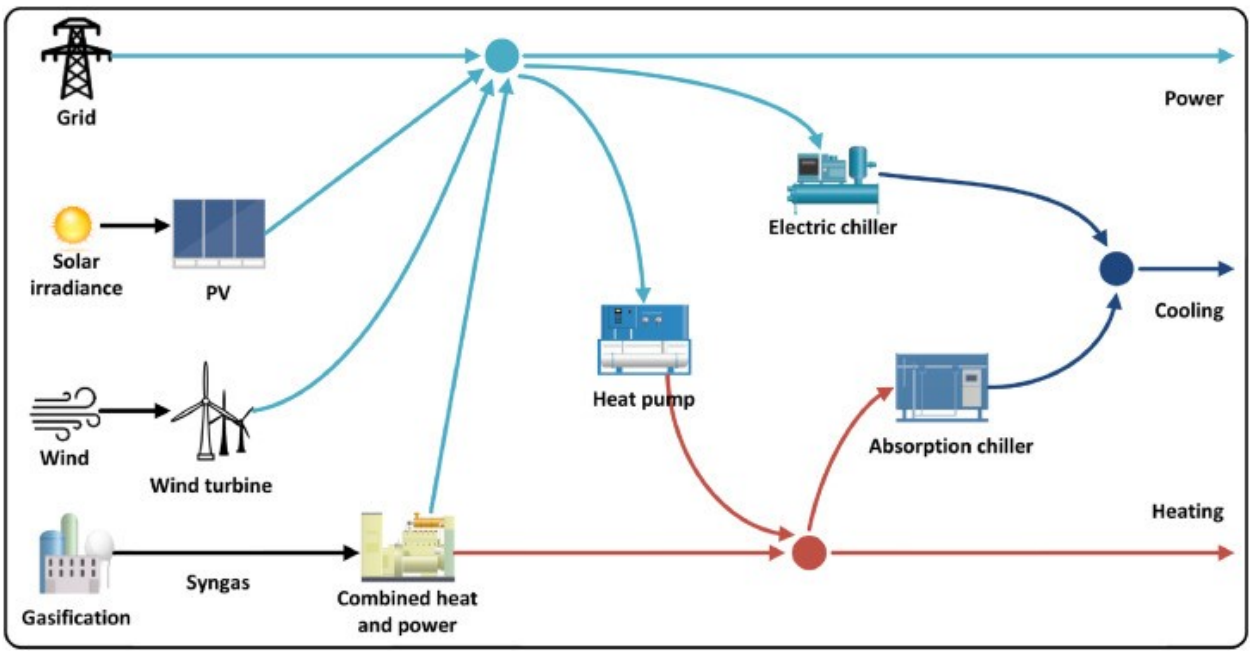


Pyrene (red), coronene (green), ovalene (grey), and circumcoronene (blue) molecules are considered in this work. Example free-edge and zig-zag sites are highlighted. Snapshots of representative heterogeneous particles are shown at low and high temperatures (solid-like and liquid-like configurations, respectively).

C4T IRP JPS: Game theory-based renewable multi-energy system design and subsidy strategy optimization

Zuming Liu, Shukun Wang, Mei Qi Lim, Markus Kraft and Xiaonan Wang, *Advances in Applied Energy*
DOI: 10.1016/j.adapen.2021.100024

Abstract: Renewable multi-energy systems have become a promising solution for deep decarbonization. However, government subsidy is needed to incentivize the deployment of renewable technologies for emission reduction. Here, we provide a game theory-based modeling framework along with tailored solution strategy for optimizing multi-energy system design and renewable subsidy strategies. We apply our modeling framework to four pilot towns in China for studying how government and consumers interact with each other to achieve their respective goals with minimum costs. We show that government subsidy policies can effectively promote renewable penetration or reduce carbon emissions, and photovoltaic panels and wind turbines absorb most of government subsidy in renewable penetration and emission cap cases, respectively. We also analyze in detail the optimal energy technology operations for meeting targets of government and pilot towns. We find that only increasing renewable penetration cannot achieve deep decarbonization; however, directly imposing carbon emission cap causes heavy government financial burden. Hence, we recommend an economic two-phase decarbonization pathway, namely first increasing renewable penetration to reduce dependence on fossil energy and then imposing a carbon emission cap to fulfill deep decarbonization. Our two-phase decarbonization pathway can be applied to other cities in China and worldwide, aiming to promote renewable energy penetration, reduce reliance on fossil fuels, and finally realize carbon neutral cities. Our proposed game theory-based modeling framework can also be extended to various temporal and spatial scales for studying how different entities can cooperate together for deep decarbonization.



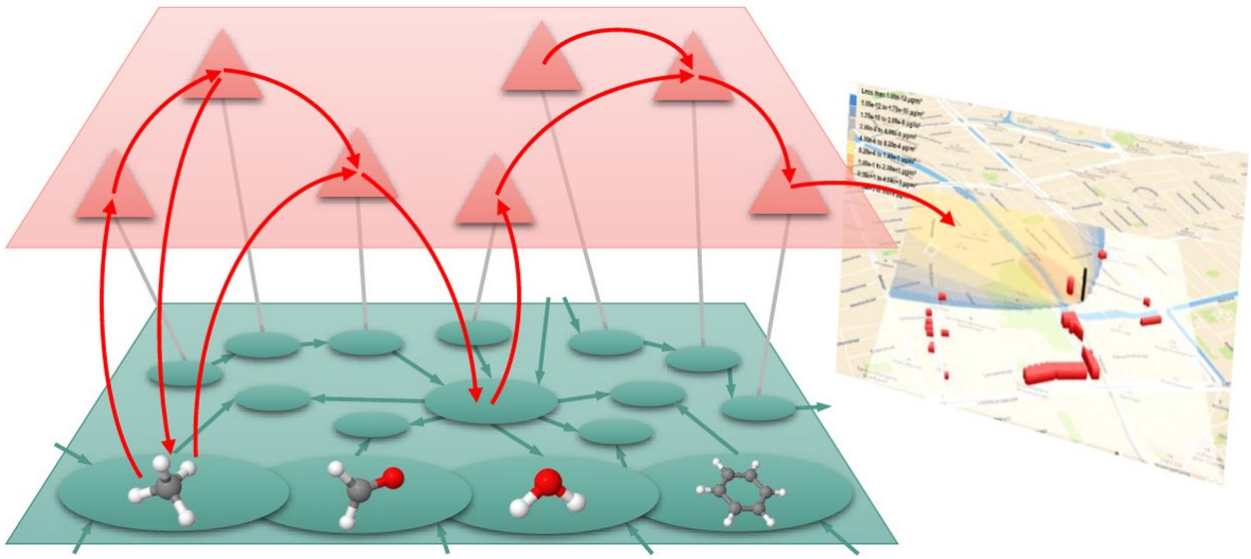
Schematic representation of a renewable multi-energy system. The solid circles indicate power, heating, and cooling distribution centres.

C4T IRP JPS: Multiscale cross-domain thermochemical knowledge-graph

Sebastian Mosbach, Angiras Menon, Feroz Farazi, Nenad Krdzavac, Xiaochi Zhou, Jethro Akroyd and Markus Kraft, *Journal of Chemical Information and Modelling*

DOI: 10.1021/acs.jcim.0c01145

Abstract: In this paper, we develop a set of software agents which improve a knowledge-graph containing thermodynamic data of chemical species by means of quantum chemical calculations and error-canceling balanced reactions. The knowledge-graph represents species-associated information by making use of the principles of linked data, as employed in the Semantic Web, where concepts correspond to vertices and relationships between the concepts correspond to edges of the graph. We implement this representation by means of ontologies, which formalize the definition of concepts and their relationships, as a critical step to achieve interoperability between heterogeneous data formats and software. The agents, which conduct quantum chemical calculations and derive the estimates of standard enthalpies of formation, update the knowledge-graph with newly obtained results, improving data values, and adding nodes and connections between them. A key distinguishing feature of our approach is that it extends an existing, general-purpose knowledge-graph, called J-Park Simulator (http://theworldavatar.com), and its ecosystem of autonomous agents, thus enabling seamless cross-domain applications in wider contexts. To this end, we demonstrate how quantum calculations can directly affect the atmospheric dispersion of pollutants in an industrial emission use-case.



eCO$_2$EP: Economically viable CO$_2$ electroreduction embedded within ethylene oxide manufacturing

Magda H. Barecka, Joel W. Ager and Alexei A. Lapkin, *Energy & Environmental Science*

DOI: 10.1039/D0EE03310C

Abstract: Electrochemical conversion of CO_2 (CO2R) into fuels and chemicals can both reduce CO_2 emissions and allow for clean manufacturing in the scenario of significant expansion of renewable power generation. However, large-scale process deployment is currently limited by unfavourable process economics resulting from significant up- and down-stream costs for obtaining pure CO_2, separation of reaction products and increased logistical effort. We have discovered a method for economically viable recycling of waste CO_2 that addresses these challenges. Our approach is based on integration of a CO2R unit into an existing manufacturing process: ethylene oxide (EO) production, which emits CO_2 as a by-product. The standard EO process separates waste CO_2 from the gas stream, hence the substrate for electroreduction is available at an EO plant at no additional cost. CO_2 can be converted into an ethylene-rich stream and recycled on-site back to the EO reactor, which uses ethylene as a raw material, and also the anode product (oxygen) can be simultaneously valorized for the EO production reaction. If powered by a renewable electricity source, the process will significantly (*ca.* 80%) reduce the CO_2 emissions of an EO manufacturing plant. A sensitivity analysis shows that the recycling approach can be economically viable in the short term and that its payback time could be as low as 1–2 years in the regions with higher carbon taxes and/or with access to low-cost electricity sources.

Proposed pathway for CO_2 recycling (R4) within EO manufacture (R1)–(R3).

IRP 1

SUSTAINABLE REACTION ENGINEERING FOR CARBON NEUTRAL INDUSTRY

IRP 1 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.

IRP 1 Principal Investigators:

Professor Alexei LAPKIN
University of Cambridge

Asst Professor Paul LIU Wen
Nanyang Technological University

Professor ZENG Hua Chun
National University of Singapore

OVERVIEW

Phase 2 of IRP 1 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.

IRP 1 is currently building up towards a more concerted effort to resolve some of the key challenges in C1 activation (selectivity and stability), as well as proposing new concepts for utilisation of alternative feedstocks, targeting both new chemistry and new process concepts. Over the last period a large number of new research directions were initiated in these topics, and the complete IRP 1 team is working towards creating a large synergistic internal project in the remaining period of C4T Phase 2.

Professor Alexei Lapkin, PI
University of Cambridge

Update on work package 1.1

Design of nano-structured catalysts

Due to the growing concerns of global warming, converting CO_2 to value added products has attracted enormous research interest. Although there are many promising achievements for converting CO_2 to C_1 products such as methanol and methane, the direct production of C_{2+} hydrocarbons has remained a great challenge.

In this report, **LI Bowen (Research Engineer, NUS)** and **Prof. ZENG Hua Chun (PI, NUS)** have thoroughly tested the previously prepared hZ5-CuZn and hZ5-CuZb@Pt catalysts for direct CO_2 hydrogenation to light hydrocarbons. The hZ5-CuZn sample consists of a hollow hexagonal shape ZSM-5 shell with both micro-/meso-porosity and embedded CuZn metals in the form of phyllosilicates. The hZ5-CuZn@Pt sample has additional Pt nanoparticles deposited on the exterior surfaces of the hollow ZSM-5 support. Both catalysts were evaluated over the temperature range of 240 to 400 °C at 30 bar. The CO_2 hydrogenation performances were given in Figure 1.1. Despite having CO and CH_4 as main products, C_2-C_4 hydrocarbons have been produced in significant amounts. However, methanol has been detected for hZ5-CuZn sample (Figure 1.1a), especially in lower temperatures, while there is no methanol detected in the exhaust for hZ5-CuZn@Pt sample (Figure 1.1b).

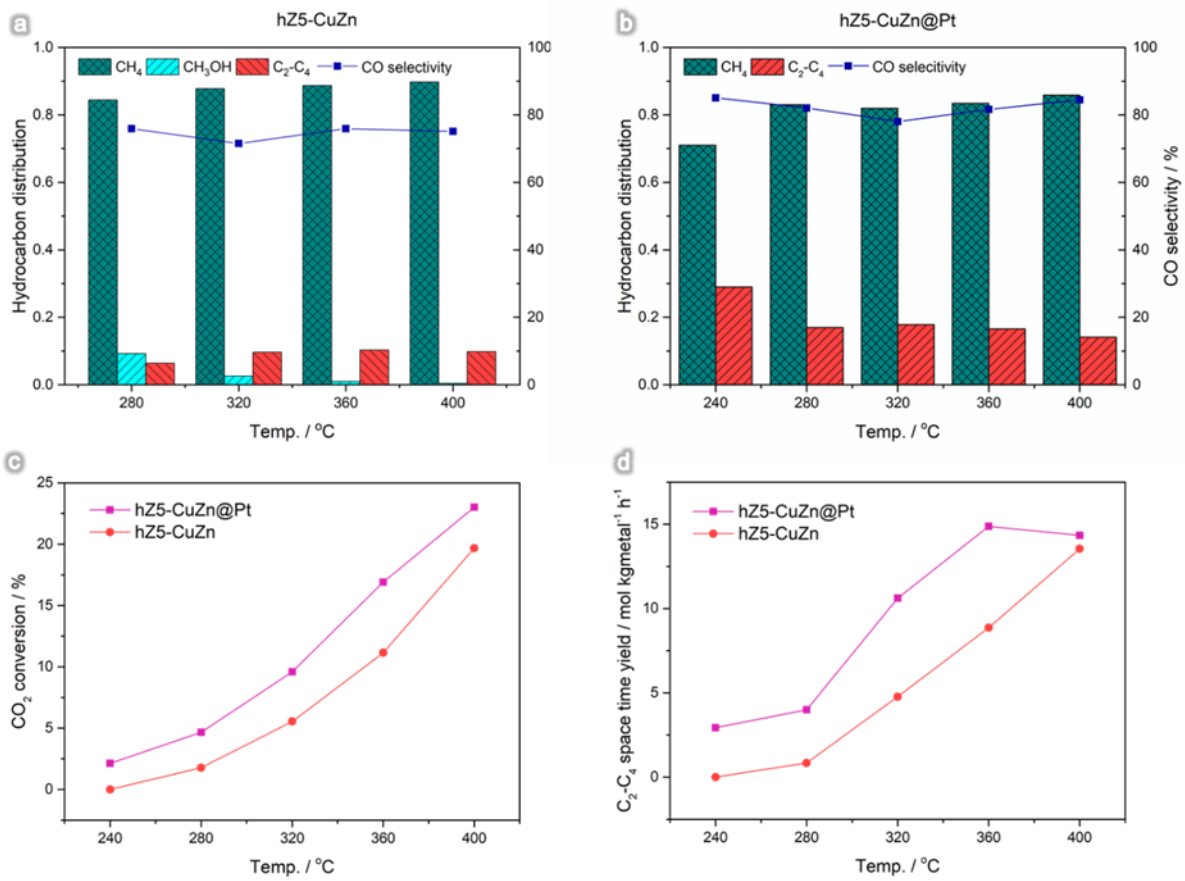


Figure 1.1: Comparison of hZ5-CuZn and hZ5-CuZn@Pt for direct CO_2 hydrogenation to light hydrocarbons. (a) CO selectivity and hydrocarbon distribution when hZ5-CuZn was used as a catalyst; (b) CO selectivity and hydrocarbon distribution when hZ5-CuZn@Pt was used as a catalyst; (c) comparison of CO_2 conversion between hZ5-CuZn and hZ5-CuZn@Pt; and (d) comparison of C_2-C_4 specific yield between hZ5-CuZn and hZ5-CuZn@Pt. Reaction conditions: 200 mg of catalyst in a stainless-steel fixed bed reactor, 50 mL/min of a mixed gas (N_2:CO_2:H_2 =15:85:255) feed was used and the catalyst was evaluated at 30 bar from 240 to 400 °C in 40 °C steps.

The introduction of Pt NPs onto the exterior surfaces has increased the yield of C_2-C_4 hydrocarbons, noting that the anchorage of Pt on the external surfaces of hZ5-CuZn (i.e., hZ5-CuZn@Pt) has also led to a slight increase in CO selectivity.

The specific space-time yield of C_2-C_4 was measured to be 14.9 mol/(kg_{metal} ·h) for hZ5-CuZn@Pt at 360 °C, which is comparable to the values reported in literature. A temperature dependent conversion of CO_2 is observed while the selectivity of C_2-C_4 hydrocarbons decreases slightly as temperature goes up. Accounting for these two factors, the maximum C_2-C_4 yield was reached at 360 °C for hZ5-CuZn@Pt sample. For the hZ5-CuZn, product yield increases at increasing temperature, in accordance with decreased methanol selectivity.

In our experiment, the residual methanol detected with the hZ5-CuZn sample suggests the existence of a methanol mediated pathway in which CO_2 was first hydrogenated to methanol by embedded CuZn and the methanol to hydrocarbon reaction was then catalysed by the ZSM-5 shell as the products diffuse out of the hollow ZSM-5 crystal. Acknowledging the complexity of CO_2 hydrogenation reactions, we believe it is inadequate to propose a defined reaction pathway leading to the observed product distribution at this point in time. Herein, instead, we can view the versatility of compositional and structural controls for our catalyst devices as a future research opportunity. We recognise the catalyst composition and structural architecture are far from ideal for production of light hydrocarbons and extensive computational resources are further required (i.e., algorithms able to optimise catalyst composition and structure based on reaction pathways and intermediates) in design and synthesis of novel catalysts with multicomponents for complex reaction systems.

For the above two catalysts (hZ5-CuZn and hZ5-CuZn@Pt), C_{5+} hydrocarbons produced were either in a negligible amount or not detected by online gas chromatography even though literature has shown ZSM-5 can convert methanol to C_{5+} products. Such a product selectivity can be attributed to the effect of this unique ZSM-5 shell structure in cooperation with loaded active metal NPs. This observation also supports the conversion pathway of methanol to hydrocarbon within the hollow ZSM-5 support (*viz*, hZ5-CuZn@Pt catalyst could be viewed as nanoscale reactors), because the microporous structure of hollow ZSM-5 shells can restrict the growth of long chain hydrocarbons.

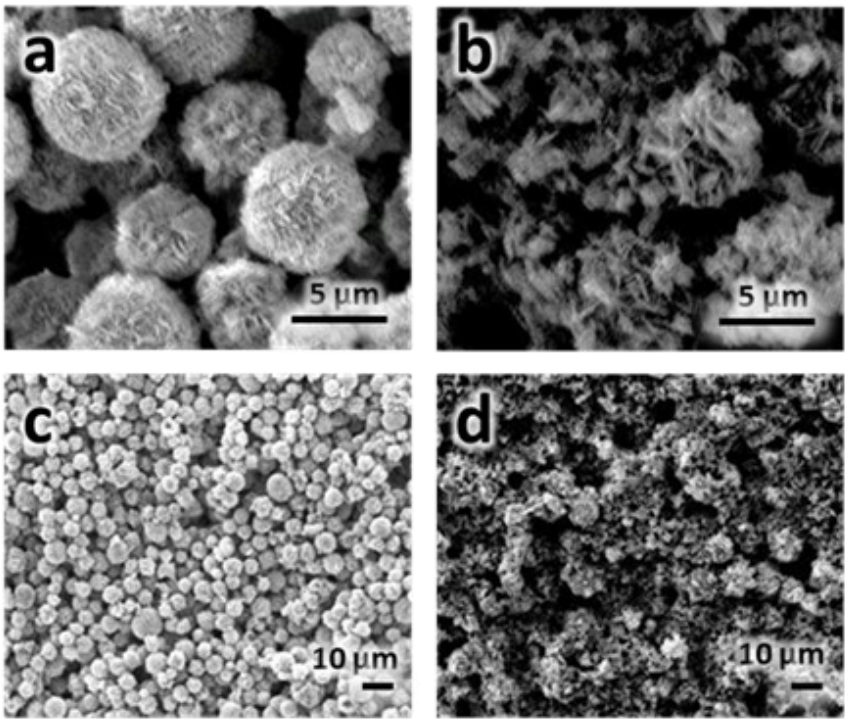


Figure 1.2: (a) SEM image of ZnAl-LDH rounded microspheres with tightly packed nanosheets,

(b) SEM image of ZnAl-LDH flower-like sphere with open nanosheet petals,

(c) SEM image of ZnAl-LDH nanospheres at low magnification, and

(d) SEM image of ZnAl-LDH nanoflowers at low magnification.

LI Bowen

Alvin LIM Ming Hao (in-kind PhD student, NUS) and **Prof. ZENG Hua Chun** have first synthesised similar sized rounded ZnAl-LDH with some form of morphology variation through a facile and low-cost hydrothermal synthesis. As with creation of monodisperse nanocatalysts, we have explored the upper bound and lower bound of synthetic parameters before the morphology becomes random in size and shape. In this way, we can consistently produce rounded spherical catalysts, ranging from tightly packed nanosheets (Figure 1.2a) to flower-like shaped assemblages with open nanosheet petals (Figure 1.2b).

Using this material, ZnAl-LDH is then calcined into ZnAl-LDO (LDO = calcined LDH), which forms our catalyst support. Copper (Cu), as the active catalyst, is then introduced via wet impregnation and calcination, creating a ZnAl-LDO/CuO material with around 6 wt% Cu. The catalyst is then reduced *in situ* and a CO_2 hydrogenation experiment is performed. Preliminary experimental results have shown some difference in catalytic performance in terms of conversion, selectivity and specific space time yield (Figure 1.2e). In summary, we intend to explore the catalyst morphology to improve on performance on key objectives.

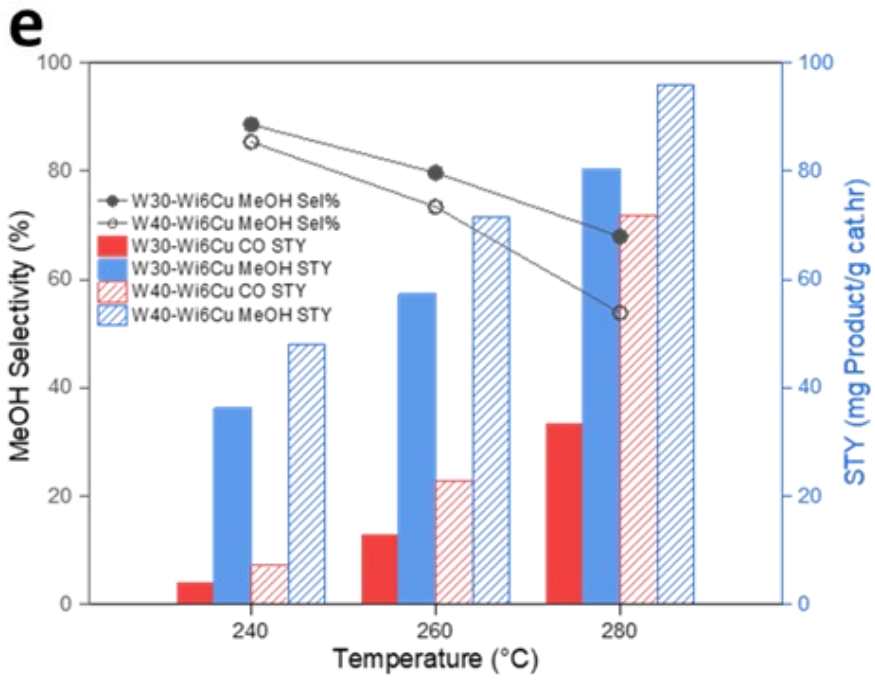


Figure 1.2: (e) Preliminary experimental results – MeOH selectivity and product STY (space-time-yield).

Alvin LIM Ming Hao

Update on work package 1.2

Novel reactions and functional molecules

Guided by Prof. Alexei LAPKIN (PI, CAM), **Dr GUO Zhen (Research Fellow, CARES)** has been engaged in three research projects: 1) development of new heuristic for chemical route searching based on molecular similarity; 2) work with PhD candidate Adarsh ARUN (CAM) on impurity predictions; 3) collaborating with PhD candidate Jana WEBER (CAM) on a paper regarding the role of digital chemistry in sustainable reaction routes. The first project was identified from a joint project in collaboration with Assoc. Prof. YAN Ning (Co-I, NUS). During the searching of reaction routes, we found that heuristics to measure the reliability of a reaction were highly desired for the automatic screening, due to the missing yields for many reactions. Therefore, a similarity-based heuristic was developed to evaluate the consistency and usefulness of a reaction in a particular reaction route. It had been demonstrated that reaction routes selected by using this new heuristic can cover those chosen based on human judgements, as shown in Figure 1.3. This work will be summarised in a paper for peer review.

The impurity project was proposed by Dr Simon SUNG (Research Fellow, CARES) and Prof. Lapkin. Currently, reaction predictions have been extensively studied using both machine learning and data mining but prediction of possible impurities has been overlooked, although knowledge in impurities should be crucial in industry. Aiming to predict all possible impurities given a query reaction, we established a framework based on data mining together with new techniques developed recently including a reaction mapper, reaction balancing and automatic identification of function groups. Basically, analogue reactions will be gathered, followed by generation of reaction templates that can be applied to the query reaction. The advantage of this approach is, compared to machine learning methods, its explicability, i.e., all possible results can be traced back to a reaction report.

For the paper about digital chemistry, Dr Guo mainly contributed to two sections: 1) a review on prediction of yields; 2) a review on high-throughput experiments.

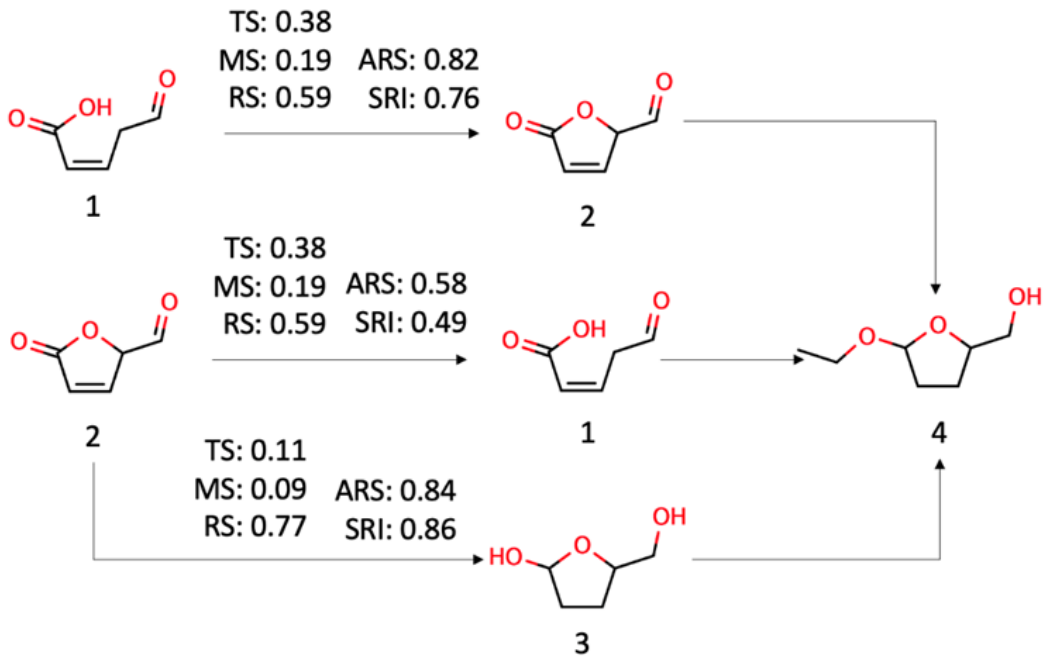


Figure 1.3: Comparison between conventional similarities (TS and MS) with new similarity-based heuristic (SRI) shows that the ranking of reactions using SRI values is more consistent to human judgements.

Dr GUO Zhen

Perman JORAYEV's (PhD student, CAM) main research focus is on transforming new discoveries into robust processes. This requires (1) prior knowledge generation to identify relevant chemical and physical parameters, and (2) using the prior knowledge to optimise the reaction. Since the last report, Mr Jorayev has completed integrating data extraction and cleaning, descriptor generation, and modelling so the entire automated workflow is now complete. The next step is to prove the accuracy and efficiency of the workflow on a case study. On the second half of the project, Mr Jorayev has tested different hardware configurations to validate optimal automated flow setup in the lab (i.e. full automation using multiple pumps vs using a single pump with a pre-mixed solution). Additionally, Mr Jorayev has carried out photon flux study using ferrioxalate actinometry to compare different light sources and quantify the energy delivered to the reaction solution. The next step in the project is to start collecting the training dataset for reaction optimisation.

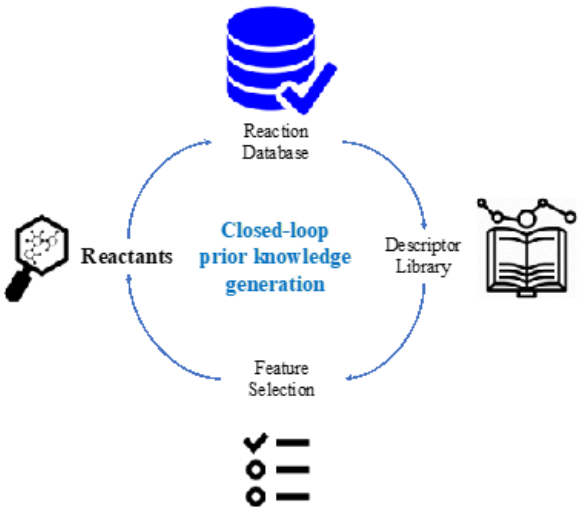


Figure 1.4: Automated prior knowledge generation to select relevant parameters for a given reaction.

Perman JORAYEV

Adarsh ARUN (PhD student, CAM) began his PhD in Chemical Engineering at the University of Cambridge in January, focusing on using reaction networks analysis in the design of circular chemical supply chains incorporating biowaste and renewable feedstocks.

He is currently working on two main projects. The first involves data mining large chemical databases such as Reaxys to predict impurities and byproducts in chemical reactions, which has the potential to aid early-stage process development. A proof-of-concept case study on impurity prediction for paracetamol synthesis has been successful, and the developed workflow is now being tested on other more complex case studies provided by the PIPS team.

The second project has been recently initiated, and involves assembling a biofeedstock or biowaste knowledge base for decision support in chemical route selection using reaction networks. This will help supplement existing research efforts in identifying sustainable pathways converting biowaste into high-value strategic and fine chemicals. Data on the regional availabilities of biowaste sources, extractable feedstock/ functionalised molecules, and pretreatment processes/technologies is being explored and gathered from wider literature. Methods such as text mining are also being investigated to automate the construction of the knowledge base.

Update on work package 1.3

Novel reactors and process technology

FAN Qianwenhao (in-kind PhD student, NTU) has been studying Co-doped $SrFeO_{3-\delta}$ perovskite materials for chemical looping air separation (CLAS). The ability of the perovskite material to release oxygen is significantly improved by doping Co to the B site. All materials with various Co substitution ratio $SrFeO_{3-\delta}$, SF; $SrFe_{0.8}Co_{0.2}O_{3-\delta}$, SFC-0.2; $SrFe_{0.5}Co_{0.5}O_{3-\delta}$, SFC-0.5; $SrFe_{0.2}Co_{0.8}O_{3-\delta}$, SFC-0.8) were synthesised using a wet chemistry method and they exhibited cubic perovskite structure (Figures 1.5a and b). The oxygen desorption properties were studied by temperature-swing experiments in TGA under different oxygen partial pressures. The N_2-TPD profile (Figure 1.5c) showed that the characteristic peak shifted to the low temperature range with increasing Co amount, indicating an enhancement in oxygen release performance. *In situ* XRD was performed to probe the evolution of the crystal structure as a function of temperature (Figure 1.6). With scan number the main peak of the perovskite phase shifted towards lower diffraction angles, indicating an increase in the unit cell parameter, which is due to the release of O_2. After cooling down to room temperature, the peak position shifted to the initial value, exhibiting thermal stability during the redox process. The same experiment, performed in air/CO_2, showed that only the position of the main perovskite peak changed as O_2 was being released, but no evidence of carbonate formation has been observed, providing evidence of applying this material in actual industrial processes. The long cycling stability of SFC oxygen sorbent was also studied at 500 °C by redox cycling in 20% O_2 and N_2 for 50 cycles (Figure 1.7). The oxygen capacity remains unchanged, and it was observed that SFC-0.5 and SFC-0.8 have higher oxygen capacity because of Co doping. In summary, after Co substitution a significant amount of oxygen vacancies were formed, enabling air separation at low temperature and producing high partial pressure of oxygen, which is necessary for a variety of chemical looping process.

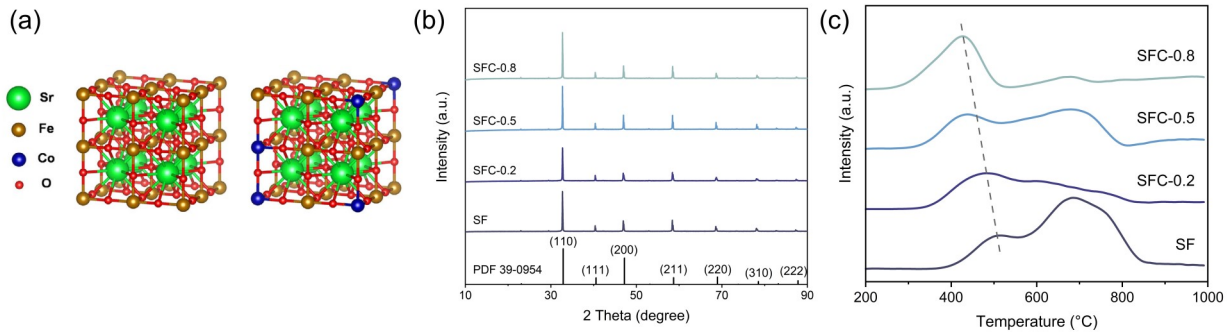


Figure 1.5: (a) Crystal structures, (b) XRD patterns, and (c) N_2-TPD profile of SF and SFC perovskites.

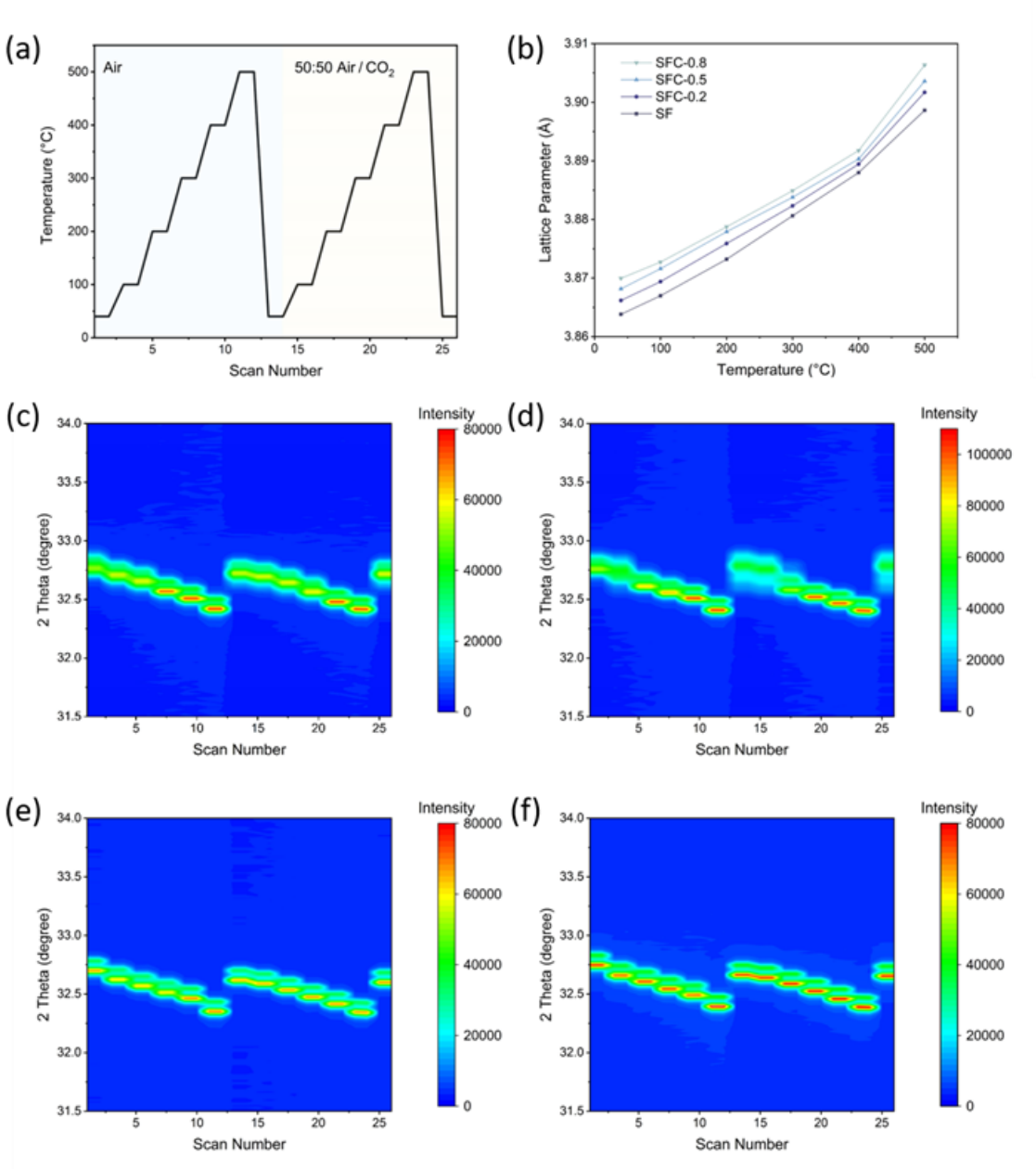


Figure 1.6: (a) In situ *XRD experimental details, (b) refined lattice parameters of SF and SFC at different temperatures, and* in situ *XRD patterns of (c) SF, (d) SFC-0.2, (e) SFC-0.5, (f) SFC-0.8 when exposed consecutively to air and 1:1 air/CO_2 at different temperatures. The scan time of one diffractogram over the 2θ range of 31-35° was ~75 s.*

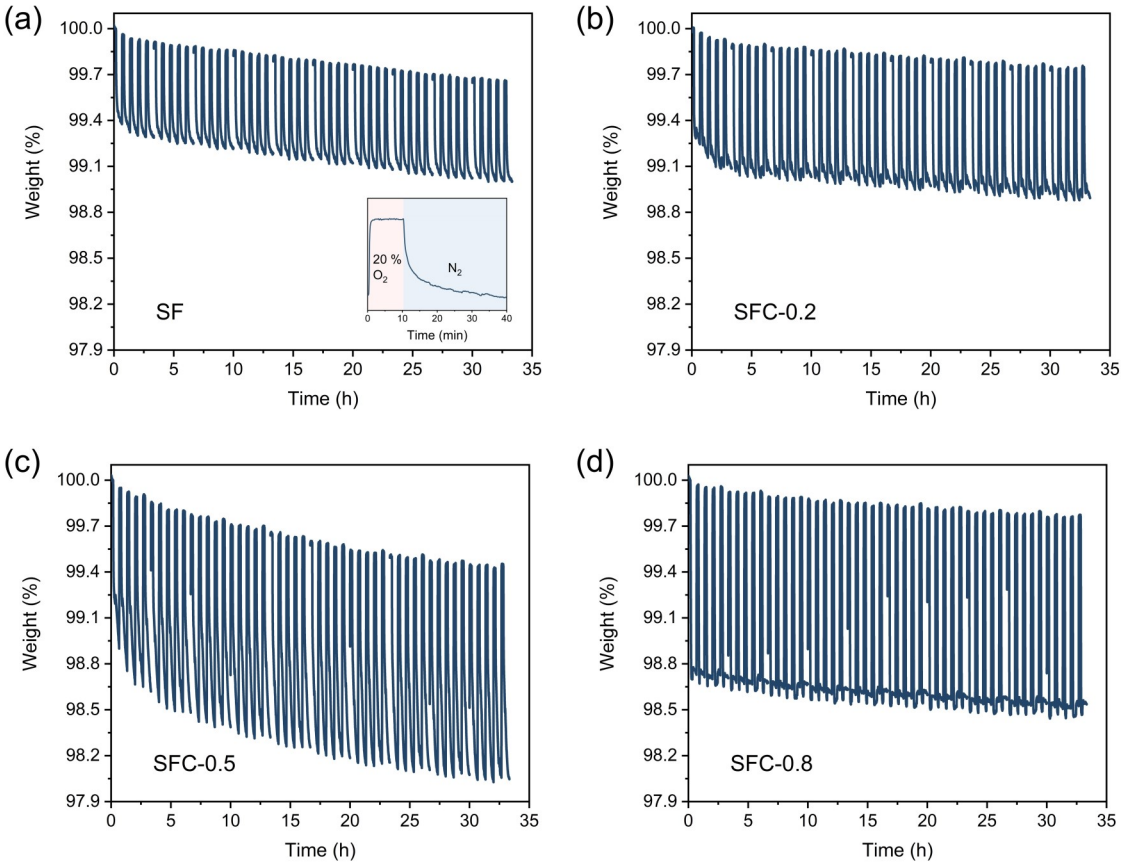
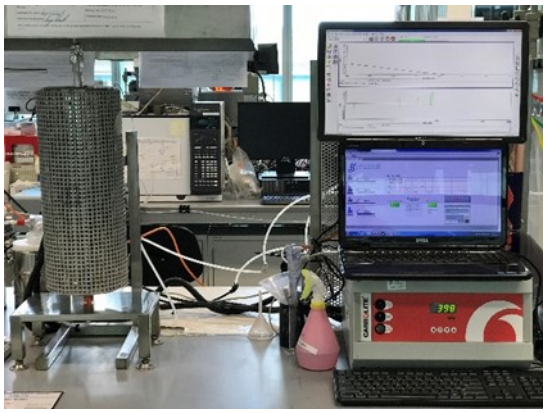


Figure 1.7: Oxygen partial pressure swing between 20% O_2 and N_2 at 500 °C for (a) SF, (b) SFC-0.2, (c) SFC-0.5, and (d) SFC-0.8.

FAN Qianwenhao

Syed SAQLINE (in-kind PhD student, NTU) has also focused on developing low-cost materials for chemical looping applications. In the previous biannual report, he had described the motivation behind using the red soil as oxygen carriers. These carriers have now been tested in a bubbling fluidised bed reactor setup (see Figure 1.8) to quantify their oxygen transfer capacity and fuel conversion.



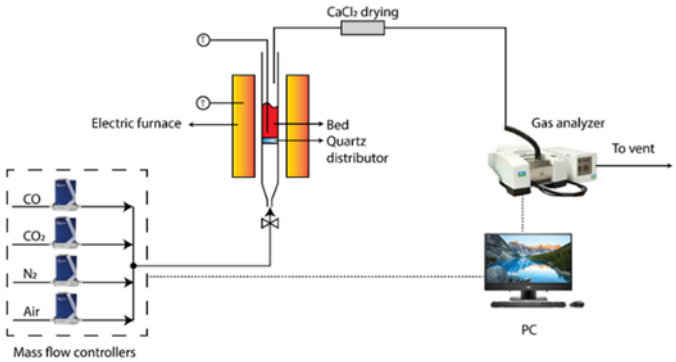


Figure 1.8: (top) Image of the setup at the IRP 1 lab, (bottom) The schematic of the CLC reactor setup.

The addition of commercial Fe_2O_3 improved chemical looping combustion (CLC) reactivity and the oxygen carrier (OC) consisting of 20 wt% Fe_2O_3 and 80 wt% red soil (20R80F) resulted in > 70% CO conversion over 100 redox cycles as well as a high amount of oxygen transfer per unit mass of OC (see Figures 1.9 and 1.10). Higher Fe_2O_3 content did not result in significant improvement. 40R60F sustained a favourable fuel conversion over 100 cycles. The performance of 100F was the best, partly owing to its higher mass density, which favours fuel conversion in a fixed volume fluidised bed.

The decline in activity of the OCs due to induced sintering caused by the temperature spike during the oxidation phase in air is evident from SEM images of the fresh and spent samples (Figures 1.11 and 1.12, on page 34). The former exhibits porous and uniform grains whereas the latter highlights the densification and sintering of particles.

Syed's plan of action for the upcoming period is to investigate the role of reducing atmosphere on the degree of reduction and oxygen carrier conversion. In addition, he also plans to use solid fuels (e.g., char and biochar) instead of gaseous fuels to explore the feasibility of using red soil in solid fuel CLC.

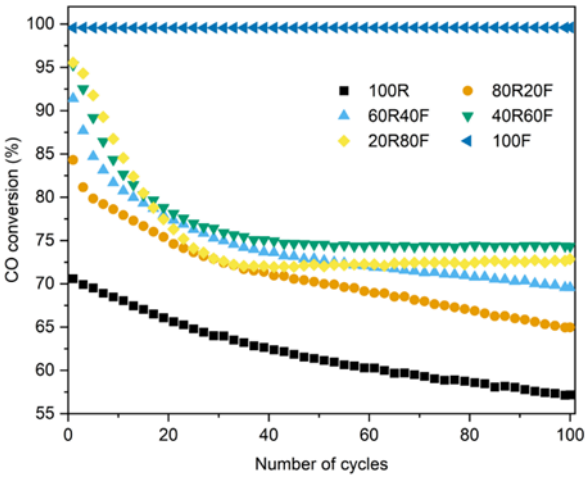


Figure 1.9: Cyclic performance of the red soil samples over 100 cycles with 10% CO as reducing gas.

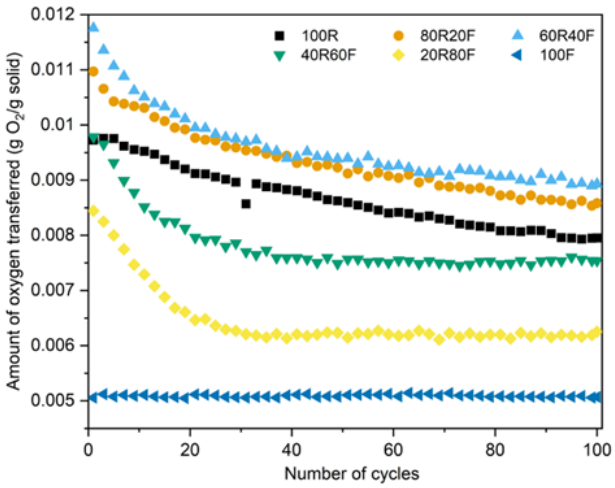


Figure 1.10: Oxygen transfer capability per gram of the prepared samples over 100 cycles.

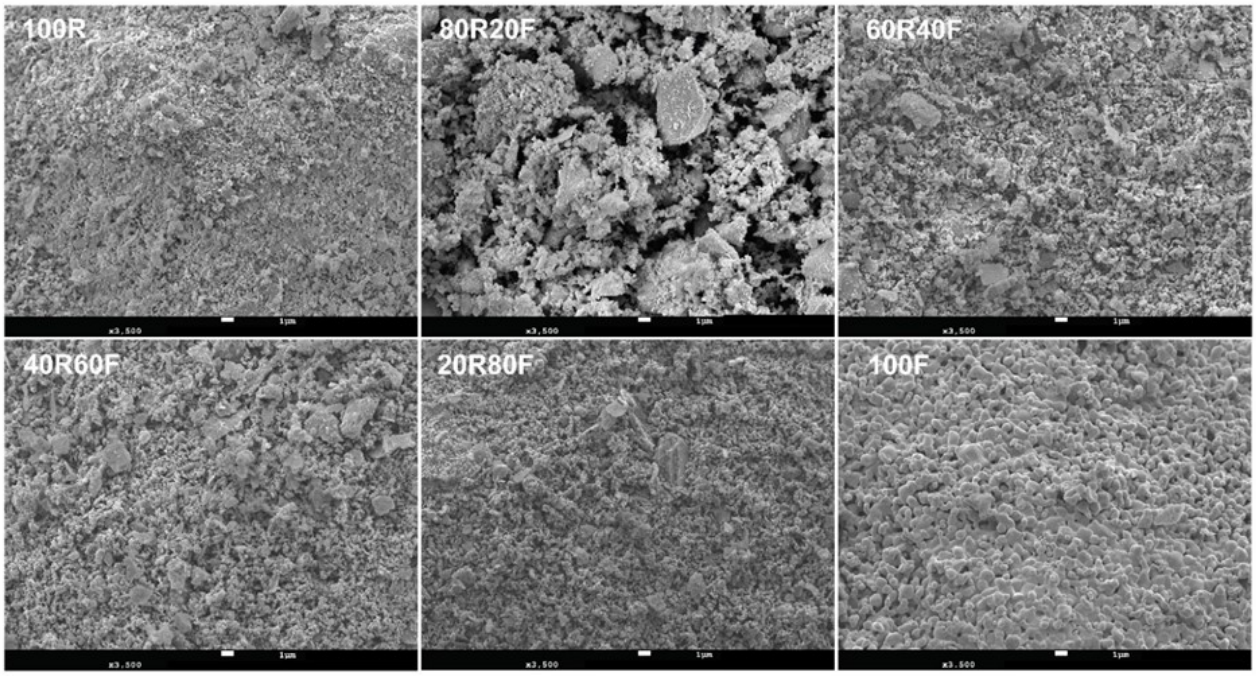


Figure 1.11: SEM images of the fresh oxygen carrier samples.

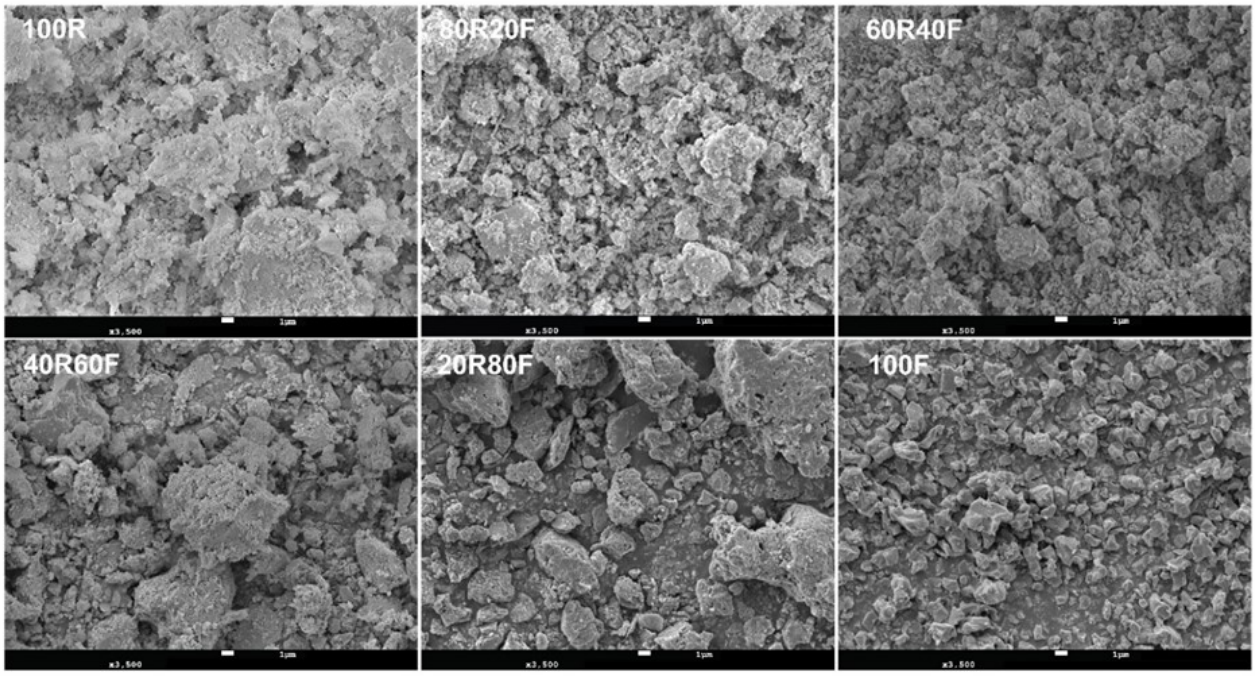


Figure 1.12: SEM images of the spent oxygen carrier samples.

Syed SAQLINE

Scientific output

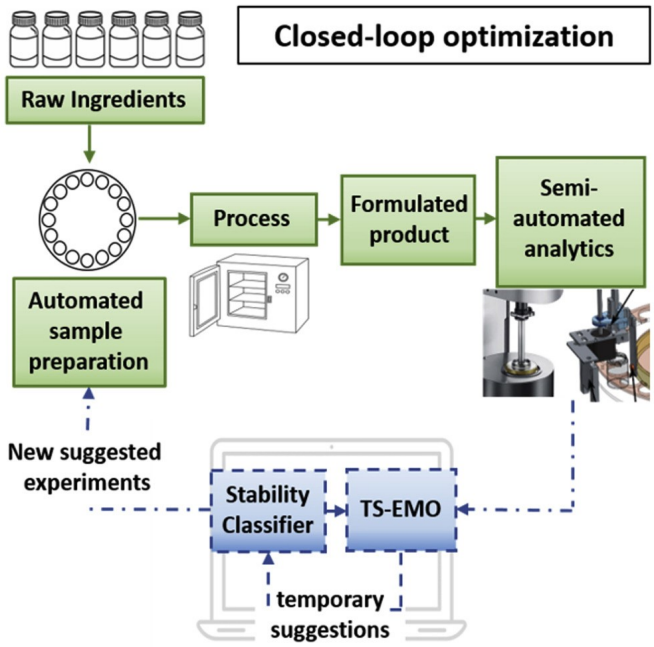
The following are the CREATE-acknowledged publications generated by IRP 1 during the reporting period, excluding those already featured in the Scientific Highlights section on page 12.

Optimization of formulations using robotic experiments driven by machine learning DoE

Liwei Cao, Danilo Russo, Daniel Salley, Abhishek Sharma, Graham Keenan, Werner Mauer, Huanhuan Gao, Leroy Cronin and Alexei A. Lapkin, *Cell Reports Physical Science*

DOI: 10.1016/j.xcrp.2020.100295

Abstract: The discovery of silica spheres by Werner Stöber and his team (known as Stöber silica) has been instrumental to many technological fields such as hollow materials research. Recent research endeavors on (physical and chemical) transformation of Stöber silica have specifically opened up a new horizon in this domain, especially in catalysis science and catalyst technology. Deliberate introduction of working spaces into Stöber silica *via* such transformations is regarded as a meaningful methodology toward fabrication of highly confined hollow nanostructures in the form of "*reactor-like nanocatalysts*" or "*catalyst-like nanoreactors*". More importantly, advanced catalytic devices with well-defined size, shape, composition, and hollowness could be obtained by these viable approaches. Concerning the further research, the present minireview gives an overview on recent advances about the synthesis and applications of hollow nanocatalysts derived from Stöber silica spheres. Firstly, we will provide the gist of current status of hollow materials research. Secondly, applicable methods for transformation of Stöber silica spheres to hollow nanostructures and hollow nanocatalysts will be elaborated. The stability and durability of SiO_2-based hollow constructs will also be elucidated. Subsequently, research snapshots of Stöber SiO_2-derived hollow nanostructures and their applicability mainly for catalytic purposes, from our research group and literature, will be discussed. Our personal perspectives on promising research opportunities and challenges in this field will also be given at the end.

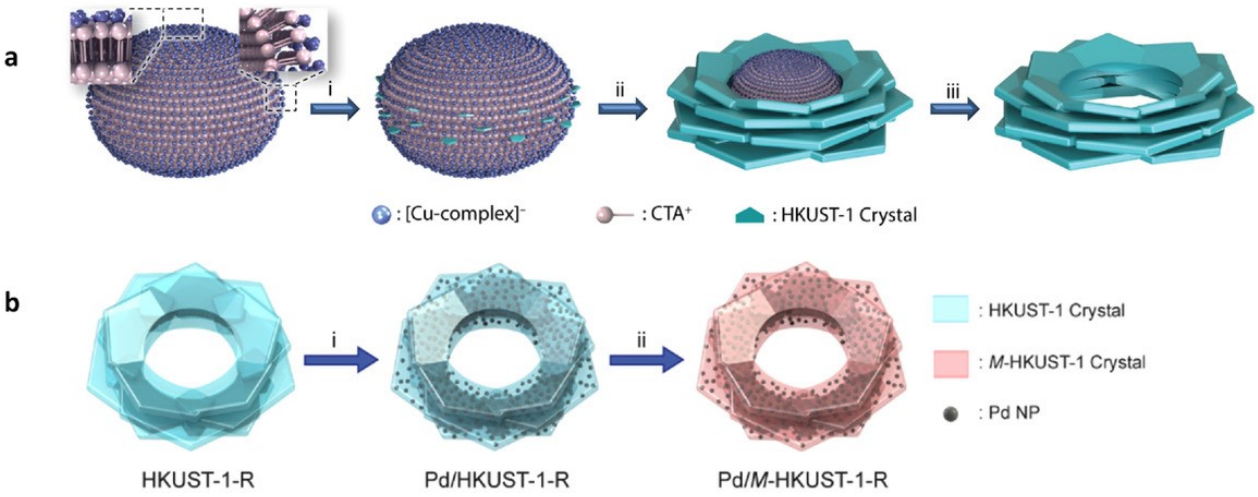


Hierarchy concepts in design and synthesis of nanocatalysts

Hua Chun Zeng, *ChemCatChem*

DOI: 10.1002/cctc.202001003

Abstract: High-performance catalytic nanomaterials (nanocatalysts) are normally more complex than their phase-pure counterparts in terms of preparation processes and physicochemical properties. Therefore, more thoughtful considerations are required on various hierarchy-related issues in their design and synthesis, especially when deciding their composition, mass, activity, selectivity, reactivity, stability, surface, texture, porosity, structure, size, shape, density, and even cost for a system under development. In this Concept article, we will address some general considerations and approaches with respect to the design and synthesis of nanocatalysts. In particular, architectural conceivability, materials selection, synthetic technique and integration strategy will be discussed. Furthermore, we will use the development of integrated nanocatalysts as examples to highlight some key hierarchical issues and snapshot a few representative practices. Finally, a number of suggestions regarding future research directions are also proposed on the basis of personal perspective.



(a) Illustration for the growth process of HKUST-1-R: (i) nucleation, (ii) growth, and (iii) removal of vesicle template. (b) HKUST-1-R undergoes an in situ reduction of Pd^{2+} to form Pd/HKUST-1-R (step i), and subsequent cation exchange with M^{n+}.

Other activities and achievements

Asst Prof. Paul LIU (PI, NTU) delivered two presentations at the *AIChE Virtual 2020 Annual Meeting* in November 2020: "Development of Capacity-Enhanced Oxygen Carriers for Chemical Looping Combustion By Exploiting Solid Solution Systems" and "Coupling Chemical Looping Combustion of Solid Fuels with Advanced Steam Cycles for CO_2 Capture: A Process Modelling Study".

Asst Prof. Liu also co-chaired two technical sessions: "Combustion Kinetics and Emissions, Catalysis and Reaction Engineering Division" and "Engineering for Combustion and Pyrolysis, Catalysis and Reaction Engineering Division".

He also received the AIChE-SLS Outstanding Young Principal Investigator Award 2020.

Perman JORAYEV (PhD student, CAM) is on the organising team for the *4th Machine Learning and Artificial Intelligence for Biochemical and Chemical Engineering Conference* in Cambridge in July 2021.

IRP 2

ELECTROSYNTHETIC PATHWAYS FOR ADVANCED LOW-CARBON CHEMICAL MANUFACTURING

In IRP 2, 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.

IRP 2 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, IRP 2 researchers have continued the focus on the development of advanced low-carbon, clean synthesis methods for the production of speciality chemicals. A combined experimental and computational approach has been applied to explore optimal device configurations for electrosynthetic reactors.

Research carried out by Dr Dai Chencheng has focused on developing microfluidic devices using thin film microband electrodes which have been fabricated in the IRP 2 clean room facilities. The microchannels have been designed through numerical modelling and fabricated for optimal electrolytic performance. The approach is currently being applied to nitrogen oxidation, with the ultimate goal of producing a new strategy for nitrate generation. Further development has also targeted new gas diffusion electrodes (GDEs) and we are exploring the incorporation of these new structures within the microfluidic devices. We have also begun to address the use of the programmable electrode-integrated membranes with GDEs, which have been a focus of a collaboration with Prof. Jim Yang Lee and Dr Zhang Tianran. This activity uses a programmable electrical stimulus to help minimise the frequency of membrane fouling, with the aim of improving the operational lifetime of the GDEs. Further electrocatalysis research has focused on developments in eCO_2RR reactions carried out by Dr Sun Libo, exploring new strategies for single atom catalysts (SACs) applications.

The work of Freyja Dagbjartsdóttir, who is sponsored by our industrial collaboration with Syngenta, has targeted new numerical approaches and models for the intelligent design of the electrosynthesis plants located in the IRP 2 laboratories. Ms Dagbjartsdóttir's work is exploring the effects of viscosity variation, influence on current density as a function of pressure and temperature. In this reporting phase she has developed data science methods using machine learning to help separate the different components within the electrolytic signal of electrocatalyst reactions. We plan to apply this new approach to the investigation the work of Dr Sun Libo and Dr Dai Chencheng.

The IRP 2 Singapore-based start-up company Datum Electronix, launched by Dr Kamal Elouarzaki and Dr Adrian Fisher, has continued to develop during the last six months. Three new AI software packages have now been completed and are available for the development of commercial low carbon synthesis technologies.

IRP 2 outreach activities have continued during COVID-19, with a focus on online courses. We have contributed to the Cambridge Science Festival in collaboration with Cambridge Zero.

Dr Adrian Fisher, PI
University of Cambridge

Update on work package 2.1

Advanced electrode architectures

Dr DAI Chencheng's (Research Fellow, NTU) recent work has been focused mainly on two areas: the electrochemical nitrogen oxidation reaction (NOR) in a flow cell with gas diffusion electrode (GDE) and microfluidic devices with thin film microelectrodes.

As introduced in the previous report, the current NOR work aims at nitrate production from electrochemical oxidation of air directly. Through the optimisation of catalyst preparation and experimental parameters, the highest nitrate production, during a two-hour chronoamperometry test, of around 1 mg h^{-1} mg^{-1} was achieved by using the $LaCoO_3$ catalyst, and the highest faradaic efficiency of around 24% was obtained by using the $LaFeO_3$ catalyst, with an applied potential of 1.8 V vs. RHE.

Microfluidic devices with thin film microelectrodes have been successfully fabricated in the clean room. The device normally consists of two parts: a glass wafer coated with thin film electrode(s), and a PDMS microchannel. The microfabrication equipment in the clean room allows the coating of various metals (e.g., Pt, Au, Ag, Cu, Ni, Co, Ti have been tried so far) and metal oxides, with different designed shapes. The microchannels can also be fabricated with different shapes and different thicknesses (normally 100 – 250 µm) based on the applications.

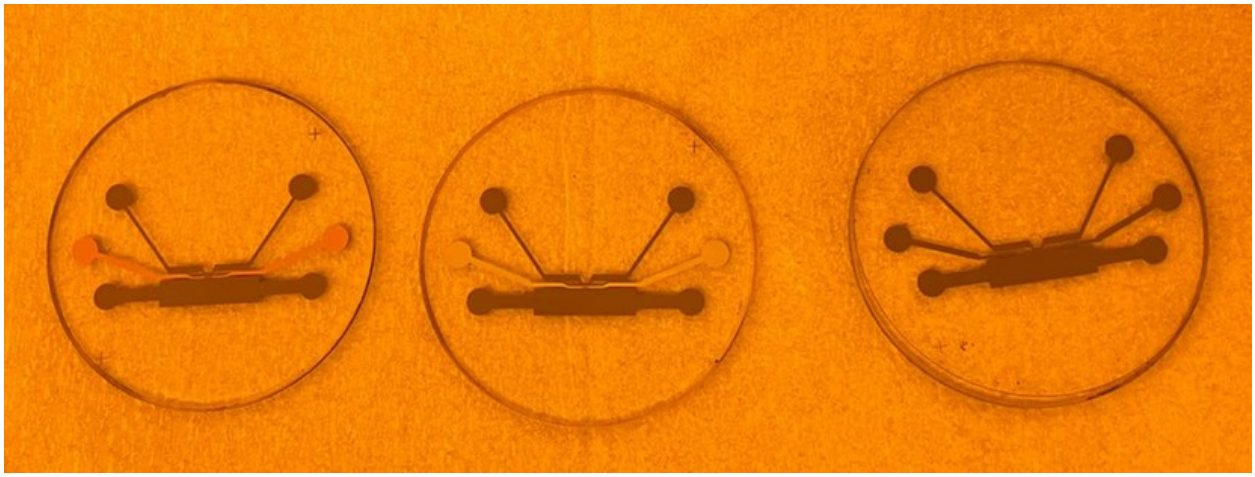


Figure 2.1: Glass wafers (diameter of 5 cm) coated with Cu, Ag and Pt (from left to right) working microelectrodes, Pt reference electrodes and Pt counter electrodes.

Dr DAI Chencheng

Update on work package 2.2

Co-generation and electrolytic synthesis reactor engineering

Dr SUN Libo (Research Fellow, NTU) reports that the research on Ni single-atom catalysts (SACS) recognises the good selectivity, high current and stability of such electrocatalysts for CO_2RR. But the preparation of these materials usually requires pyrolysis, graphitisation and an etching process, which is still complicated and not economic for the practical use of such electrocatalysts. Thus, one alternative way is using molecule catalysts, which can avoid the problems met for the SACS. However, Ni-based molecule catalysts such as nickel phthalocyanine (NiPc) always exhibit good selectivity towards the CO_2 reduction to CO, yet the current density is not good, and the catalysts may easily decay when large overpotential is applied.

Here, as inspired by previous research on the Co quaterpyridine ligand which showed that the incorporation of pyrazine could help to increase the activity of Co-based complexes, such a functional group was introduced to decorate the phthalocyanine ligand and a series of new Ni-based phthalocyanine derivatives were prepared. These materials exhibited rather high selectivity to CO, excellent stability and high current. For instance, the current could reach 18 mA cm^{-2} at -0.75 vs. RHE; the selectivity of FE is almost 100% in 0.1 M $KHCO_3$. It also kept good selectivity the whole testing range (> 95%) and the loading of catalyst is also rather low, at the 10^{-8} mol cm^{-2} level.

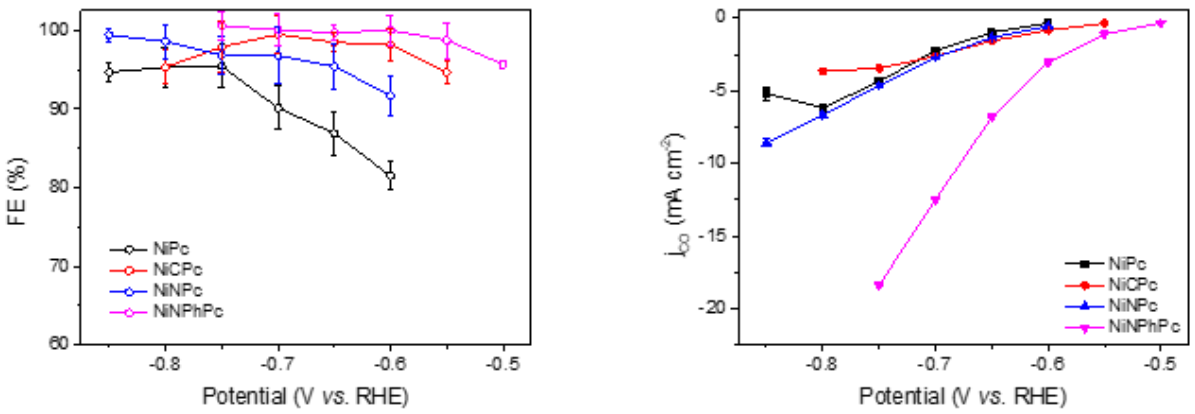


Figure 2.2: (a) Faradaic efficiency of CO, (b) Partial current density of CO.

Dr SUN Libo

Update on work package 2.3

Micro-variable pressure and temperature electrosynthesis plant

Freyja Björk DAGBJARTSDÓTTIR'S (PhD student, CAM) research interests lie in investigating novel electrochemical systems where a complex relationship exists between chemistry and mass transport. The aim is to develop numerical and analytical descriptions of electrochemical systems that can be used to investigate, design and monitor these systems.

Recently her focus has been on innovative ways of analysing Fourier transform AC voltammetry (FTacV) signals by using large quantities of simulated signals and data science methods such as machine learning to make the method more accessible to the user and open up the technique to applications beyond catalyst investigation.

With Dr DAI Chencheng, Ms Dagbjartsdóttir has also been working on establishing a microfabrication process at CARES to make electrochemical microfluidic devices that can be used as sensors and reactors. Microfluidic devices have very well defined mass transport so she intends to use them to validate some of the analytical and numerical models she has previously constructed.

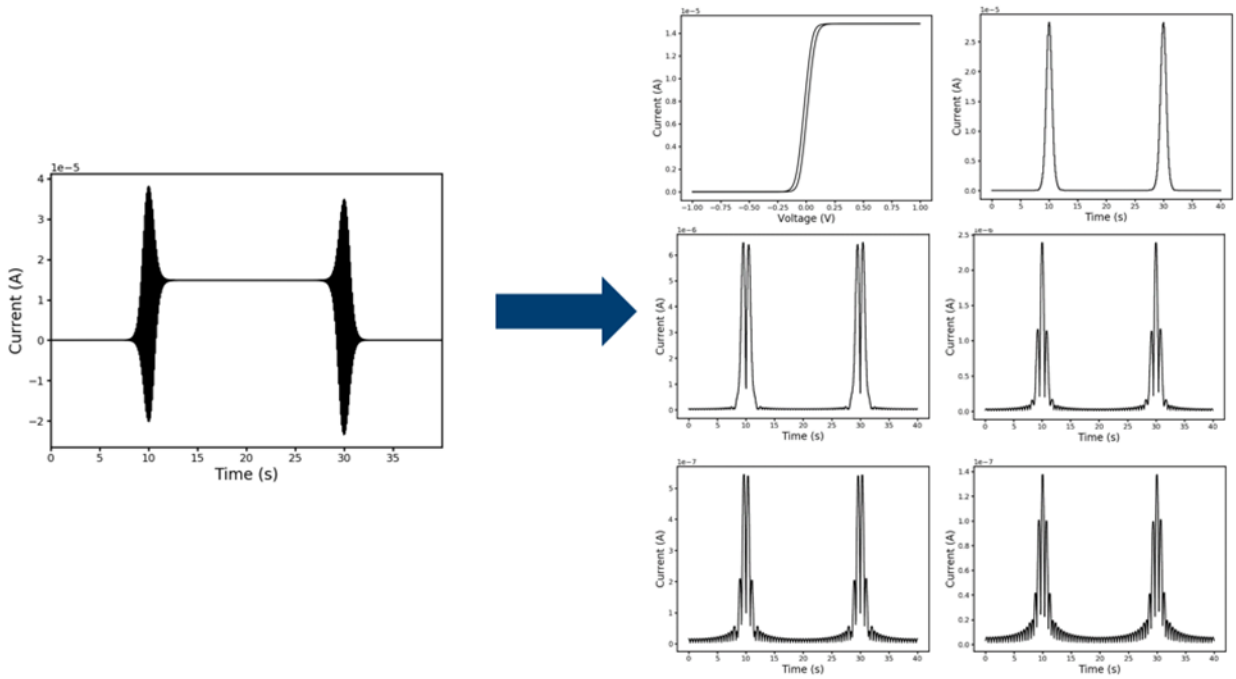


Figure 2.3: (left) A typical raw FTacV signal and (right) the same signal after FT processing. The signal is produced using the MECSim software package. [http://www.garethkennedy.net/MECSim.html]

Freyja DAGBJARTSDÓTTIR

Scientific output

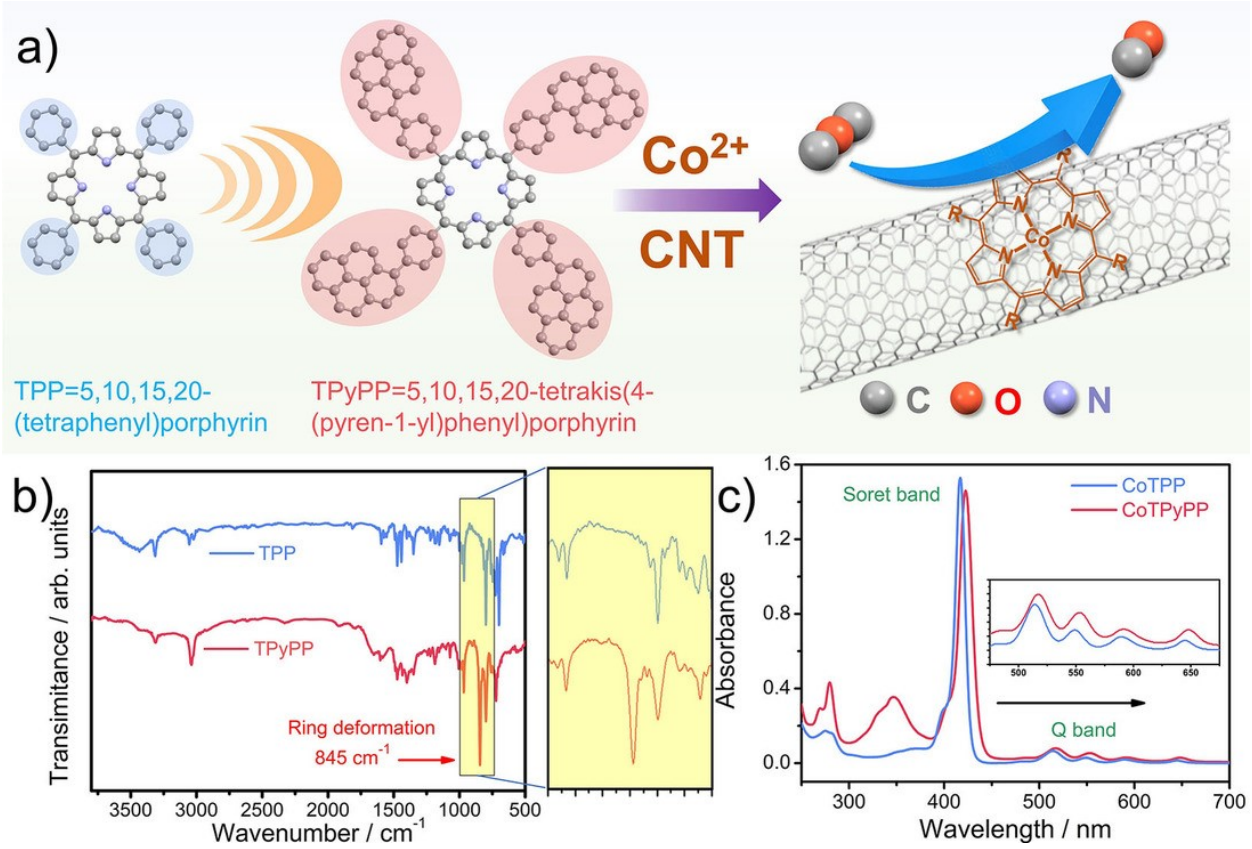
The following are the CREATE-acknowledged publications generated by IRP 2 during the reporting period, excluding those already featured in the Scientific Highlights section on page 12.

Enlarging the π-conjugation of cobalt porphyrin for highly active and selective CO_2 electroreduction

Shuo Dou, Libo Sun, Shibo Xi, Xiaogang Li, Tan Su, Hong Jin Fan and Xin Wang, *ChemSusChem*

DOI: 10.1002/cssc.202100176

Abstract: Heterogeneous molecular catalysts have attracted considerable attention as carbon dioxide reduction reaction (CO_2RR) electrocatalysts. The π-electron system of conjugated ligands in molecular catalysts may play an important role in determining the activity. In this work, by enlarging π-conjugation through appending more aromatic substituents on the porphyrin ligand, altered π-electron system endows the as-prepared 5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl) porphyrin Co^{II} with high Faradaic efficiency (ca. 95 %) for CO production, as well as high turnover frequency (2.1 s^{-1} at −0.6 V vs. RHE). Density functional theory calculation further suggests that the improved electrocatalytic performance mainly originates from the higher proportion of Co d_{z2} orbital and the CO_2 π* orbital in the HOMO of the $(Co–porphyrin–CO_2)^-$ intermediate with larger π-conjugation, which facilitates the CO_2 activation. This work provides strong evidence that π-conjugation perturbation is effective in boosting the CO_2RR.



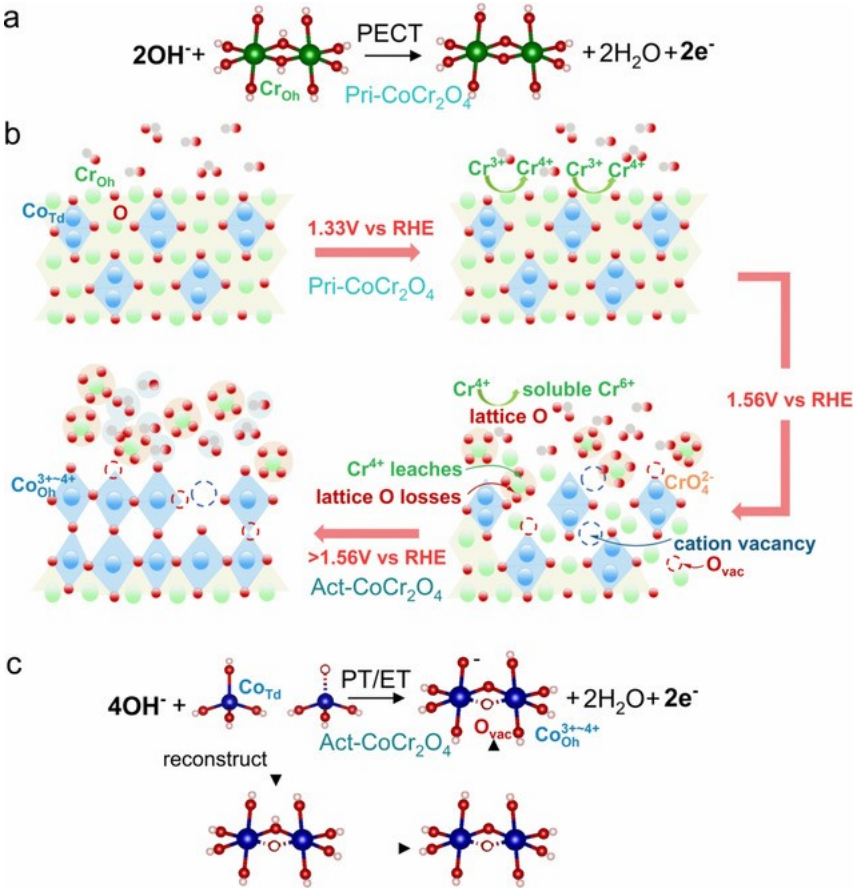
a) Molecular structures of TPP and TPyPP and synthesis of Co–porphyrins/CNT for CO_2RR.
b) FT-IR results of TPP and TPyPP.
c) UV/Vis absorption spectra of CoTPP and CoTPyPP.

Anodic oxidation enabled cation leaching for promoting surface reconstruction in water oxidation

Yan Duan, Jun Yan Lee, Shibo Xi, Yuanmiao Sun, Jingjie Ge, Samuel Jun Hoong Ong, Yubo Chen, Shuo Dou, Fanxu Meng, Caozheng Diao, Adrian C. Fisher, Xin Wang, Günther G. Scherer, Alexis Grimaud and Zhichuan J. Xu, *Angewandte Chemie International Edition*

DOI: 10.1002/anie.202015060

Abstract: A rational design for oxygen evolution reaction (OER) catalysts is pivotal to the overall efficiency of water electrolysis. Much work has been devoted to understanding cation leaching and surface reconstruction of very active electrocatalysts, but little on intentionally promoting the surface in a controlled fashion. We now report controllable anodic leaching of Cr in $CoCr_2O_4$ by activating the pristine material at high potential, which enables the transformation of inactive spinel $CoCr_2O_4$ into a highly active catalyst. The depletion of Cr and consumption of lattice oxygen facilitate surface defects and oxygen vacancies, exposing Co species to reconstruct into active Co oxyhydroxides differ from CoOOH. A novel mechanism with the evolution of tetrahedrally coordinated surface cation into octahedral configuration via non-concerted proton-electron transfer is proposed. This work shows the importance of controlled anodic potential in modifying the surface chemistry of electrocatalysts.



Activation conditions on the surface evolution mechanisms for $CoCr_2O_4$.
a) Proton electron concerted transfer for Pri-$CoCr_2O_4$.
b) Scheme of $CoCr_2O_4$ surface change before OER testing after being applied increased potentials.
c) Proton electron non-concerted transfer for Act-$CoCr_2O_4$.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IRP 3

COMBUSTION FOR CLEANER FUELS AND BETTER CATALYSTS

To formulate the fuel of the future, IRP 3 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.

IRP 3 Principal Investigators:

Professor Markus KRAFT
University of Cambridge

Professor XU Rong
Nanyang Technological University

Assoc Professor YANG Wenming
National University of Singapore

OVERVIEW

Notwithstanding the still ongoing pandemic, we have continued our experimental activities in the laboratory in this reporting period, investigating the potential of a poly(oxymethylene) dimethyl ether (PODE) to reduce soot emissions from internal combustion engines when blended with conventional diesel fuels. We have now obtained differential mobility particle size results in engines as well as soot volume fraction data in controlled laboratory flame setups, including a comparison with other oxygenated blend components. These results represent a further step towards a quantitative understanding of how oxygenated fuels can contribute to a reduction in soot emissions.

In the area of flame-synthesised inorganic functional nanostructured materials, we have added another characterisation technique to our list of capabilities. We are now able to conduct temperature programmed oxidation (TPO) to characterise the quantity and distribution of oxygen vacancies in titanium dioxide (TiO_2). This technique is superior to currently adopted characterisation methods that are able to detect oxygen vacancies but cannot simultaneously determine the position and abundance of defects. This method being at our disposal promises deeper insights into structure-activity relationships of catalyst materials.

Additionally, we have built a prototype system that allows continuous particle collection in a flame synthesis reactor in order to produce quantities with uniform properties which are sufficient for catalytic tests and material characterisation. This forms a key step in addressing the challenges of low yield and poor reproducibility. Furthermore, the setup enables characterising the distribution of collected particles which will help to shed light on the particle formation mechanism and thus achieve improved control of particle properties.

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 utilisation. The research activities are conducted under the collaboration of NUS and Cambridge researchers. The study on various fuels and additives in engine research continues as the pandemic eases in the last few months. With the use of the DMS particle sizer, Dr Zong and his fellow researchers were able to investigate both nucleation mode particles (0-50 nm) and accumulation mode particles (50-1000 nm) in engine emissions. In the study, poly (oxymethylene) dimethyl ethers ($PODE_3$) showed the ability to reduce accumulation mode particles by blending with diesel. Based on the experimental results, a summary chart was designed to predict the particle reduction under different blending ratio and engine loads. Besides this, Dr Zong also started modelling the same engine with CMCL Innovations engineers. The simulation shows good agreement with the experimental data on both combustion characteristics and emissions.

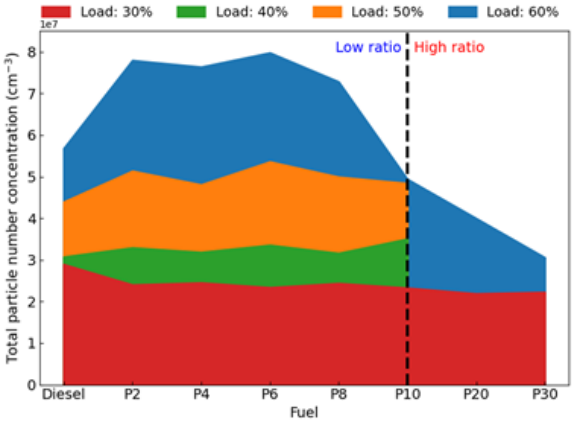
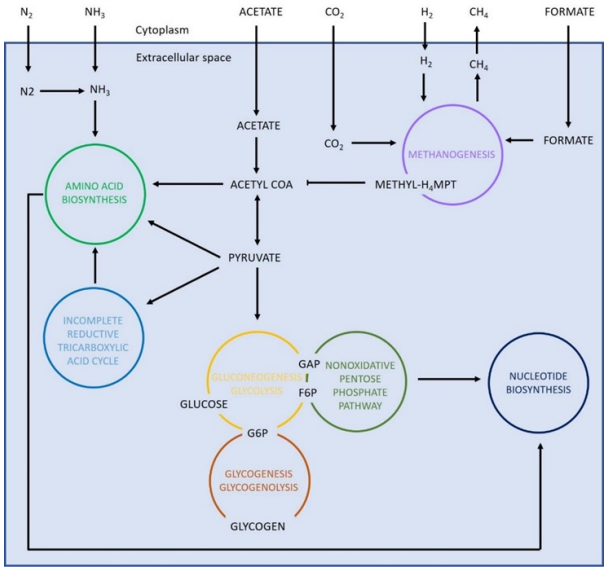


Figure 3.1: Emission reduction of $PODE_3$ additive under different blending ratio and engine loads.



Clifford VO Chi Hung's (PhD student, NUS) main research interest lies in the biological fixation of CO_2 using the archaeon *M. maripaludis* S2. Unlike many other microbes which require organic feedstock, this microorganism can convert CO_2 into CH_4 without any organic carbon input. In the last six months, Mr Vo studied the intracellular amino acid concentration profile of *M. maripaludis* S2. In addition, he characterised the molecular and catalytic properties of purified acetyl coenzyme A synthetase, an enzyme involved in acetate production in this microbe. A manuscript for this study is being prepared.

Figure 3.2: Major metabolic subsystems in M. maripaludis S2 *and their interactions. H_4MPT, tetrahydromethanopterin; GAP, glyceraldehyde-3-phosphate; F6P, fructose-6-phosphate; G6P, glucose-6-phosphate.*

Clifford VO Chi Hung

TAN Yong Ren (PhD student, CAM) is currently investigating soot formation in flames when blending different oxygenated fuels with jet fuel. The selected oxygenated fuels are dimethoxymethane (DMM), polyoxymethylene dimethyl ethers ($PODE_3$), dimethyl carbonate (DMC) and ethanol (EtOH). The oxygenated fuels were studied due to their practical value as fuel additives in engines. Mr Tan blended the oxygenated fuels with jet fuel at 5% to 20% blending percentage and used colour-ratio pyrometry to measure the soot volume fraction of the flame. This aimed to understand and compare the effectiveness of each oxygenated fuel in reducing the sooting tendency of the fuel blend. As observed in Figure 3.3, the increase in the volumetric blending of the oxygenated fuels increases the reduction of the maximum wing soot volume fraction of the flames at varying degrees, with ethanol (EtOH) decreasing the soot volume fraction most effectively, followed by dimethyl carbonate (DMC), polyoxymethylene dimethyl ethers ($PODE_3$) and lastly dimethoxymethane (DMM).

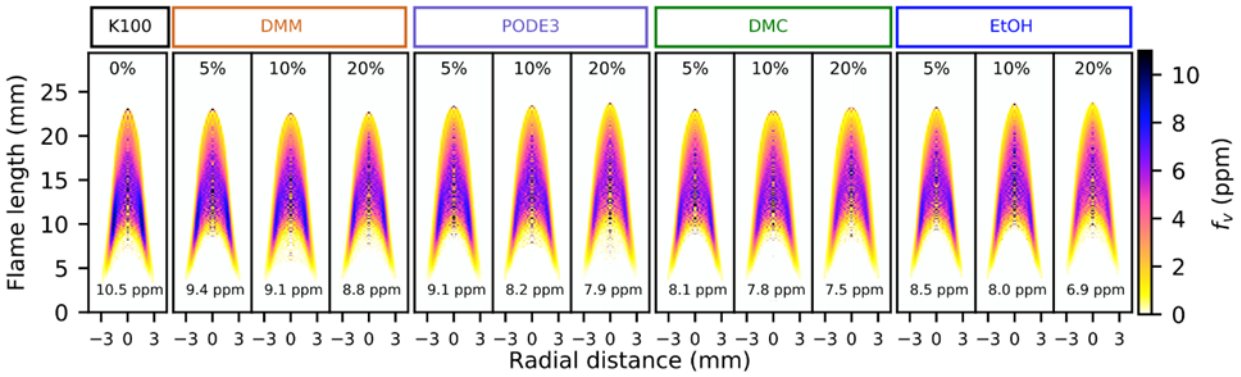


Figure 3.3: The soot volume fraction, f_v, profiles for the oxygenated fuel-blended jet fuel wick-fed laminar diffusion flames. The percentage of dimethoxymethane (DMM), polyoxymethylene dimethyl ethers (PODE3), dimethyl carbonate (DMC) and ethanol (EtOH) in each fuel blend is indicated at the top of each image. The maximum flame wing soot volume fraction is indicated at the bottom of each flame.

TAN Yong Ren

Update on work package 3.2

Refinery, fuel and engine of the future — modelling

Chemical mechanisms, PAH chemistry, after-treatment

Dr Laura PASCAZIO's (Research Fellow, CAM) main research interest lies in the study of combustion-generated carbonaceous nanoparticle (also known as soot) formation using computational methods. The understanding of the soot inception mechanism remains one of the most debated topics in the combustion scientific community. Recently, Dr Pascazio has been focusing on crosslinking reactions that may lead to particle formation at high temperatures. She has recently published a paper in the *Proceedings of the Combustion Institute* in which a new crosslinking reaction between two pentagonal rings around the periphery of planar pericondensed aromatic molecule is proposed in the context of soot formation. The work was also presented at the *38th International Symposium on Combustion* in January. Jointly with **Dr Jacob MARTIN (former Research Fellow, CARES)**, she is now submitting a paper on the importance of localised π-radicals in soot formation. These compounds were found to bond strongly enough for stability at flame temperature and are found to react rapidly through physically stabilised internal rotors. Currently, Dr Pascazio is writing a literature review for a new project on the automation of reactive force field parameterisation using web-based technologies.

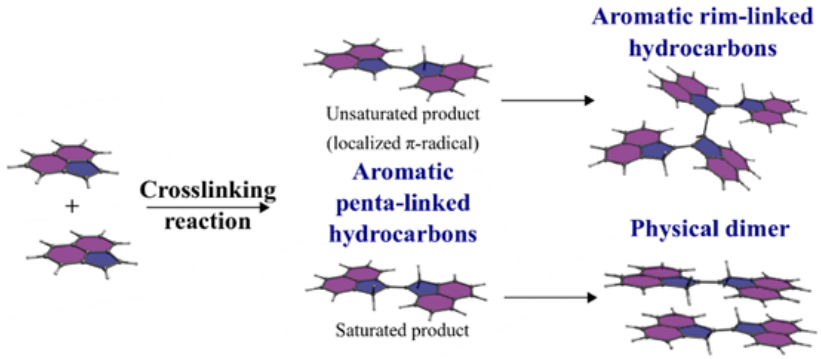


Figure 3.4: Aromatic penta-linked hydrocarbons in soot nanoparticle formation.

Dr Laura PASCAZIO

Angiras MENON's (PhD student, CAM) work focuses on using *ab initio* quantum chemical methods such as density functional theory to model the optical, kinetic and thermodynamic properties of polycyclic aromatic hydrocarbons (PAHs). The aim of this research is to utilise these computational chemistry tools to try and identify which PAHs contribute to the formation of carbonaceous nanoparticles in combustion conditions. A project involving computing the rates of bridge forming (cross-linking) reactions between PAHs containing different edge types has been completed and published in conjunction with Dr Jacob MARTIN (former Research Fellow, CARES). The key findings of this work are that reactions between aryl-type σ-radical PAHs and localised π-radical PAHs are among the fastest of the cross-linking reactions. These two edge sites also form a cross-link with substantial bond energies, suggesting that they are stable in flame environments, whereas some other widely suggested candidate PAHs, like de-localised π-radical PAHs and standard flat PAHs do not form very strong bonds. It was also seen that larger PAHs can bond and stack, with larger localised π-radical PAHs having a substantial enhancement in equilibrium constants due to the rim bonding. This work has suggested that localised π-radical PAHs could be potential precursors to soot formation. Otherwise, Mr Menon has primarily been writing his PhD thesis, titled "Modelling the optical, kinetic, and thermodynamic properties of soot precursor molecules", which he successfully defended in November 2020.

Update on work package 3.3

Better, cheaper, cleaner nanostructures — experimental

Flame synthesis of thin films of mixed metal oxide nanoparticles

Dr SHENG Yuan (Research Fellow, NTU) has mainly been working on the catalytic application of flame-synthesised materials including Ni-Fe phosphide/phosphate-carbon composite films, copper oxides and TiO_{2-x}. He has identified the high sensitivity of the structure of Ni-Fe phosphide/phosphate-carbon composites toward flame equivalence ratio as the key factor in the irreproducibility of the experiments. The critical equivalence ratio for incipient carbon growth has been determined and found to correlate to the best oxygen evolution performance of the resulting film that can be reproduced now with an improved synthesis protocol (Figure 3.5). He has also been studying the ethylene oligomerization activity of Ni catalysts supported on flame-synthesised TiO_{2-x}/Al_2O_3 and the methylcyclohexane dehydrogenation activity of Pt/Al_2O_3 catalysts.

Recently, Dr Sheng has been increasingly involved in the eCO_2EP project (see page 95). He has developed CuO_x/carbon paper gas diffusion electrodes by flame synthesis that operate in a 1 cm^2 flow cell for CO_2 reduction at a total current density of 0.5 A/cm^2. Moreover, he has designed a 100 cm^2 flow cell for pilot-scale demonstration and optimised the gas/electrolyte flow fields using computational fluid dynamics (Figure 3.6).

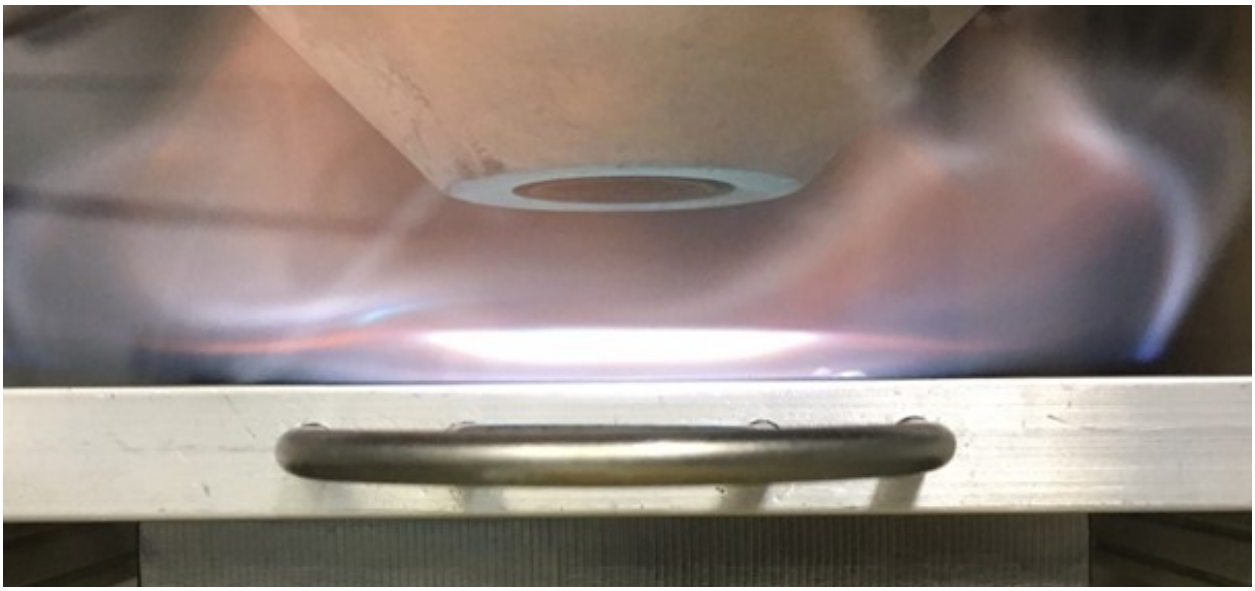


Figure 3.5: The flame synthesis of Ni-Fe phosphide/phosphate-carbon composite films.

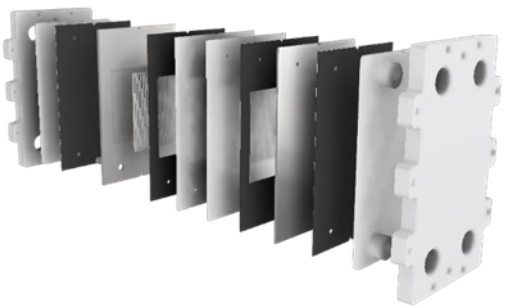


Figure 3.6: 3-D illustration of the 100 cm^2 flow cell.

Dr SHENG Yuan

WU Shuyang's (PhD student, NTU) research lies in the area of flame synthesised defective TiO_2 for energy and environmental applications. Over the past six months, his research mainly focused on developing the temperature programmed oxidation (TPO) method to characterise the quantity and distribution of oxygen vacancies in TiO_2. Generally, the TPO process typically involves the adsorption of oxygen on the surface and subsequent diffusion of the adsorbed oxygen species from the surface to the bulk via oxygen vacancy (OV) sites. As such, the temperature and area of TPO peaks can reveal the distribution of the defects in the particle. TPO is applied for the first time to differentiate and quantify oxygen vacancies at the surface, grain boundary and bulk of TiO_{2-x}. Most of the currently adopted characterisation methods are able to detect OVs such as electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM), X-ray absorption fine structure (XAFS), time-resolved photoluminescence spectroscopy (TRPL) and positron annihilation lifetime spectroscopy (PALS). However, these methods cannot simultaneously determine the position and abundance of defects at the same time. With the assistance of the TPO technique, a deeper understanding of "structure-activity" correlations on catalyst materials should be achieved.

As shown in Figure 3.8, the TPO profiles of flame-made TiO_{2-x} (6, 10 and 15 min) can be resolved into four sub-peaks. The first two peaks below 300 °C are associated with OVs at the surface and sub-surface. Among TiO_{2-x}-6 min, 10 min and 15 min, a clear trend can be observed. Firstly, the temperatures of these two peaks decrease with the increase of deposition time. Secondly, the sum of the two peak areas continuously drops from 19.2 to 14.7 and then 11.6 mmol. Two more TPO peaks appear above 300 °C. They are expected to be contributed by OVs in the bulk, since at higher temperatures oxygen species can diffuse through the lattice to the bulk. For samples with longer deposition time among TiO_{2-x} (6, 10 and 15 min), the temperatures of these two peaks are higher which is likely due to a larger activation energy of oxygen diffusion in more crystalline samples. The appearance of two peaks (P3 and P4) indicates defects of different nature in their bulk structures. It is interesting to note that the area of P3 peak increases almost twice from TiO_{2-x}-6 min to TiO_{2-x}-10 min. Combining these two results, the P3 peak can be assigned to OVs at the grain boundaries, while P4 to OVs in the bulk lattice. For sample TiO_{2-x}-30 min which is white, TPO results show that all types of defects have been greatly reduced. For comparison, the TPO profile of P25 TiO_2 shows that there is only a trace amount of OVs on the surface and in the bulk. Based on these data, the estimated x value in TiO_{2-x} is in the range of 0.054 - 0.134 with generally smaller x for longer deposition time.

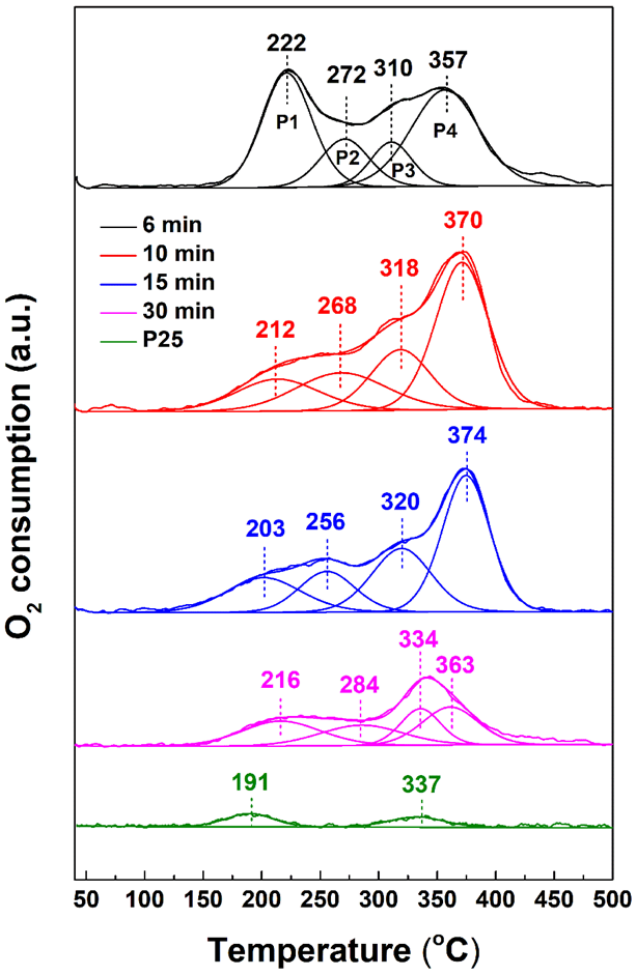


Figure 3.7: TPO profiles of flame-made TiO_{2-x} and P25 TiO_2.

WU Shuyang

Update on work package 3.4

Better, cheaper, cleaner nanostructures — modelling

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

Dr Manoel MANUPUTTY (Research Fellow, NTU) has been working to explore the use of flame synthesised metal oxides as catalyst supports for important chemical processes such as TiO_2 and TiO_2/Al_2O_3 in ethylene oligomerization. Recently, Dr Manuputty has been focusing on overcoming the challenges of low yield and poor reproducibility during flame synthesis which are due to the interval collection system used in the flame reactor. A preliminary prototype includes a simple modification to the reactor to allow a continuous particle collection which can produce up to 1 g of oxides with homogeneous properties per synthesis batch. Such quantities are required for catalytic tests and material characterisations. In addition, Dr Manuputty is working on characterising the radial distribution of particles collected on the stagnation plate to better understand the particle formation mechanisms and thus achieve a better control of particle properties in the flame synthesis system.

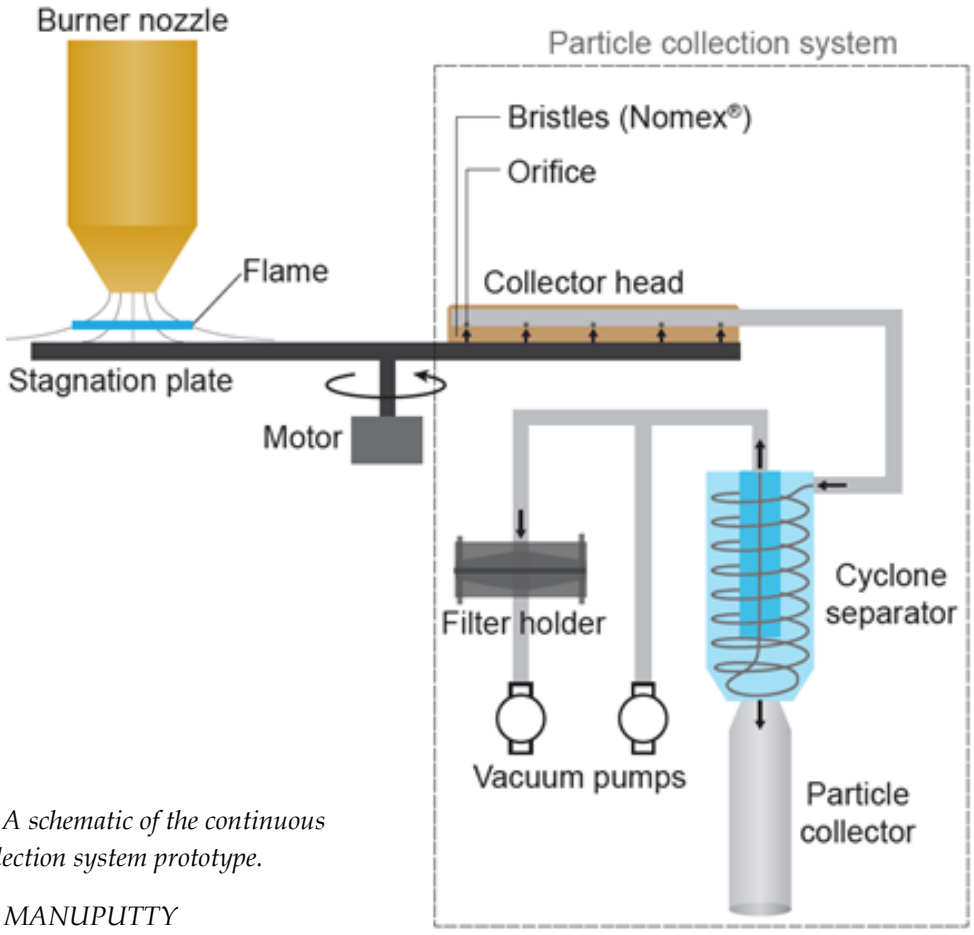


Figure 3.8: A schematic of the continuous particle collection system prototype.

Dr Manoel MANUPUTTY

Scientific output

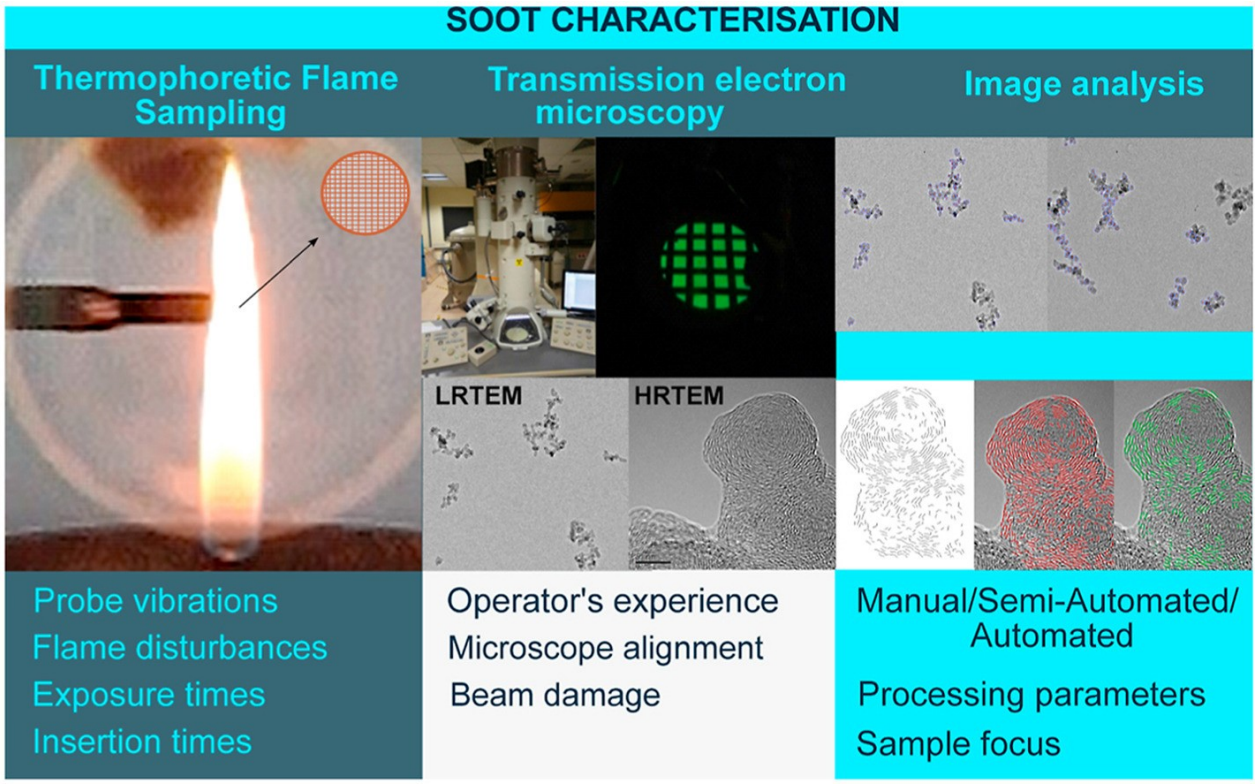
The following are the CREATE-acknowledged publications generated by IRP 3 during the reporting period, excluding those already featured in the Scientific Highlights section on page 12.

On the thermophoretic sampling and TEM-based characterisation of soot particles in flames

Maria Botero, Jethro Akroyd, Dongping Chen, Markus Kraft and John R. Agudelo, *Carbon*

DOI: 10.1016/j.carbon.2020.09.074

Abstract: Thermophoretic sampling and TEM imaging are common techniques used to characterise soot particles in flames. In this paper, we present a multi-scale evaluation of operating conditions and methodological aspects of these techniques, and based on our own experimental observations, show how these can influence the characterisation of the particles. Regarding the thermophoretic sampling of soot particles in flames, we evaluated the influence of exposure time, transit times, multiple-insertions, probe design and vibrations in the capture of representative samples, and present a series of recommendations. For the nano-structural characterisation of soot particles using HRTEM combined with fringe analysis we evaluated the influence of microscope alignment and image quality in the mapping of fringes and the calculation of metrics, concluding that the fringe lengths and interfringe spacing are very sensitive to particle focus. Also, the parameters used in the image transformation process are critical and require optimisation for different magnifications and microscopes. Finally, the effect of beam damage was studied, confirming a time of approximately 6 min during which both nascent and mature particles can be imaged without noticeable nanostructural damage. The use of lower microscope electron voltage can further minimise the impact of beam damage.

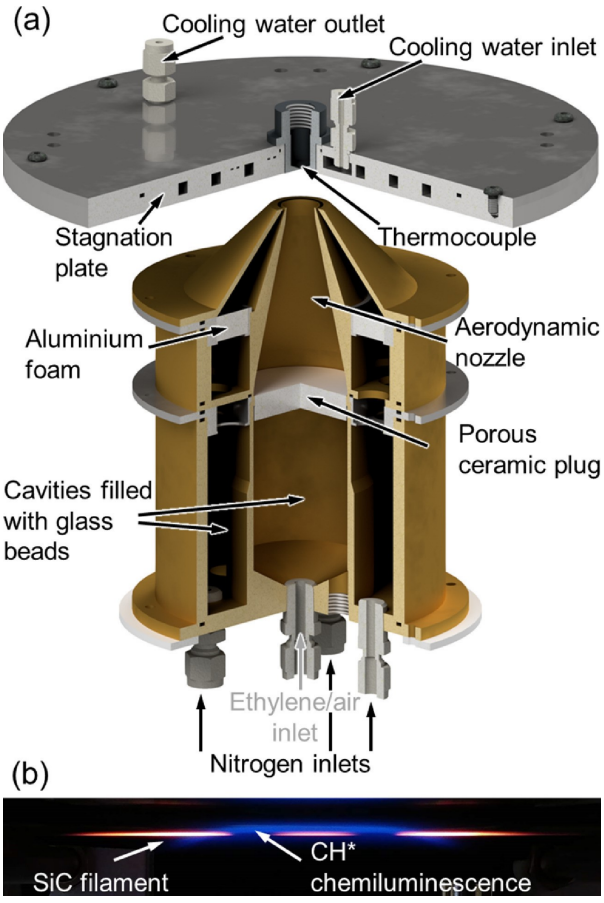


Temperature and CH* measurements and simulations of laminar premixed ethylene jet-wall stagnation flames

Jochen Dreyer, Eric Bringley, Manoel Manuputty, Jethro Akroyd and Markus Kraft, *Proceedings of the Combustion Institute*

DOI: 10.1016/j.proci.2020.06.106

Abstract: New experimental 2D measurements are reported to characterise the flame location, shape and temperature of laminar premixed ethylene jet-wall stagnation flames when the equivalence ratio, exit gas velocity and burner-plate separation distance are varied. Bandpass-filtered optical measurements of the CH* chemiluminescence were used to provide information about the shape and location of the flames. Thin filament pyrometry (TFP) using a 14 μm diameter SiC filament was used to make line measurements of the temperature to reconstruct the full 2D temperature field for the first time in premixed, jet-wall stagnation flames. The comparison of CH* measurements with (intrusive) and without (non-intrusive) the presence of the SiC filament showed that the filament resulted in minimal disturbance of the flame when the filament was placed downstream of the flame front. However, the flame was observed to attach to the filament, resulting in more significant disturbance, when it was placed upstream of the flame front. The flames were simulated using both 1D and 2D models. The 2D simulations were used to provide estimates of the velocity, kinematic viscosity and thermal conductivity required to calculate the gas temperature from the TFP data. The 1D simulations showed excellent agreement with the experimentally observed centreline quantities, but required the strain boundary condition to be fitted in order to match the experimentally observed flame location. The 2D simulations showed excellent agreement without the need for any fitting, and correctly predicted the flame shape, location and temperature as the experimental conditions were varied. A comparison of the set of simulated temperature-residence times along different streamlines showed relatively uniform distributions within each flame. However, the most uniform set of temperature-residence time distributions did not correlate with the flattest flame.

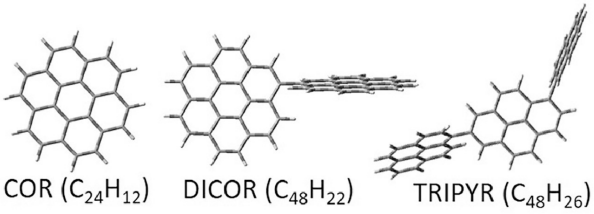


Atomic insights into the sintering process of polycyclic aromatic hydrocarbon clusters

Dingyu Hou, Qingzhao Chu, Dongping Chen, Laura Pascazio, Markus Kraft and Xiaoqing You, *Proceedings of the Combustion Institute*

DOI: 10.1016/j.proci.2020.06.368

Abstract: In this work, we studied the sintering process of two homogeneous polycyclic aromatic hydrocarbon (PAH) clusters with diameters in the range of 3–6 nm using molecular dynamics (MD) simulations. The sintering process was quantified through monitoring the solvent accessible surface area (SASA) and the distance between the center of mass (COM) of the two PAH clusters. The effect of temperature and crosslinking level of PAH clusters on sintering was investigated. The results show that the sintering rate of two PAH clusters at a certain temperature T is largely dependent on the melting point (T_{MP}) of the PAH cluster. When T is higher than T_{MP}, the characteristic sintering time (τ_s) is around 10−2 ns and sintering is not affected by the crosslinking level as the PAH clusters are liquid-like. In contrast, when T is much lower than T_{MP}, the PAH clusters sinter rather slowly with $\tau_s > 5$ ns, and the sintering process is hindered by the crosslinks between PAH molecules within solid-like PAH clusters due to the enhanced steric effect.



Monomers of the PAH clusters.

Reactive localized π-radicals on rim-based pentagonal rings: Properties and concentration in flames

Angiras Menon, Jacob W. Martin, Gustavo Leon, Dingyu Hou, Laura Pascazio Xiaoqing You and Markus Kraft, *Proceedings of the Combustion Institute*

DOI: 10.1016/j.proci.2020.07.042

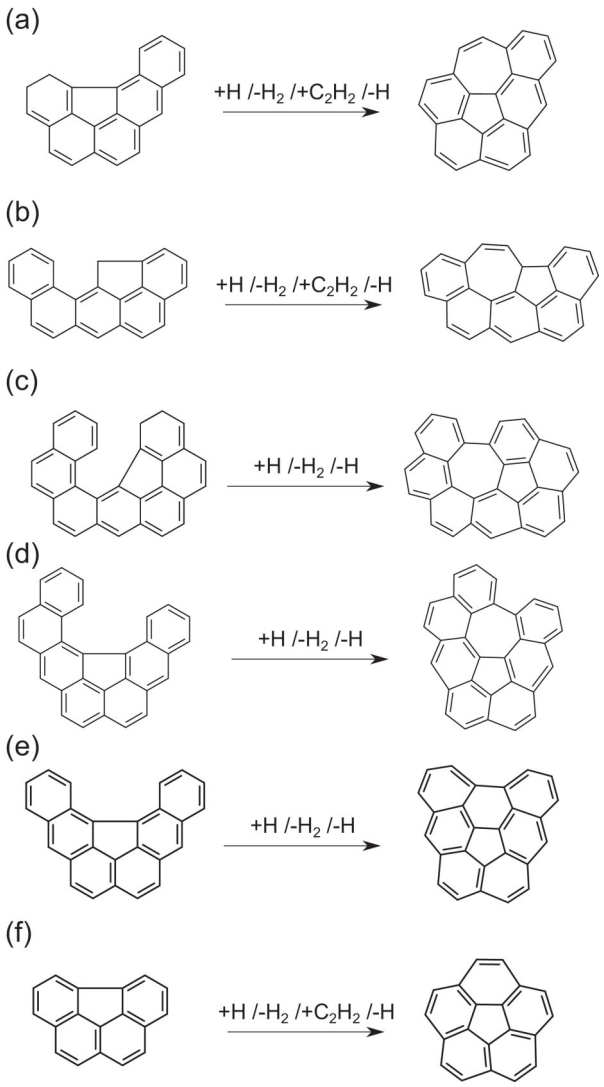
The impact of localized π-radicals on soot formation is explored by considering their electronic structure and computing their relative concentrations in flame conditions. Electronic structure calculations reveal that the presence of localized π-radicals on rim-based pentagonal rings is due to aromaticity. We further calculated a complete mechanism for the formation and elimination of the site from hydrogen additions and abstractions. A batch reactor with flame concentrations of $H^{\bullet}$ and H_2 was used to determine the time-dependent concentration of localized π-radicals. Low temperatures (< 1000 K) favored the fully saturated rim-based pentagonal ring. Soot nucleation temperatures (1000–1500 K) give way to unsaturated rim-based pentagons being favored. Localized π-radicals on rim-based pentagonal rings are found to be in higher concentration than the aryl-type σ-radical on the rim-based pentagon (mole fractions of 10−6–10−7) in below < 1500 K, consistent with recent experimental observations. Higher temperatures favor the σ-radical and the concentration of the localized π-radical on rim-based pentagons becomes negligible. A kinetic Monte Carlo treatment of multiple sites indicates that multiple localized π-radicals are possible on a single molecule. These results reveal the importance of localized π-radicals on rim-based pentagonal rings for PAH chemistry leading to formation of soot nanoparticles in flames involving aromatic rim-linked hydrocarbons (ARLH).

Kinetic Monte Carlo statistics of curvature integration by HACA growth and bay closure reactions for PAH growth in a counterflow diffusion flame

Gustavo Leon, Angiras Menon, Laura Pascazio, Eric Bringley, Jethro Akroyd and Markus Kraft, *Proceedings of the Combustion Institute*

DOI: 10.1016/j.proci.2020.06.352

Abstract: This paper uses a Kinetic Monte Carlo model that includes processes to integrate curvature due to the formation of five- and seven-member rings to simulate polycyclic aromatic hydrocarbons (PAHs) growing in lightly sooting ethylene and acetylene counterflow diffusion flames. The model includes new processes to form seven-member rings via hydrogen-abstraction-acetylene-addition and bay closure reactions on sites containing partially embedded five-member rings. The model additionally includes bay closure and HACA bay capping reactions for the integration of five-member rings. The mass spectra of PAHs predicted by the model are assessed against experimental data, and the distribution of embedded five-member rings and seven-member rings is studied as a function of spatial location, molecule size and frequency of events sampled in the simulation. The simulations show that the formation of seven-member rings and the embedding of five-member rings is a competitive process. Both types of rings are observed more frequently as the simulation proceeds from the fuel outlet towards the stagnation plane. Approximately 15% of the events that integrate curvature resulted in the formation of a seven-member ring coupled to an embedded five-member ring, and the remaining 85% of events embedded five-member rings via the formation of six-member rings. The proportion of PAHs containing embedded five-member rings and/or seven-member rings is observed to be a function of PAH size, passing through a maximum for PAHs containing 15–20 six-member rings. However, the proportion of PAHs containing both types of ring increases with PAH size, where upwards of 10% of PAHs containing at least one five-member ring and 15 or more six-member rings also contain a seven-member ring.

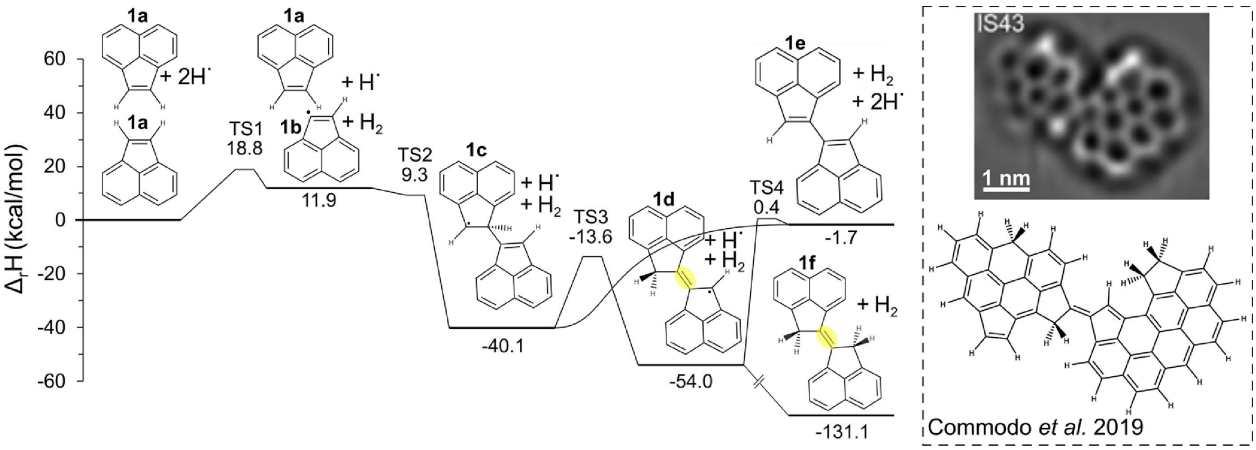


Curvature integration jump processes.

Aromatic penta-linked hydrocarbons in soot nanoparticle formation

Laura Pascazio, Jacob W. Martin, Angiras Menon, Dingyu Hou, Xiaoqing You and Markus Kraft,
Proceedings of the Combustion Institute
DOI: 10.1016/j.proci.2020.09.029

Abstract: A new crosslinking reaction between two pentagonal rings around the periphery of planar pericondensed aromatic molecules is proposed and its impact on soot nanoparticle formation explored. The reaction mechanism was computed, using density functional theory, between an aryl-type σ-radical on a rim-based pentagonal ring attacking another rim-based pentagonal ring. A hydrogen migration allowed for the formation of a double bond forming a planar aromatic penta-linked hydrocarbon (APLH) complex, recently experimentally observed. The clustering of this planar species is compared with a pericondensed polyaromatic hydrocarbon (PCAH) and an aromatic aryl-linked hydrocarbon (AALH) using molecular dynamics and metadynamics. Similar clustering is found for the investigated species compared with a pericondensed structure of similar mass indicating enhanced physical interactions after forming the crosslink. Finally, a further crosslink is possible between the unsaturated pentagonal ring sites forming an aromatic rim-linked hydrocarbon (ARLH) complex of considerable stability. This was confirmed by simulating the stable molecular dynamics of such a complex with on-the-fly quantum forces from a quantum semi-empirical method, revealing possible reactions under flame conditions that might play a role in soot nucleation.



Potential energy diagram for the formation of a planar crosslinked aromatic molecule with a double bond (highlighted) connecting rim-based pentagonal rings of the aromatic subunits at 0 K. A similar species observed experimentally has been also reported for comparison:

Commodo, Mario, Katharina Kaiser, Gianluigi De Falco, Patrizia Minutolo, Fabian Schulz, Andrea D'Anna, and Leo Gross. 2019. 'On the Early Stages of Soot Formation: Molecular Structure Elucidation by High-Resolution Atomic Force Microscopy'. Combustion and Flame *205 (July): 154–64. https://doi.org/10.1016/j.combustflame.2019.03.042. Used with permission CC BY-NC-ND 4.0.*

Other activities and achievements

Dr ZONG Yichen (Research Fellow, NUS) gave a virtual presentation titled "Performance of diesel engine fueled with $PODE_3$ at partial loads" at the *International Conference on Applied Energy 2020*, 1-10 December 2020. Co-authors of the presentation were Zhu Qiren, Yang Wenming and Markus Kraft.

CARES IRP 3 researchers (shown by *) gave the following virtual presentations at the *38th International Symposium on Combustion*, 24-29 January 2021:

- "Atomic insights into the sintering process of polycyclic aromatic hydrocarbon clusters" (Dingyu Hou, Qingzhao Chu, Dongping Chen, Laura Pascazio*, Markus Kraft*, Xiaoqing You)
- "Aromatic penta-linked hydrocarbons in soot nanoparticle formation" (Laura Pascazio*, Jacob W. Martin*, Angiras Menon*, Dingyu Hou, Xiaoqing You, Markus Kraft*)
- "Kinetic Monte Carlo statistics of curvature integration by HACA growth and bay closure reactions for PAH growth in a counterflow diffusion flame" (Gustavo Leon, Angiras Menon*, Laura Pascazio*, Eric Bringley, Jethro Akroyd*, Markus Kraft*)
- "Surface properties of heterogeneous polycyclic aromatic hydrocarbon clusters" (Kimberly Bowal, Laura Pascazio*, Hongyu Wang, Dongping Chen, Markus Kraft*)
- "Reactive localized π-radicals on rim-based pentagonal rings: properties and concentration in flames" (Angiras Menon*, Jacob W. Martin*, Gustavo Leon, Dingyu Hou, Laura Pascazio*, Xiaoqing You, Markus Kraft*)
- "Temperature and CH* measurements and simulations of laminar premixed ethylene jet-wall stagnation flames" (Jochen Dreyer, Eric Bringley, Manoel Manuputty*, Jethro Akroyd*, Markus Kraft*)

Dr Laura PASCAZIO (Research Fellow, CARES) gave a virtual presentation at the *UK Consortium on Turbulent Reacting Flows (UKCTRF) Annual Meeting*, 30-31 March 2021. Co-authors of the presentation were Jacob MARTIN, Angiras MENON, Jethro AKROYD and Markus KRAFT.

Dr Laura PASCAZIO received the Combustion Institute (British Section) award for virtual registration at the *38th International Symposium on Combustion*. The grant covered the full registration cost for the symposium.

Prof. Markus KRAFT (PI, CAM) gave a talk titled "Carbonaceous nanoparticle formation in flames" for the Combustion Webinar series on 29 August 2020.

Prof. Markus KRAFT gave a talk titled "Titania nanoparticles structure and composition" at the *Nanoparticle Synthesis in Spray Flames* short course hosted by Heidelberg University on 9 February 2021.

IRP 4

BETTER, CLEANER HEAT USAGE

Better, Cleaner Heat Usage is a new IRP 4 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. IRP 4 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.

IRP 4 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 significant problems by a series of connected work packages, including fundamental studies on particulate emissions from marine engines burning fossil or alternative fuels, waste heat utilisation methods such as the use or Organic Rankine Cycles and the associated turbomachinery, high-efficiency heat exchangers, and estimates and measurements of pollutant dispersion from ships and its reception in port and urban areas.

The reporting period is in the middle of the pandemic, which reduced the pace of the research for many reasons. Work from home was not always as productive as we would have liked, given that access to supercomputers and high-performance clusters for the large datasets from the Computational Fluid Dynamics in WP1 and WP4 was slower. Also, there was no opportunity to travel and hence exchange ideas, however this was mitigated to a large extent by regular online meetings. But more importantly, there was a restructuring of the personnel working on the project, with the post-docs in WP2 and WP4 leaving. We are recruiting to fill these vacancies presently.

Professor Epaminondas Mastorakos, PI
University of Cambridge

Update on work package 4.1

Engine combustion — best fuel, best operating condition

Shrey TRIVEDI (Research Assistant, CAM) reported that in the previous update, the initial stages of the simulations of a heavy-duty MTU396 research engine using STARCD (an industry-standard CFD code) coupled with the Conditional Moment Closure turbulence-reaction interaction model, were presented (Figure 4.1). These have been improved further to achieve excellent agreement with the measurement data in terms of pressure trace and trends with NOx and engine-out soot as a function of operating condition. Figure 4.2 shows the pressure trace comparison between CFD and experiments for three different cases with varying start of injection (SOI) of fuel. Variations in duration of injection and oxidiser mass-fraction have also been analysed. The simulations provide an estimate of soot mass through a semi-empirical two-equation model. Further, a postprocessing tool based on Incompletely Stirred Reactor (ISR) concept is under development which takes the frozen flow field from an existing CFD solution and on it applies more a sectional soot model to predict soot particle size distribution.

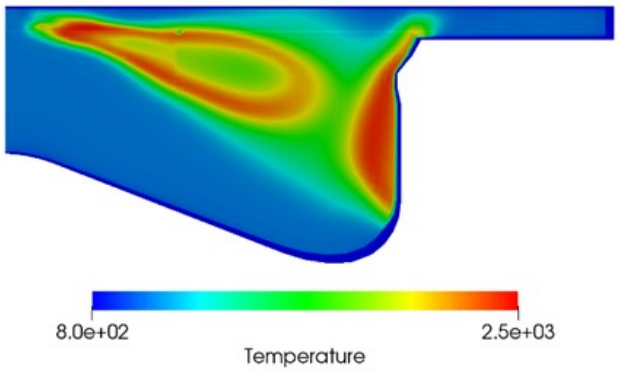


Figure 4.1: Slice of Temperature field taken from the MTU396 research engine.

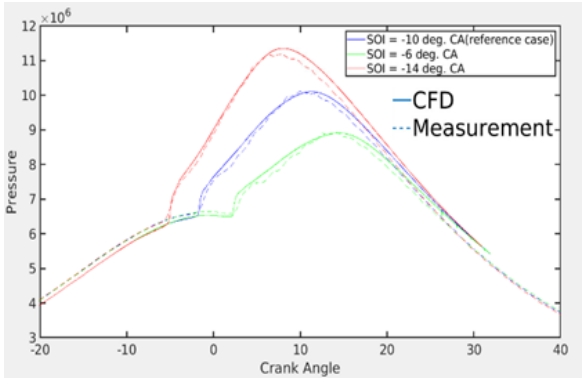


Figure 4.2: Pressure trace comparison between CFD and Experiments for SOI variation cases.

Shrey TRIVEDI

Update on work package 4.3

High-efficiency heat exchanger

Dr Ravi RANJAN (Research Fellow, CARES) has been working on three dimensional numerical simulations of the finned tube heat exchangers to study their thermo-hydraulic performance. Four tube sizes (*circular*, *oblique*, *flat* and *tilted flat*) are selected in this study, where the oblique tube has a similar cross-sectional area compared to its circular counterpart, whereas flat and titled flat tubes have a similar surface 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, flat tube and tilted flat tube heat exchanger and compare their results against the conventional circular finned tube heat exchanger.

Overall, the finned flat tube heat exchanger has outperformed other candidates during air-side investigation. In Figure 4.3, the strength of the wake region (flow separation) observed at the downstream of the various tube geometries has been shown at the air flow velocity of 0.914 m/s. The circular tube showed the highest wake formation at the downstream of flow field, whereas the flat tube showed the lowest. This directly concludes that with the increase in fluid flow resistance, the pressure drop across the various tube geometries increases. The flat tube showed a higher heat transfer performance and lower pressure drop compared to its counterparts. This compound effect of superior heat transfer performance and lower pressure drop has also resulted in a lower fan power requirement to produce comparable air-side heat transfer performance for the finned flat tube heat exchanger.

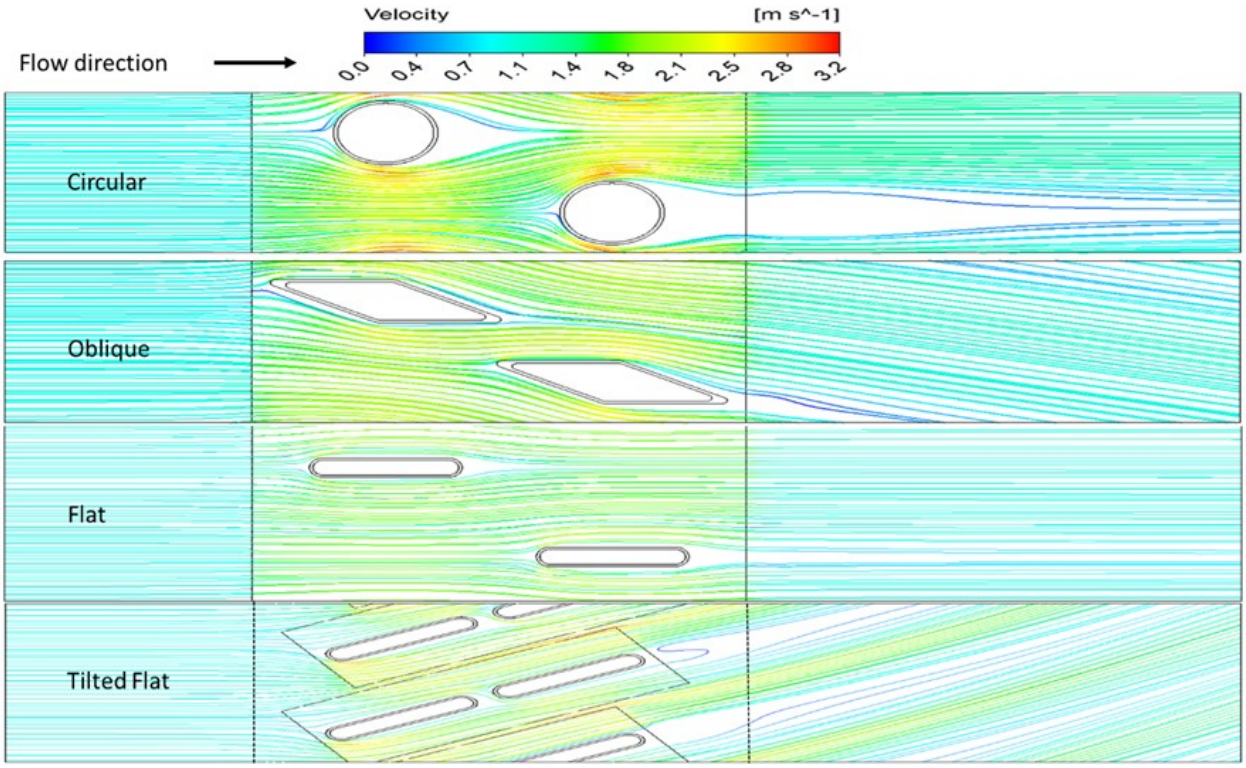


Figure 4.3: Air flow field across various tube geometries at inlet air velocity of 0.914m/s.

Air-side performance

In general, the size and strength of wake regions increases with the increase in flow rate, which is clearly shown in Figure 4.4. Both at lower flow rate and higher flow rate, the wake region observed in the case of the circular tube are quite significant. These wake regions are the flow separations taking place after it detaches from tube surface and forms a wake at the downstream. It leads to the increase in flow resistance which finally contributes to the drop in pressure across the tube. The slenderer shape with less frontal area leads to less flow separation as shown in oblique, flat and tilted flat tubes, thus contributing to a lower pressure drop compared to its circular counterpart. The lower footprint of tube geometry also produces lower flow resistance and flow separation. Overall, the footprint of the flat and tilted flat tube are lower than the oblique and circular tubes, which results in a lower pressure drop as shown in the case of flat and tilted flat tubes.

The pressure drop across various tube geometries is shown in Figure 4.5. The pressure drop is found to be the highest in the circular tube and the lowest in the tilted flat tube. At a lower flow rate, the pressure drop differences are lower and increased with the increase in flow rate. This is directly related to the fact that with increasing flow rate, flow separation and wake region increase.

The outlet air temperature of the flat tube and oblique tube is consistently lower compared to the circular tube and tilted flat tube as shown in Figure 4.6. The heat transfer performance depends on both the size of wake region and the early reattachment of the flow. Oblique, flat and tilted flat tubes showed smaller wake regions compared to the circular tube, however the lack of early reattachment of flow in the tilted flat tube is apparent, which results in inferior heat transfer performance.

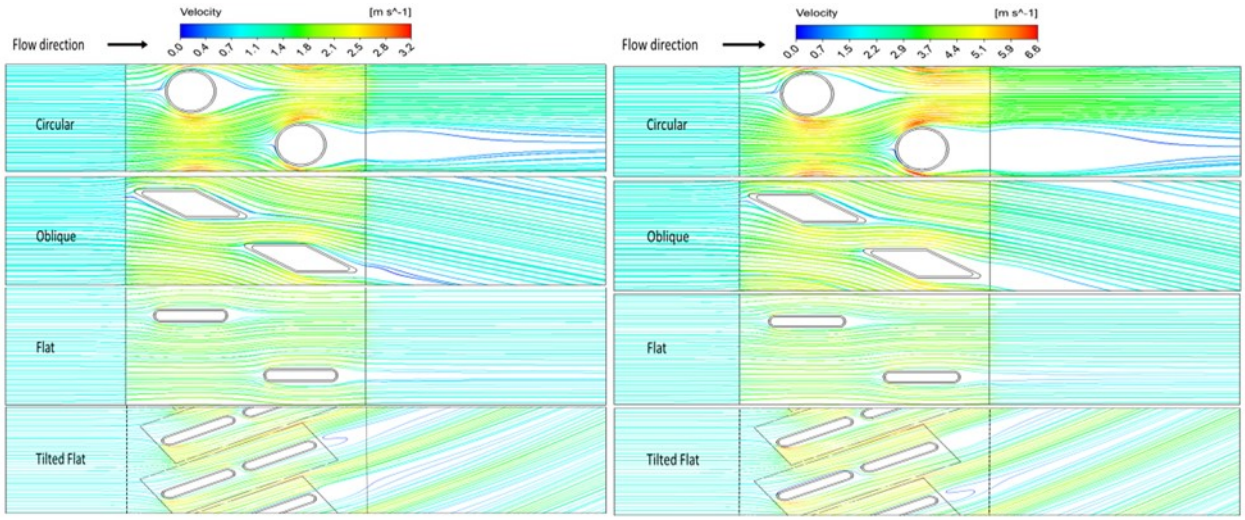


Figure 4.4: Air flow across various tube geometries at inlet air velocity of 0.914 and 2.03m/s.

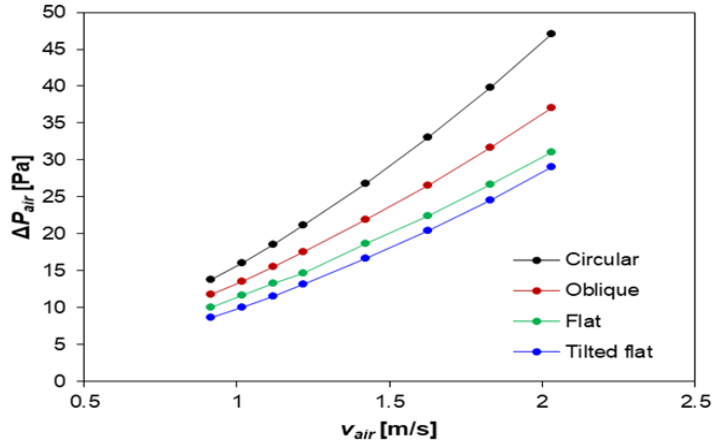


Figure 4.5: Comparison of pressure drop across various tube geometries.

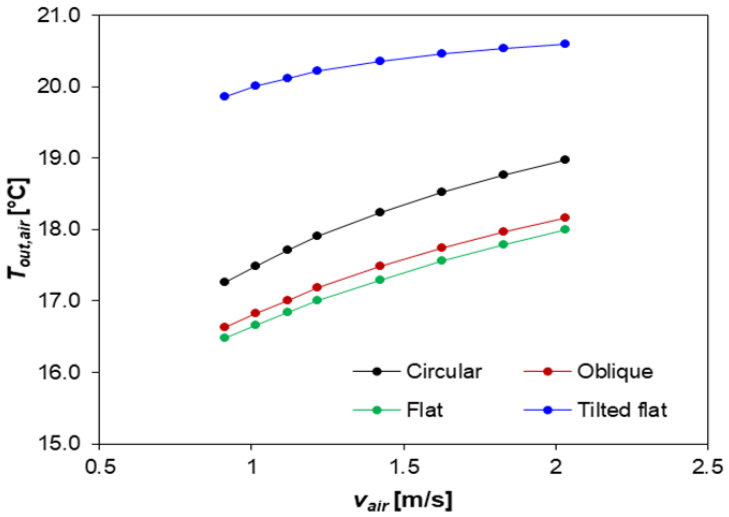


Figure 4.6: Comparison of air outlet temperature across various tube geometries.

In Figure 4.7, the calculation for cooling produced per unit fan power for various tube geometries is reported at 80% of fan power. The coupled effect of superior heat transfer performance and lower pressure drop offered by the flat tube has enabled it to deliver higher cooling power per unit fan power at most of the air flow rate conditions, as shown. It may be concluded that a lower fan power is required to provide comparable air-side heat transfer performance of a finned flat tube heat exchanger.

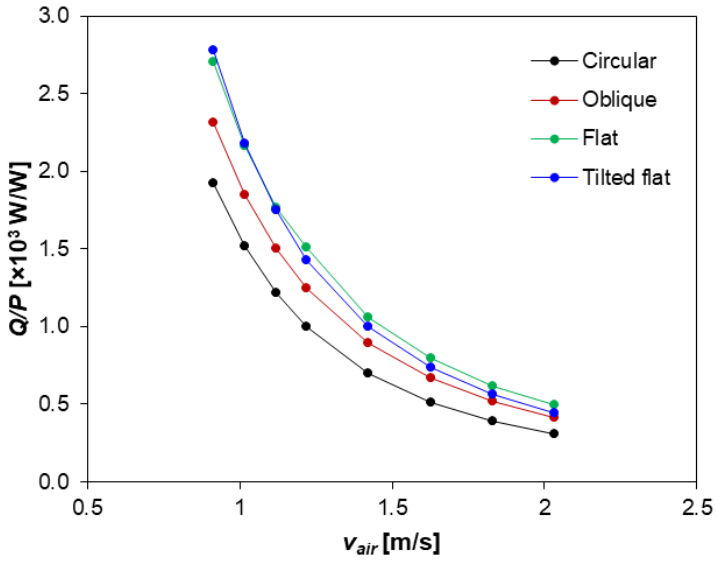


Figure 4.6: Cooling produced per unit fan power of various tube geometries.

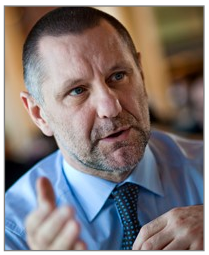
Dr Ravi RANJAN

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.

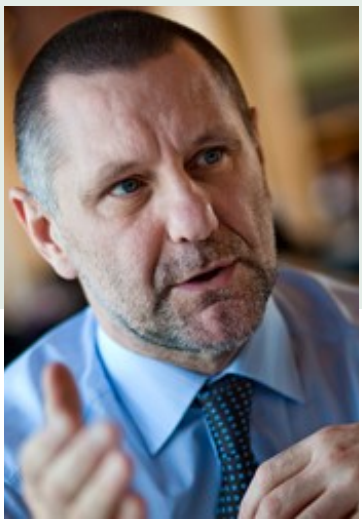
IRP BB Principal Investigators:



Professor Steve EVANS
University of Cambridge

Professor S. VISWANATHAN
Nanyang Technological University

Assoc Professor Kenneth HUANG Guang-Lih
National University of Singapore



OVERVIEW

Over the past six months, the IRP BB team has continued to investigate alternative business models for the adoption of sustainable innovations and technologies. A manuscript is in progress on this topic. BB and IRP 2 are also working together to investigate how to optimise the use of renewable energy that could be generated on-site by local electro-chemical manufacturers.

A survey that will measure attitudes towards clean technology adoption has been sent out to organisations and nearly all data has been gathered. The IRP BB researchers are also looking into the impact of major international policies and treaties on clean-tech innovations and capabilities, as well as examining attitudes towards clean energy adoption across SMEs and big industries in Singapore.

BB is continuing its close collaboration with the technology IRPs to identify the most promising technologies for adoption by industry. They are also working with the UK government on decarbonisation roadmaps.

Professor Steve Evans, PI
University of Cambridge

Update on work package BB.1

Business model innovation potentials

Research continues on evaluating alternative business models for adopting sustainable innovations and technologies. Most of the findings of this paper have been shared in previous reports. As the Research Fellow working on this project has left the services of C4T, there has been a delay in completing the final manuscript of the paper. It should be completed in the next six months.

In collaboration with IRP 2, the team is working on investigating production scheduling problems that can take advantage of on-site generation of renewable energy (when available) to support local electro-chemical 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. Initially we formulated it as a dynamic programming problem under joint centralised manufacturing and decentralised manufacturing that is supplied by on-site generation solar energy. The formulation was recently changed to model a continuous review inventory system. With this formulation, it is hoped to generate results and insights more quickly.

Update on work package BB.2

Policy formulation, customer and industry perceptions

Under this work package, work continues to quantify the effect of international policies on clean technology innovation. The team is also working on understanding industry perceptions and attitudes and has finished 90% of the fieldwork phase for the survey.

In WP2, the research focus is on the impact of major international policies and treaties on technological innovation and clean-tech capabilities. Examination of their impact continues on the trajectories of chemical and clean technologies in Singapore compared with China. Based on the patented innovation dataset and firm level dataset we have collected and obtained, the researchers have been examining and quantifying these policy impacts as well as any moderating factors from both the macro industry level and micro firm level using the respective datasets. Analyses and reports of the empirical results on this important research topic are continuing. Different potential internal and external factors which could influence or moderate the results are being tested using different model specifications in the difference-in-differences estimation models. In addition, the researchers are in the process of interpreting the policy and managerial implications of this evidence-based research. The ultimate goal is to make policy recommendations that will better foster clean technology and related technological innovations by enhancing and improving the innovation capabilities of companies in the chemical and energy industries.

To achieve this research goal, the value of patented innovations in China across different industries must first be understood and estimated, including those of the chemical and environmental technology industries. To examine this key research question, the researchers collect and con-

duct the analysis using the large-scale, comprehensive annual Inventors Survey database (ISDB) collected by China National Intellectual Property Administration (CNIPA), which consists of 12,869 firms linked to 30,693 patents granted between 2010 and 2012. This paper is now under third-round revise and resubmit at *Technological Forecasting and Social Change*, which is a leading journal in technology assessment, technology policy and technological forecasting and has a high Journal Citation Reports impact factor (2019) of 5.846.

As a part of WP2, the survey to understand the attitudes and perceptions of managers in Singapore organisations towards clean energy adoption has been implemented data collected from about 180 participants who are in the top management in their respective organisations (CEOs, CTOs, business owners, sustainability managers, technology experts). The last phase with about 20 -30 participants is underway. The results on the current data look promising and are being tested for various hypotheses posed while designing the survey study. The 200 participants (targeted number) represent Singapore-based organisations from industrial as well as non-industrial sectors. The industrial and non-industrial participants are further sorted in subsectors, and hypotheses are being tested for the main as well as sub-categories. The study of the industrial sector versus non-industrial sector has provided interesting inferences regarding the perception of the role of leadership in the Singapore organisations with regard to sustainable actions. The comparison between the current data on big and small industrial participants have indicated different motivations and deterrents for adoption of clean technology. In addition to these studies, several sector-specific results, e.g. for government organisations, financial sectors and big emitting industries will be documented in the manuscript, which is in progress.

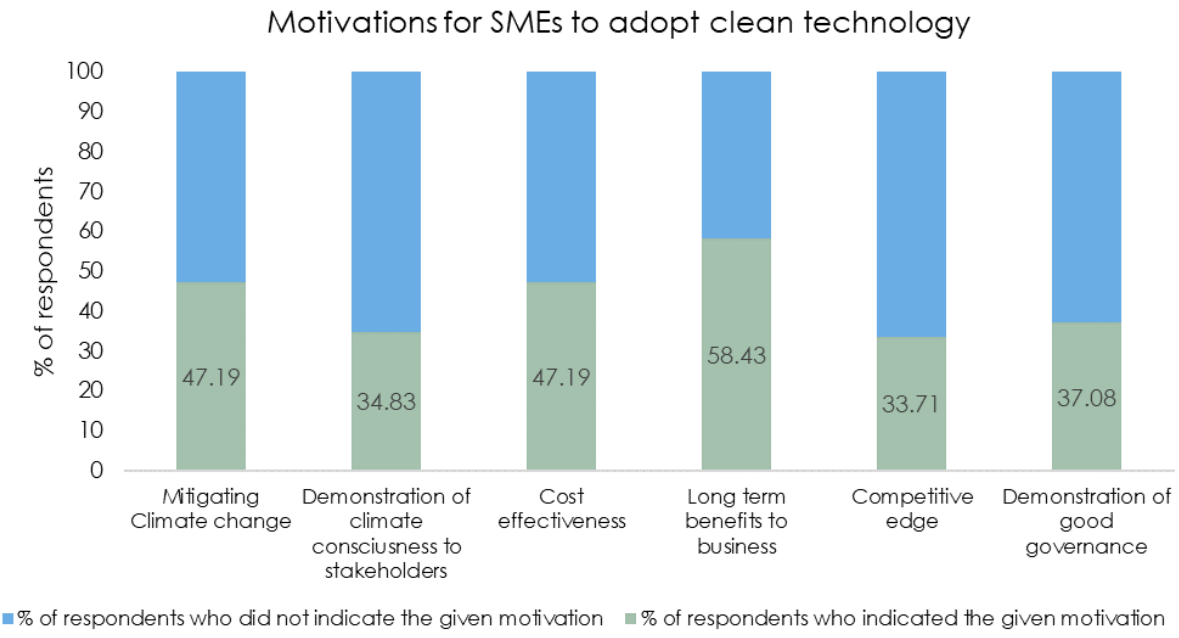


Figure 5.1: Motivations for small and medium-sized enterprises to adopt clean technology.

For the theoretical understanding of perceptions, a framework is being developed on the basis of Belief-Action-Outcome model that can elucidate the data based on a combination of cognitive psychology theories and organisational behaviour theories. After the manuscript publication (hopefully within six months) the second phase of this project will commence, possibly by Q1 of 2022. This will include sector-specific insights via interviews and another survey designed to specifically understand implementation of CO_2 reduction technologies in big industries in Singapore. Some sample results based on current data are shown in Figures 5.1 and 5.2.

The figures show the motivations for adoption of clean technology for big industries as indicated by the survey results so far. From these results, the main motivation for the big industry is mitigation of climate change followed by long-term benefits to the business. Considering that big industries are the biggest emitters, this demonstrates climate consciousness on their part and recognition that it will help in long term for their business too. On the other hand, for the smaller industries, long terms benefits and cost effectiveness are the most important motivations than climate change itself. Climate change itself is not a consideration for them, as small industries still struggle to quantify their carbon footprint and thus contribution to climate change. Gaining a competitive edge is, currently, not the most important consideration for both types of industries indicated here, though it might gain importance as more and more companies adopt clean technology. Also, as compared to SMEs, big industries clearly are more concerned about the stakeholders and are subject to more scrutiny, while the ESG data is becoming more a part of investment decisions.

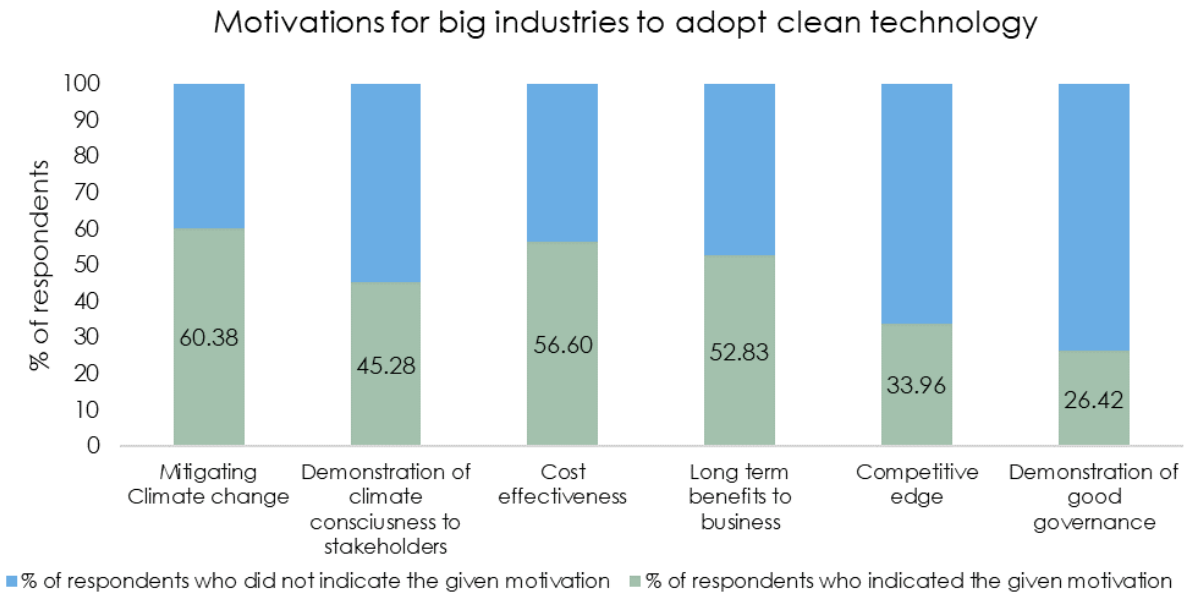


Figure 5.2: Motivations for big industries (more than 1,000 employees) to adopt clean technology.

Update on work package BB.3

Future roadmap for industrial decarbonisation, including international comparisons

IRP BB continues to work closely with the technology IRPs, including meetings with emerging (and potential) spin-outs from IRP 1, IRP 2 and IRP 3. The researchers have also been collecting and analysing decarbonisation reports for Singapore as well as the ASEAN region to gain insights into regional industrial decarbonisation. IRP BB has also been working separately with the UK government on their decarbonisation roadmaps.

A literature and methodological review of roadmapping techniques that may be suitable for the specific use case is now complete; he multi-level perspective ('MLP') as developed by Geels & Schot was chosen [1, 2] (the dominant graphical description of their model is copied below for reference). The initial use case is focused on the electrochemistry of IRP 2.

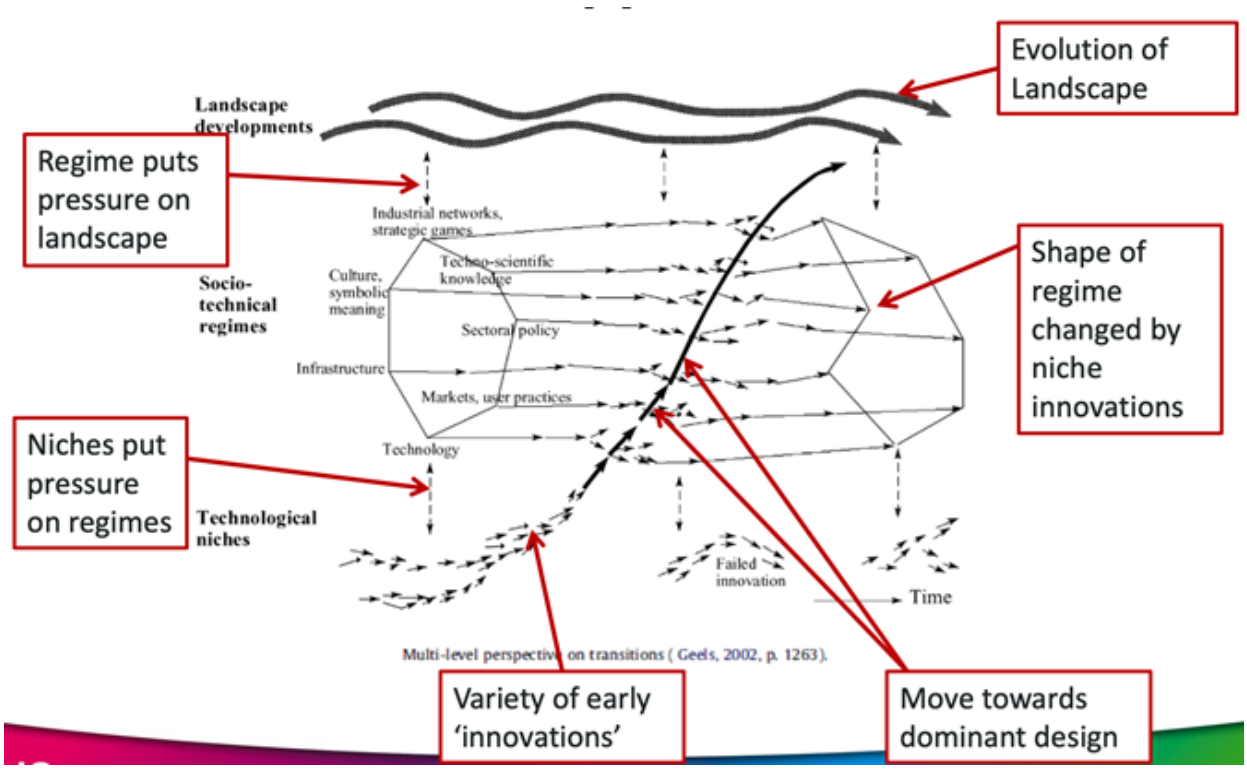


Figure 5.3: Graphical description of Geels and Schot's multi-level perspective model. Taken from Steward, Tom. 2012. 'A Brief Introduction to the Multi-Level Perspective (MLP)'. 2012. http://projects.exeter.ac.uk/igov/wp-content/uploads/2012/12/DOWNLOAD-Multi-Level-Perspectives.pdf.

[1] F. W. Geels and J. Schot, "Typology of sociotechnical transition pathways," Res. Policy, vol. 36, no. 3, pp. 399–417, Apr. 2007, doi: 10.1016/j.respol.2007.01.003.

[2] F. W. Geels, B. Sovacool, T. Schwanen, and S. Sorrell, "Accelerating innovation is as important as climate policy," Policy Forum, vol. 357, no. 6357, pp. 1242–1244, 2017.

IRP JPS

THE J-PARK SIMULATOR

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

IRP JPS Principal Investigators:

Professor Markus KRAFT
University of Cambridge

Assoc Professor Raymond LAU Wai Man
Nanyang Technological University

Professor Iftekhar KARIMI
National University of Singapore

OVERVIEW

Over the past six months, the J-Park Simulator (JPS) has progressed on several fronts with regard to developing new capabilities for enhancing the existing JPS architecture. This step is crucial in order to make use of the full potential of Semantic Web technologies in the JPS. For instance, we have been working on developing a Knowledge Graph (KG) Router which equips the JPS infrastructure with new capabilities that removed the dependency of the JPS agents on the hardware (servers) where the knowledge graph is deployed. Consequently, migrating the knowledge graph to a new set of servers or replacing an existing server with a new one will no longer require any modification in the agents. We have also addressed the knowledge graph storage dependency issue by abstracting storage access to allow JPS agents to interact with the knowledge graph through SPARQL queries and updates in a storage agnostic manner. Furthermore, we have developed knowledge graph tools to perform common tasks such as renaming of IRIs and cloning of data from one repository to another. The tools are designed to be robust and capable of processing large numbers of RDF triples, and with the aim to make usage of the knowledge graph and agent development easier. Apart from these, an IRI Resolution Agent was created to address the resolvability of IRIs of instances represented using ontologies in the knowledge graph. This factor is critical in accessing data and the semantics in the JPS, and has been underpinned by the directory listing feature of web servers. The JPS knowledge graph is rapidly increasing and has tens of gigabytes of ontologised data represented using RDF/OWL. In order to reduce the load on the servers, the developed IRI Resolution Agent will capture any request for an instance IRI and perform a SPARQL query against the JPS knowledge graph to identify its availability, as well as retrieve all data, metadata, semantics, and links to other instances.

In addition, we have been working on upgrading the novel Question Answering system for chemical data in the JPS knowledge graph – also known as "Marie". This work involves the implementation of: 1) faster query mechanism based on the Linked Data Fragment concept, and 2) automatic deployment mechanism based on Docker technology. We are also in the process of developing "what-if" scenario analysis for energy generation from different sources and their impacts on climate change, as well as gauging and understanding complex relationships between UN sustainable development goal indicators such as environmental goal indicators and economic goal indicators.

Professor Markus Kraft, PI
University of Cambridge

Update on work package JPS.1

Big data — sensors and data modelling

Dr Jethro AKROYD (Senior Research Fellow, CARES), **Dr Sebastian MOSBACH (Senior Research Fellow, CARES)** and **Dr Feroz FARAZI (Research Associate, CAM)** have been working on developing "what-if" scenario analysis for the energy generation from different sources and their impacts on climate change, as well as in gauging and understanding complex relationships between UN sustainable development goal indicators such as environmental goal indicator and economic goal indicator. To this end, Dr Farazi assessed the suitability of implementing digital twins using Semantic Web technologies in this context. As challenges posed by climate change are inherently interdisciplinary, the development of solutions requires the consideration of economic, engineering, environmental, and social factors over a range of geographic scales. It may also require the development of new concepts, for example, to facilitate the consideration of societal practices and patterns of consumption in the analysis of different solutions. These factors are strongly interconnected and it is widely appreciated that interoperable, collaborative models that span multiple disciplines are necessary, perhaps in the form of digital twins supported by artificial intelligence. Therefore, the Semantic Web technologies, that offer the potential to increase the interoperability between heterogeneous data formats as well as models via formalising the representation of data and services, has been established to be suitable for this purpose.

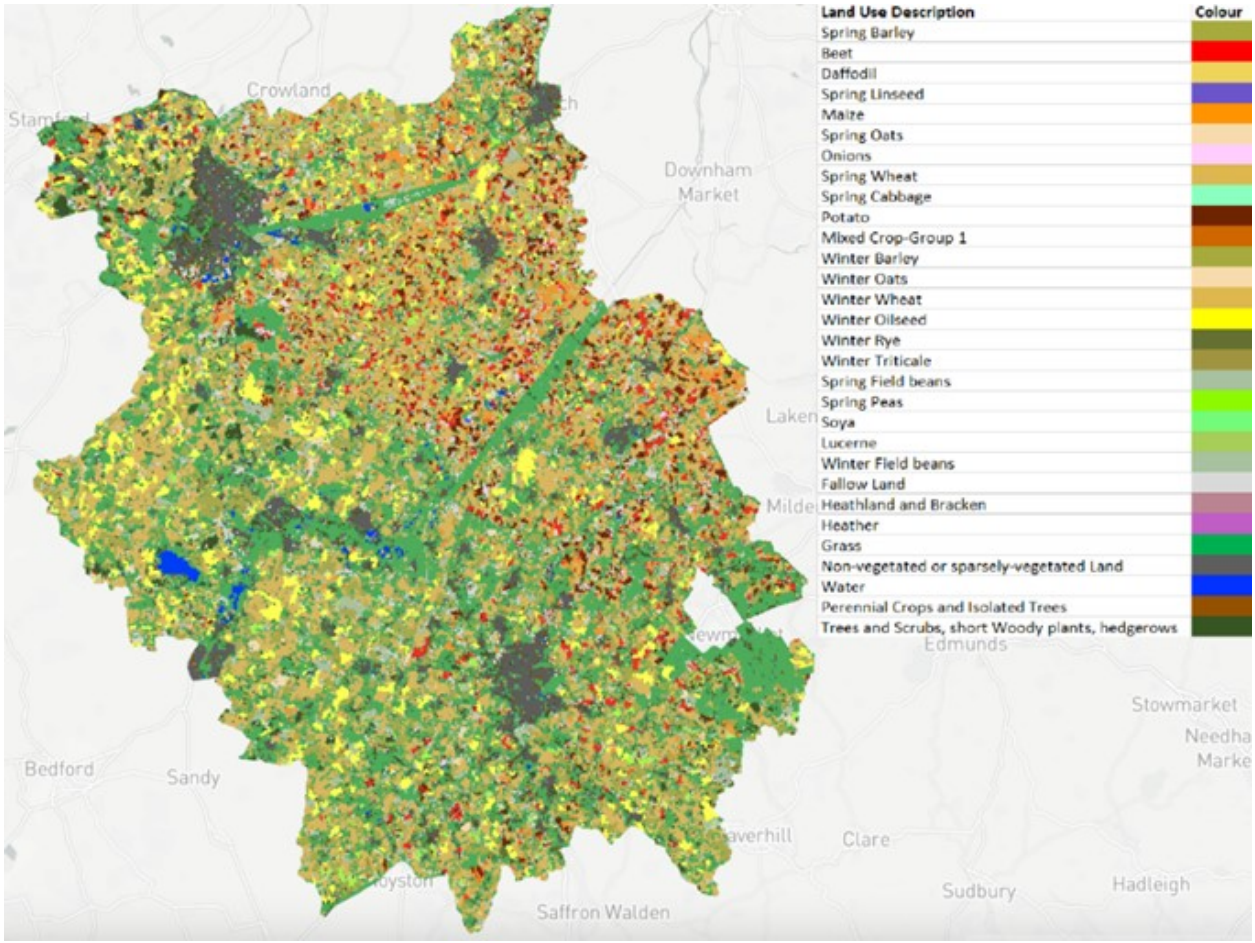


Figure 6.1: Depiction of land use information about Cambridgeshire, UK, using MapBox, with data retrieved from OntoLandUse and OntoCropMapGML in the form of land use codes (originally sourced from the Crop Map of England 2019).

The transformation of the energy system is driven by economic factors, the need to reduce greenhouse gas emissions and to achieve higher efficiency. Singapore's potential to implement renewable energy solutions e.g., biomass, to reduce its carbon footprint is limited. Moreover, progress, advancement and cost reduction of solutions depend considerably on their global application. Hence, Singapore needs to develop solutions involving other parts of the world, in particular with our agricultural producing neighbours. Consequently, Dr Akroyd, Dr Mosbach and Dr Farazi have developed four ontologies (OntoCropMapGML, OntoLandUse, OntoCropEnergy, and OntoSDG) for describing the concepts relevant to such scenario analyses. OntoCropMapGML, the ontology for representing crop map data published in GML format, together with the GML structure, is used as the basis for creating the CropMapGML to RDF converter. The CropMapGML to RDF converter is used to parse land data and metadata, including the geometry, land use code, bounding box, area, length and identifier from an input GML file, and represent them using RDF. The OntoLandUse ontology is developed by analysing land-use codes applied in the UK to indicate the type of use i.e., type of crops produced in agricultural land, for a piece of land designated by a hexagon for a rural payment scheme that assists farmers. As UK land-use codes are readily and publicly available, we have utilised them in the first instance to develop the OntoLandUse ontology. As a next step, the ontology will be extended to include other regions' land-use codes. The OntoCropEnergy ontology represents crop yield, gross calorific value, and net calorific value of different crops while the OntoSDG ontology is developed to represent the UN sustainable development goals, targets, indicators, relationships between the goals and targets, the targets and indicators, the positive or negative influence of an indicator on another, the different indicators of locations, as well as the environmental indicators of industrial facilities, e.g., power plants. Dr Farazi has also developed a tool called "EntityRDFizer", which is underpinned by an ABox Generation data template, to create instances of crops, land use codes and the sustainable development goal indicators in the knowledge graph.

Figure 6.2: Screenshot of an interactive tool displaying the value of UN Sustainable Development Goal Indicator 9.4.1 for Power Plants in the UK. The Indicator is the CO_2 produced per unit of manufacturing value-added. The colour of the points corresponds to the value of the indicator, and the radius of the point corresponds to the capacity of the plant.

As part of the dynamic geospatial knowledge graph development, Dr Farazi, in close collaboration with **Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES)**, Dr Akroyd and **Mr Tom SAVAGE (in-kind MPhil student, CAM)**, has also been working on the geospatial search functionality and semantic representation of hexagonally spilt land parcel data for the UK. Similarly, as land parcel data for the UK are readily and publicly available, we have utilised it in the first instance.

Update on work package JPS.2

Surrogate models and superstructure

Dr Jethro AKROYD (Senior Research Fellow, CARES), **Dr Sebastian MOSBACH (Senior Research Fellow, CARES)**, **Dr Feroz FARAZI (Research Associate, CAM)** and **Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES)** have been involved in driving forward the overall JPS architecture. For instance, they have enhanced the JPS architecture by developing a Knowledge Graph (KG) Router which equips the JPS infrastructure with new capabilities that removed the dependency of the JPS agents on the hardware (servers) where the knowledge graph is deployed. Therefore, migrating the knowledge graph to a new set of servers or replacing an existing server with a new one will no longer require any modification in the agents.

Triple stores are used in the project for storing knowledge graphs. Some example triple stores are RDF4J, Blazegraph, and GraphDB. However, different triple stores have different structures for endpoint IRIs. With the development of the KG Router, the JPS agents and users are not required to be aware of the specific details of the often-lengthy endpoint IRIs. Furthermore, the JPS infrastructure needs to be triple store agnostic. For this aspect, **Dr Casper LINDBERG (Research Fellow, CARES)** has been working on modifying the JPS base libraries (JPS_BASE_LIB) to improve the interactions with and maintenance of the knowledge graph. Dr Lindberg, in close collaboration with Dr Farazi, Dr Mosbach and Mr Chadzynski, has addressed the storage dependency issue by abstracting storage access to allow JPS agents to interact with the knowledge graph through SPARQL queries and updates in a storage agnostic manner.

This involves two main components:

- RemoteKnowledgeBaseClient , and

- FileBasedKnowledgeBaseClient, both of which implement abstract methods declared in KnowledgeBaseClientInterface. The RemoteKnowledgeBaseClient was developed using Jena JDBC, an open-source API built with the integration of SPARQL features over different types of data storage. This component enables the JPS agents to issue SPARQL query, insert and delete operations virtually on any triple store. The component has been tested against the RDF4J and Blazegraph triple stores to verify the uniformity of its query and update functionalities before integrating into the JPS base libraries. The FileBasedKnowledgeBaseClient was developed using Jena RDFConnection, an open-source SPARQL operations API that provides a unified set of operations for working on RDF data loaded from file-based storage into a Jena dataset. This component extends SPARQL query and update functionalities to OWL files in a manner consistent with the RemoteKnowledgeBaseClient.

In addition, Dr Lindberg has been developing knowledge graph tools to perform common tasks such as renaming of IRIs and cloning of data from one repository to another. The tools are designed to be robust and capable of processing large numbers of RDF triples, and with the aim to make usage of the knowledge graph and agent development easier. Dr Lindberg is in the process of integrating the new abstracted storage access methods with the existing scenario agent implementation in order to support the "parallel world" framework.

Dr Farazi has also developed an IRI Resolution Agent to address the resolvability of IRIs of instances represented using ontologies in the knowledge graph. This factor is critical in accessing data and the semantics in the JPS, and has been underpinned by the directory listing feature of web servers. The JPS knowledge graph is rapidly increasing and has tens of gigabytes of ontologised data represented using RDF/OWL. In order to reduce the load on the servers, the developed IRI Resolution Agent will capture any request for an instance IRI and perform a SPARQL query against the JPS knowledge graph to identify its availability, as well as retrieve all data, metadata, semantics, and links to other instances.

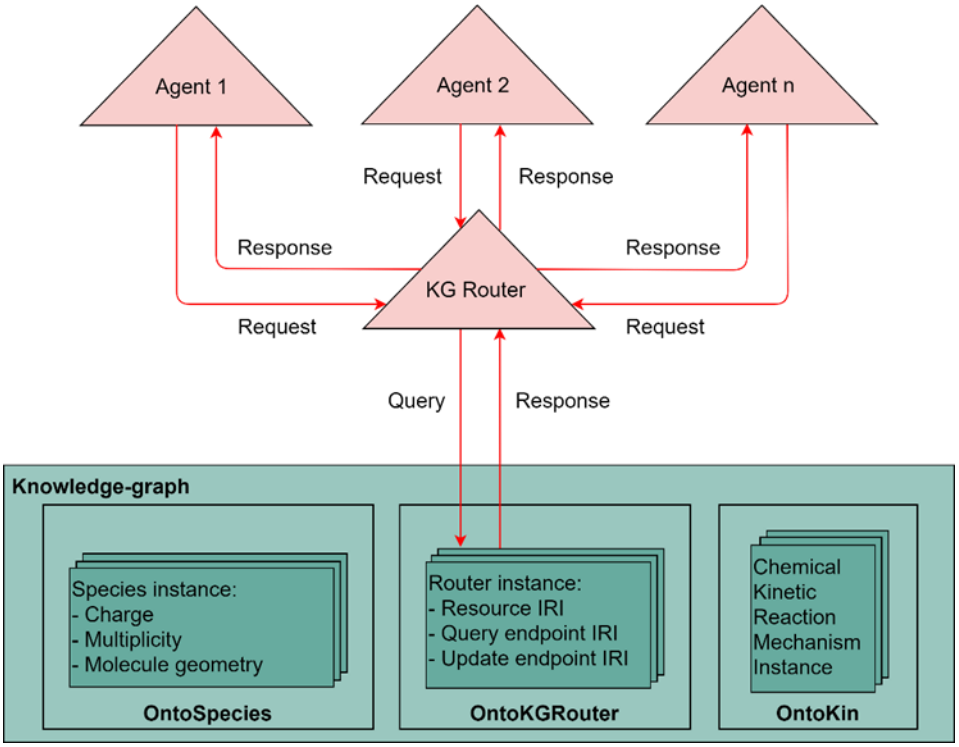


Figure 6.3: The KG Router receives a request from an agent to provide the query or update endpoint of a specific resource in the knowledge graph by querying OntoKGRouter and returning the endpoint to the requesting agent.

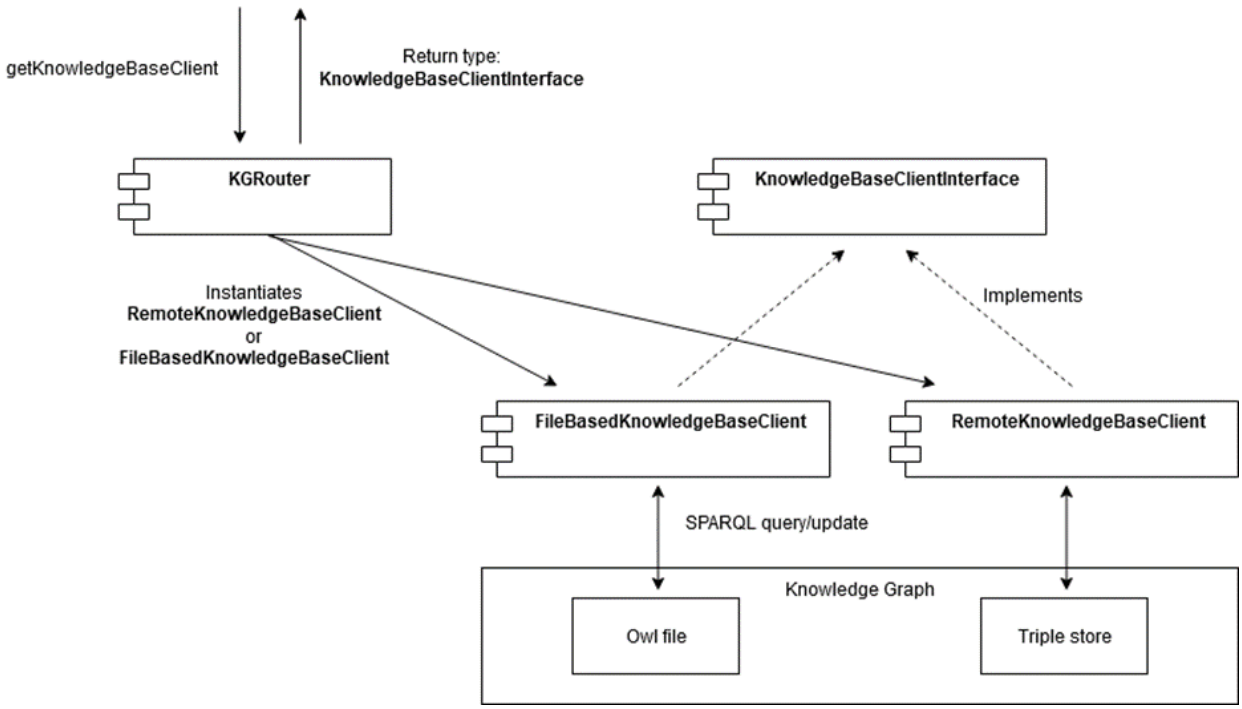


Figure 6.4: Diagram of the KnowledgeBaseClient and KGRouter implementation – for technology agnostic knowledge graph interactions. KnowledgeBaseClientInterface is an interface implemented by the Remote-KnowledgeBaseClient class, to access triple stores, and the FileBasedKnowledgeBaseClient class, to access OWL files. The KGRouter class instantiates either a RemoteKnowledgeBaseClient or FileBasedKnowledgeBaseClient depending on the requested resource (file path or IRI), and returns an object of the abstracted type Knowledge-BaseClientInterface.

Ms Laura ONG (Software Developer, CARES) together with Mr Chadzynski has extended the functionality of existing JPS agents to ensure their compliance with the new JPS Agent framework as described in the previous reporting period. This involves utilising various validation methods to verify that data, in the form of JSON packets, are sent in the correct type and format to the corresponding agents in the framework. Furthermore, Ms Ong has removed numerous hardcoded strings from the agents to enable the agents to read files via JSON parameters that it receives from the other agents. Ms Ong also supported Mr Chadzynski in implementing the JPS Agent Interface framework (described in the previous reporting period). With this implementation, each agent inherits the "JPSAgent" class and its "processRequestParameters" method, as well as implements the appropriate "validateInput" method. The "validateInput" method verifies if the input(s) that an agent receives is valid e.g., whether a string is an IRI or a Boolean, and returns "true" if the input(s) is valid; otherwise returns "false". If the "validateInput" method returns "true", the JPS agent continues with its task; or else the "processRequestParameters" method logs an error and the JPS agent terminates its task.

Ms Ong has also improved the deployment process by revising legacy projects such as the Arbitrage Spotter, Mass Exchange Network and Semakau Island Smart Grid projects, as well as providing documentations for the deployment process. In addition, together with **Mr Russell FOO (Intern, CARES)**, Ms Ong has developed unit tests and operating system agnostic features in the "JPS_BASE_LIB" package to improve the performance of the deployment process in non-Windows servers.

Mr Foo, in close collaboration with Mr Chadzynski, has designed and developed an automated Python virtual environment building system. This work is motivated by the fact that multiple projects in the JPS utilise Python libraries e.g., machine learning libraries. This new provision significantly reduces the number of manual steps required during the deployment of any project with mixed – Java and Python – dependency requirements. The provision is being utilised by multiple projects e.g., a prototype of an ontology matching framework.

Mr Chadzynski is also heavily involved in supporting and providing guidance to the JPS team concerning documentation, questions on software design, agent development and non-functional requirements such as performance and scalability.

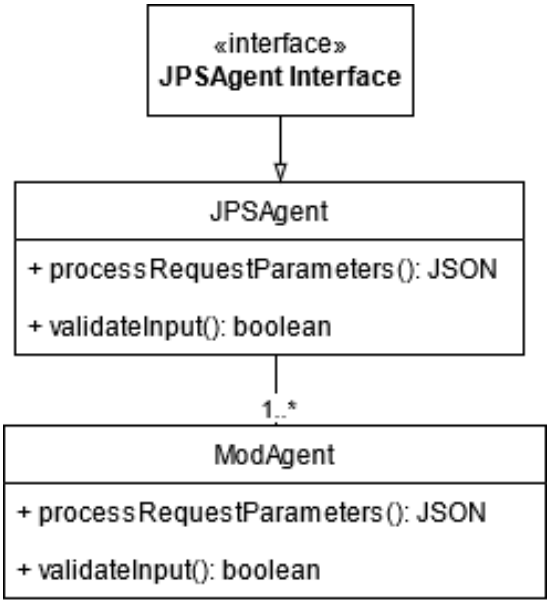


Figure 6.5: UML class diagram for JPS Agent implementation. The "JPSAgent Interface" is an abstract class from which the "JPSAgent" class inherits the "processRequestParameters" and "validateInput" methods. Any typical JPS agent (represented as "ModAgent" in the figure) utilising this framework will thus inherit and implement the corresponding "processRequestParameters" and "validateInput" methods based on the types of input and function it possesses.

Update on work package JPS.3

Implementation

Dr Aravind DEVANAND (Research Fellow, CARES) and **Mr Gourab KARMAKAR (Research Engineer, CARES)**, in close collaboration with **Dr Feroz FARAZI (Research Associate, CAM)**, **Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES)** and **Dr Nenad B. KRDZAVAC (Senior Software Developer, CARES)** have completed the development of the ElChemo framework, as described in the previous reporting period, which establishes cross-domain semantic interoperability between modelling tools used in the chemical and electrical engineering disciplines. Mr Chadzynski has supported Dr Devanand and Mr Karmakar in the system architecture design, which includes constructing a number of high-level abstractions in order to avoid repetition code for processing relevant digital representations. In this reporting period, Dr Devanand and Mr Karmakar have also programmed both the gPROMS and MATLAB agents to execute via the command line instead of a graphical user interface. Furthermore, the go:RUN functionality in gPROMS was utilised to configure the chemical system model such that it can be run on the High Performance Computing (HPC) system using the SLURM resource manager. Figure 6.6 illustrates the step-by-step activities of the components in the gPROMS agent. Dr Devanand and Mr Karmakar, together with Mr Chadzynski, have extended the existing asynchronous watcher to periodically monitor jobs and changes to existing files in the gPROMS agent workspace. Dr Devanand and Mr Karmakar have also redesigned both the gPROMS and MATLAB agents to ensure their compliance with the new JPS Agent framework. A RDF4J repository was also constructed to store the annotated metadata information about the output files generated by the agents. This metadata information includes location, date of creation and the agent that created it. The annotated output files, using the SPIN constraint agents, are checked for any constraint violation as shown in Figure 6.7. The ElChemo framework will terminate when any constraint violation is detected. Dr Devanand and Mr Karmakar have prepared and submitted a paper (under review), titled "ElChemo: A Cross-Domain Interoperability in a Chemical Plant" which describes the main ideas and results of this work.

Mr Karmakar also collaborated with **Mr Bryan LEE Zhen Yuan (NTU student)**, who is developing a model to generate the electrical engine's reactive power profile based on the active power profile obtained from the gPROMS agent. This work will improve the robustness and fidelity of the existing electrical system model employed in the ElChemo framework.

Dr Devanand also collaborated with **Mr Benjin LAU (NTU student)**, who is improving the existing carbon tax model employed in the carbon tax use case, in order to consider more types of alternative energy sources as well as the electrical network constraints when determining the optimal configuration for the power generators.

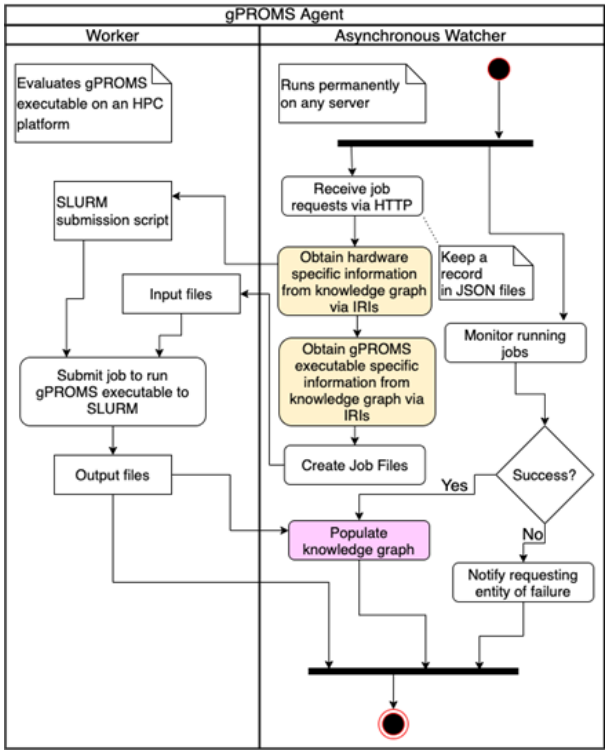


Figure 6.6: UML activity diagram of the gPROMS agent that enables the execution of gPROMS simulation asynchronously on an HPC platform upon HTTP requests. The yellow shaded actions represent the data retrieval operation of the agent from the knowledge graph, whereas the magenta shaded action represents the knowledge graph populating operation of the agent.

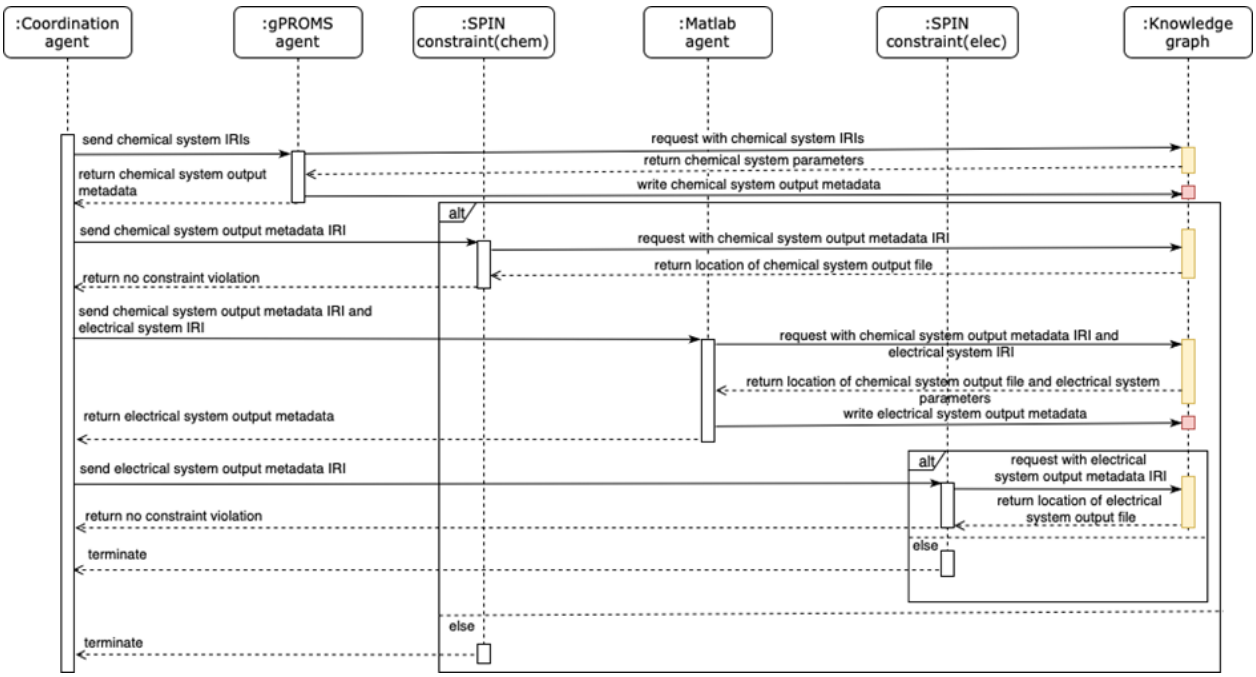


Figure 6.7: UML sequence diagram of ElChemo framework depicting the interaction between the different agents and the knowledge graph. Actions where the agent retrieves data from the knowledge graph are shaded in yellow and those where the agent populates the knowledge graph are shaded in magenta.

Ms Laura ONG (Software Developer, CARES) has redesigned the Energy Demand Side Management use case to ensure its compliance with the new JPS Agent framework, as well as to improve its modularity. Despite involving multiple components and distinct functions, the previous Energy Demand Side Management use case utilises a monolithic block of Python code to query and retrieve all the necessary data such as solar irradiation, electrical characteristics and behaviours from the knowledge graph. Subsequently, the same block of code executes the game theory simulation using the retrieved inputs. Ms Ong redesigned the monolithic block of code by separating the respective components (residential, industrial and commercial players), as well as the game theory framework into individual functions such that they can be packaged as distinct agents. The agents are able to apply the semantic web stack to query and retrieve information from the knowledge graph, and modify its data values by writing back into the knowledge graph. The revised use case employs a coordination agent to coordinate the distinct agents in order to fulfil the objective of reducing the peak to average ratio, which in turn, leads to lower stress on the main grid and hence providing cost savings for the customers. The enhanced modularity of the implementation provides the use case with the possibility to consider other game types or decision support frameworks.

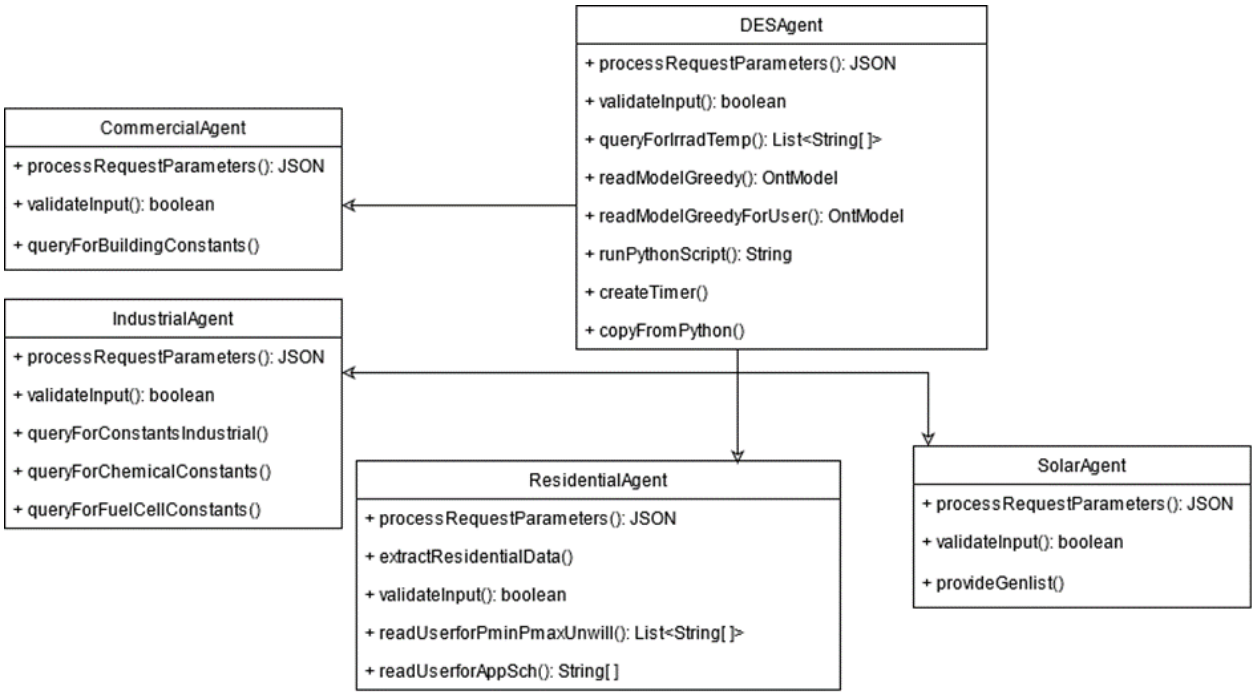


Figure 6.8: UML class diagram for Energy Demand Side Management use case.

Ms Wanni XIE (in-kind PhD student, CAM) has been working on the development of the Digital Twin knowledge graph and its implementation in the "parallel world" framework. This work is motivated by the research question of which potential hybrid energy supply pattern(s) can support the goal of zero carbon emission. As energy consumption, power plant and grid data for the UK are readily and publicly available, we have utilised them in the first instance to develop the "UK Digital Twin knowledge graph" as a proof of concept. This work can easily be extended and applied to other regions where data are available, in particular Singapore. Ms Xie is in the process of constructing the portions of the knowledge graph that are describing real world entities semantically i.e., "base world". The base world is a reflection of the current state of our world and can be connected to various real-time data sources. The UK Digital Twin knowledge graph is organised by means of layered orthogonal structuring principle as shown in Figure 6.9. Two domain ontologies, OntoEIP and OntoCAPE, have been adopted to describe and instantiate the power plants and energy consumption in the knowledge graph (represented as "Level 1" in Figure 6.9). Multiple power flow models with variant fidelities will be developed and applied to address the research question. Consequently, portions of the knowledge graph (represented as "Level 2" and "Level 3" in Figure 6.9) are designed to allow the co-existence of the semantic descriptions for different grid topologies (different levels of abstraction depicting the internal connectivity between the bus nodes and electrical lines) and grid models. The UK Digital Twin knowledge graph also describes and instantiates data and metrics (represented as "Level 4" in Figure 6.9) derived from the base world and grid models e.g., indicators measuring CO_2 emission and renewable energy share.

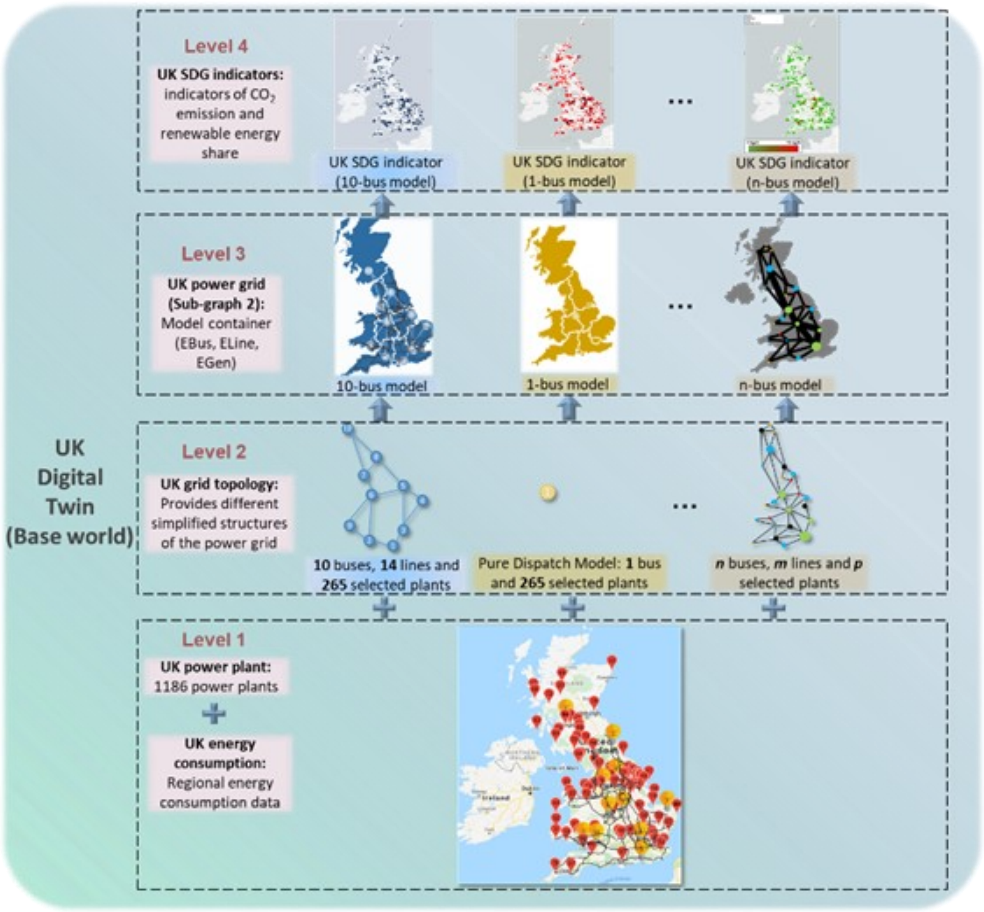


Figure 6.9: An overview of the UK Digital Twin knowledge graph.

Mr John ATHERTON (PhD student, CAM) has been working on improving the UK power grid modelling. Similarly, as necessary data for the UK are readily and publicly available, we have utilised them in the first instance as a proof of concept. For instance, Mr Atherton updated the existing Optimal Power Flow (OPF) agent to permit greater functionality by replacing multiple prior redundant versions of the code with a consolidated and updated agent. With the new implementation, new and prior functionalities can be used in greater depth e.g., the agent can now call different input / output files, hence permitting multiple parallel execution without the risk of overwriting any data. Furthermore, together with Ms Ong, he has implemented new unit tests as well as revised previous unit tests for the new OPF agent.

In addition, Mr Atherton has applied new techniques for visualising the data of generators as shown in Figure 6.10. As part of this work, he has also found and updated data that are faulty. Moreover, he has created in-built tests within the visualisation to detect for such errors automatically.

Mr Atherton has also written a paper about the geospatial effects of the placement for power loads and generators in the UK with respect to the implementation of a carbon tax on the current UK power generation infrastructure. With the UK shifting from a "top-up" to an entirely national-level determined tax rate, this paper provides a policy relevant analysis alongside comparing a national-level aggregated to regional-level dispersed model – thus also providing insight into UK power grid modelling. He is in the process of conducting a detailed literature analysis pertaining to major UK energy researchers as well as an investigation into the major data sources available.

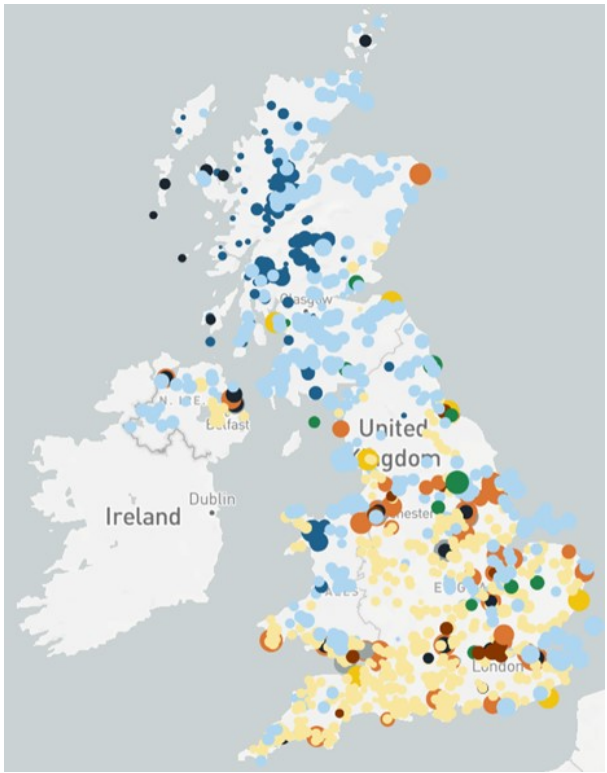


Figure 6.10: Visualisation of the power generators in the UK. The size of the circles corresponds to the capacity of the generator while the colour of the circles corresponds to the type of the generator.

Update on work package JPS.4

Model analysis and visualisation

Ms Shaocong ZHANG (Software Developer, CARES) has applied her previous work (a prototype of an ontology matching framework that performs data consolidation by taking advantage of JPS' multi-level and multi-domain design for terminology definition) to conduct matching for all 100 power plant instances and 5,000 power plant instances from DBPedia and JPS respectively. In this process, Ms Zhang observed that the performance and scalability of the existing framework have to be enhanced in order to be applicable. Consequently, she revised the matching methods, in particular the string-matching methods, as well as adjusted the model parameters, to improve the matching accuracy rate. In addition, together with **Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES)**, **she** has redesigned the relevant agents to be operating system agnostic, hence enabling the agents to be deployable on the High Performance Computing (HPC) system for better computational performance.

Mr Xiaochi ZHOU (PhD student, CAM) has been working on upgrading the novel Question Answering (QA) system for chemical data in the JPS knowledge graph – also known as "Marie". This work involves the implementation of: 1) faster query mechanism based on the Linked Data Fragment concept, and 2) automatic deployment mechanism based on Docker technology. As querying over a large-scale knowledge graph with billions of triples is both time and computational consuming, Mr Zhou conducted a literature review on fast SPARQL query to establish familiarity with, and to understand current research in this area. Based on the literature review, he concluded that the Linked Data Fragment (LDF) concept is a potential candidate to improve both the query speed of Marie and to alleviate the work load of its SPARQL endpoint. The essence of the LDF concept is to only implement a triple pattern service, which returns triples when given any one or two of the triple (subject, predicate, and object), on the server-end. The client-end will subsequently utilise the triples retrieved from the server-end and conduct SPARQL operations including Join, Union and Filter. Since the work load on the server-end is largely alleviated compared with a conventional RDF triple store, the availability of the SPARQL endpoint is increased. Furthermore, due to the high reusability of the triple search results, the overall query speed of the SPARQL endpoint is also improved. Accordingly, Mr Zhou implemented a Java-based LDF serv-

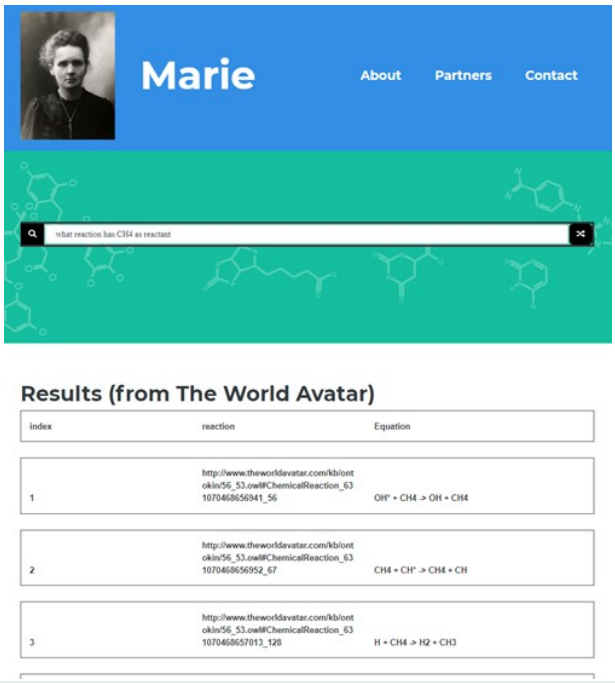


Figure 6.11: Screenshot of the Marie web-interface.

er within the JPS that provides fast search for the most time-consuming queries in Marie – questions related to OntoKin (ontology for chemical kinetic reaction mechanisms). This new implementation reduces the typical query time from approximately 2 minutes to around 7 seconds. He is in the process of extending the LDF server to provide SPARQL endpoints for other ontologies in the JPS knowledge graph e.g., OntoChemExp (ontology for experimental data).

Being a complex project, Marie relies on numerous dependencies and environments for its deployment. Therefore, Mr Zhou has created a Docker image to automate tasks associated with the deployment, which includes configuring, building and managing agents. Docker technology has been chosen as it can package an application, its dependencies and environments in a virtual container that can be run on any operating system e.g., Linux, Windows, or macOS. He is also in the process of creating new Docker images to include the LDF service.

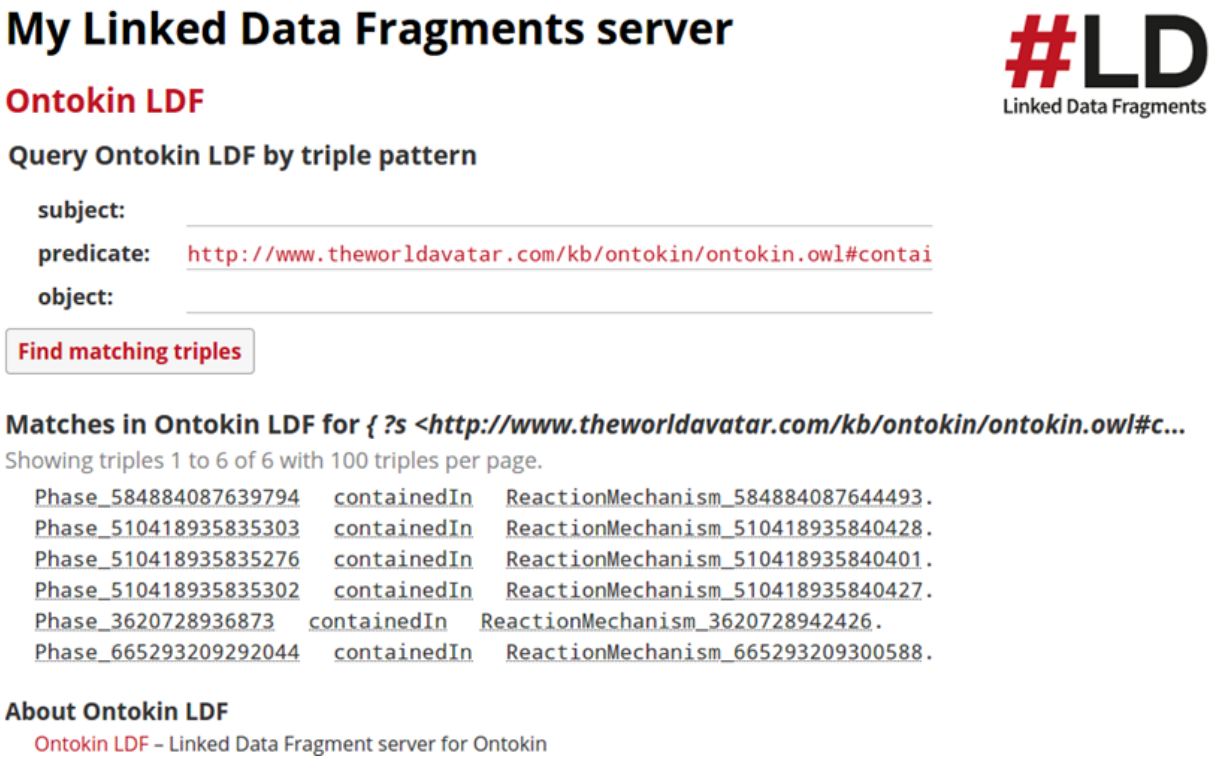


Figure 6.12: Linked Data Fragment (LDF) sever for OntoKin.

Scientific output

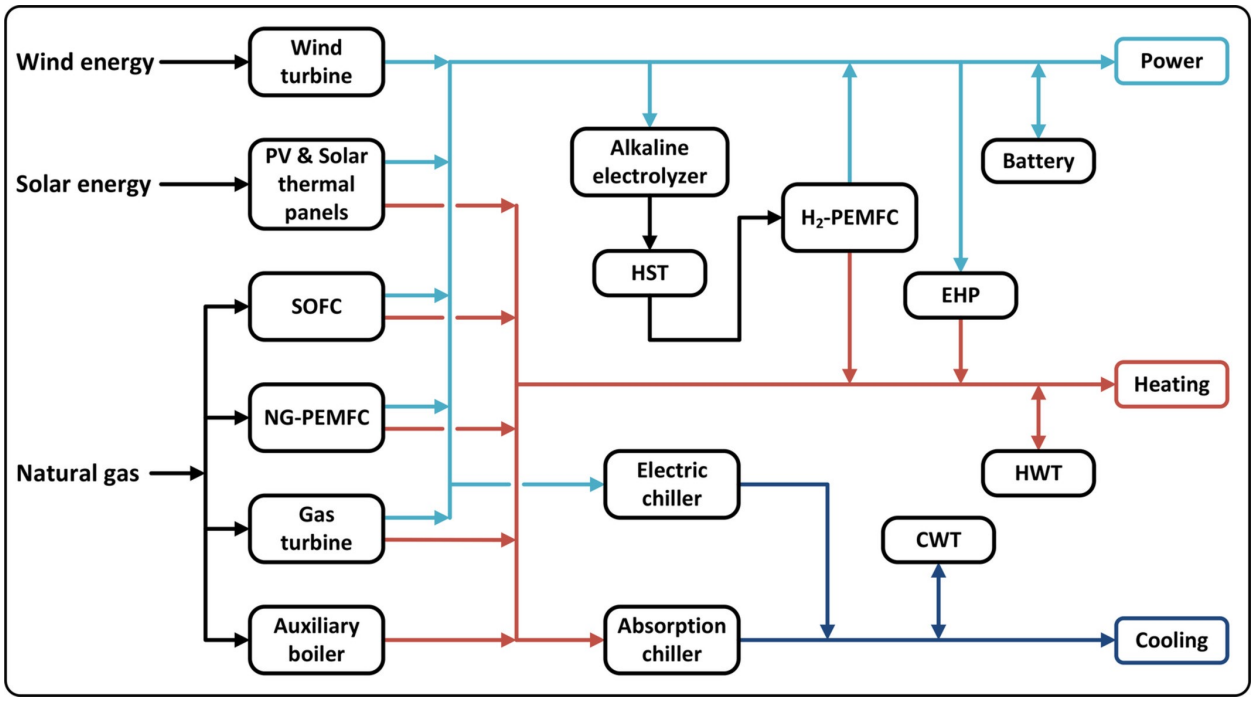
The following are the CREATE-acknowledged publications generated by IRP JPS during the reporting period, excluding those already featured in the Scientific Highlights section on page 12.

Simultaneous design and operation optimization of renewable combined cooling, heating and power systems

Zuming Liu, Mei Qi Lim and Markus Kraft, *AIChE Journal*

DOI: 10.1002/aic.17039

Abstract: Combined cooling, heating, and power (CCHP) systems are promising solutions for conserving energy and reducing emissions. This article proposes a new mixed-integer linear programming (MILP) model for simultaneous design and operation optimization of a renewable CCHP system, considering component nonlinear operating characteristics and performance degradation with time. A bi-objective MILP problem is solved to achieve a trade-off between total annual cost (TAC) and greenhouse gas emissions (GHGe). A case study of a commercial region is employed to demonstrate our proposed methodology. The results shows, in comparison with conventional cost minimization, our solution features a tardy increase of 12.8% in TAC and a sharp reduction of 75.5% in GHGe. Moreover, we find that ignoring performance degradation leads to an overestimation of 2.3–13.7% in system economic performance. The proposed methodology provides an effective and flexible framework for optimal design and operational analysis of renewable CCHP systems.



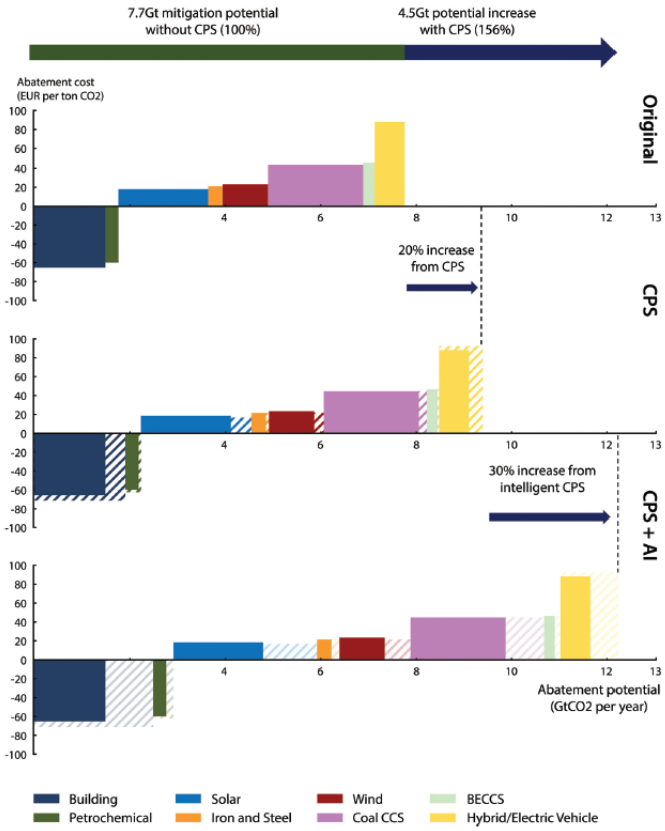
Schematic representation of a renewable combined cooling, heating, and power system. CWT, chilled water tank; HST, hydrogen storage tank; HWT, hot water tank; NG, natural gas; PEMFC, proton exchange membrane fuel cells; SOFC, solid oxide fuel cells.

Other activities and achievements

Prof. Markus KRAFT (PI, CAM) gave a talk titled "Intelligent Decarbonisation of Cities" at the *Applied Energy Symposium: Low Carbon Cities & Urban Energy Systems* conference, 10-17 October 2020. The talk addressed how diverse kinds of data can be made mutually legible by developing a semantic, extendible representation of relationships between them, what is known as a knowledge graph. This process, if demonstrated, will help planners and designers generate more reliable information and knowledge about cities – sites, neighbourhoods, areas or systems – and how they change.

Prof. Markus KRAFT gave a talk titled "Computational Modelling Cambridge Ltd.—A Cambridge professor's journey from researcher to director of an SME" for the *CARES Commercialisation Talks Series* on 20 October 2020.

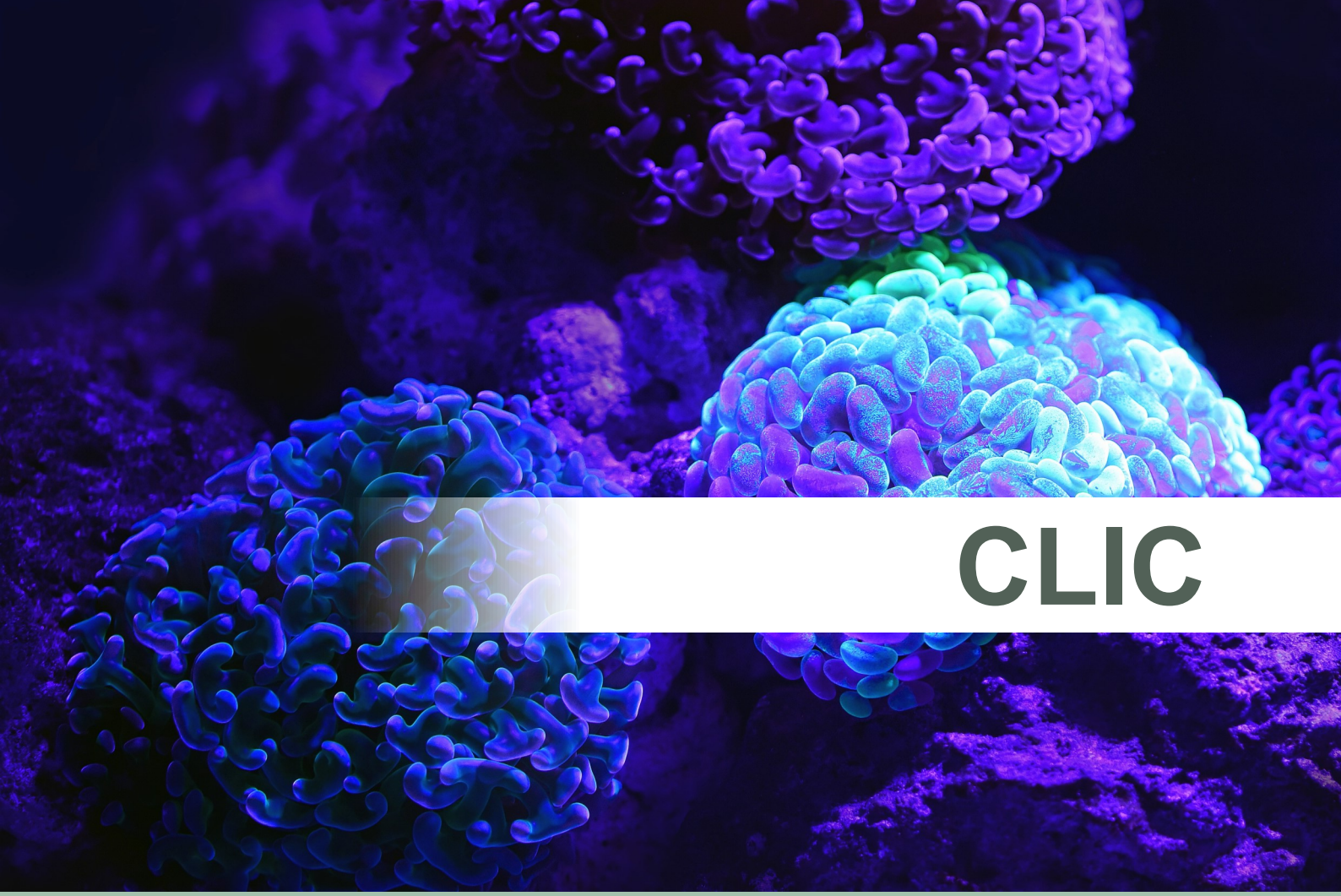
Prof. Markus KRAFT gave a talk titled "Intelligent Decarbonisation" for the *Lee Kuan Yew School of Public Policy* on 31 March 2021. The talk addressed how digitalisation and AI can help to address the problems of climate change and a possible uncontrolled, future general artificial intelligence. Concentrating The World Avatar project, which uses AI technologies including machine learning and knowledge graphs, Prof. Kraft explained some of the underlying ideas of these technologies and look at specific examples to illustrate how these technologies can offer solutions to difficulties created by vast amounts of data, data silos and lack of interoperability. The talk demonstrated how this technology will not only help planners to create an environmentally friendly, healthy and low-carbon world but also find new materials and increase our understanding of scientific fundamentals.



An image from a publication that Prof. Kraft showed during his "Intelligent Decarbonisation" talk. The graph displays the Marginal Abatement Cost Curve, which shows which carbon reduction measures save the most money.

Taken from:

The impact of intelligent cyber-physical systems on the decarbonization of energy. Oliver Inderwildi, Chuan Zhang, Xiaonan Wang and Markus Kraft, Energy & Environmental Science *13(3), 744-771, (2020).*



CLIC

CENTRE FOR LIFELONG LEARNING AND INDIVIDUALISED COGNITION

CLIC is a flagship programme in the Science of Learning initiative to harness advancements in neuroscience to develop cognitive training programmes for the improvement of lifelong flexible learning, focusing initially on adolescents and young adults, but also envisaging work with infants and older adults. This is a strategic global initiative for the University of Cambridge and NTU that brings together multidisciplinary expertise from over 30 investigators in the areas of neuroscience, psychology, linguistics and education across the two universities.

CLIC Directors:

Professor Annabel CHEN Shen-Hsing
Nanyang Technological University

Professor Zoe Kourtzi
University of Cambridge

OVERVIEW

As technology and globalisation are changing the nature of labour markets and increasing the demand for high levels of skill, the need for individuals to be able to develop new skills during their working careers is becoming increasingly pressing. Singapore's SkillsFuture programme promoted by the Ministries of Education, Manpower and Trade & Industry aptly recognises that societies need workers that have the capacity for flexible behaviour; that is, the ability to adapt to change, problem-solve in new situations based on previous experience and achieve in jobs that are likely to emerge over the next few decades. This individual capacity for cognitive flexibility is central to the modern digital age with its rapidly changing settings at home and work. As we recognise the need for flexible behaviour and transferable skills in our workforce, we need our education systems to ensure that citizens are equipped with the cognitive flexibility they need to develop these skills for the future. Yet there is currently a gap in evidence-based training programmes that can effectively support and promote cognitive flexibility across the life course.

CLIC aims to develop an integrated model of flexible learning by: 1) understanding the neurodevelopmental mechanisms of learning that support cognitive flexibility; 2) investigating the neurobiological and social factors that mediate the relationship between learning and cognitive flexibility in individuals and 3) developing user-led training interventions to improve cognitive flexibility across the life span and in real-world settings.

For Phase 1, the CLIC PIs are organised into four workgroups spearheading **Cognition**, **Social**, **Education** and **Neuroimaging** aspects of the research respectively.

The Cognition workgroup has produced one journal manuscript describing a novel Remote Guided Testing methodology that was developed specifically for CLIC. This is currently under review at a Tier 1 journal.

The Social workgroup has currently hired or are preparing offer letters for four Research Assistants, one Research Associate and two Research Fellows. These research staff were selected to represent diverse and complementary skills sets. There are still positions to fill for two Research Assistants/Associates and one Research Fellow.

The Education workgroup has recruited three Research Associates. This team will work closely in all aspects of the research in the school panel to advance the field of education neuroscience.

The Neuroimaging workgroup has hired one Research Fellow and one Research Associate. A Research Assistant will join the team in May 2021. These research staff will be supporting the intervention study involving the socio-cognitive and neuroimaging measures, as well as data management for the project. The search and interviews for two Research Fellows to support the neuroimaging and pulse sequence implementation components are still ongoing.

Professor Annabel Chen Shen-Hsing, Director
Nanyang Technological University

Professor Zoe Kourtzi, Director
University of Cambridge

Update on work package 1

Neurocognitive model of flexible learning

The Cognition work package has completed a full pilot study which was led by Deputy Director **Asst Prof. Victoria LEONG (PI, NTU)**. The study involved N=85 healthy young adults who completed 14 different tasks measuring cognitive flexibility, structure learning, working memory, inhibition and intelligence. The main purpose of the pilot was to validate a new Remote Guided Testing (RGT) method for testing participants virtually using web-based platforms (Figure 7.1), which would eliminate the need for face-to-face contact in the event of future COVID-19 related social restrictions. Data quality was assessed using detailed trial-level measures (missed trials, outlying and excluded responses, response times), as well as overall task performance measures. The results indicated that, across all measures of data quality and performance, RGT data was statistically-equivalent to data collected in person in the lab (Figure 7.2), confirming that the RGT method yields high quality data and can be used as an alternative to face-to-face testing. A manuscript reporting these results has been submitted to the *Journal for Medical Internet Research* (a Tier 1A journal) and is now under review. A further small pilot is now being planned to assess the suitability of a range of creativity tasks for inclusion in the main study.

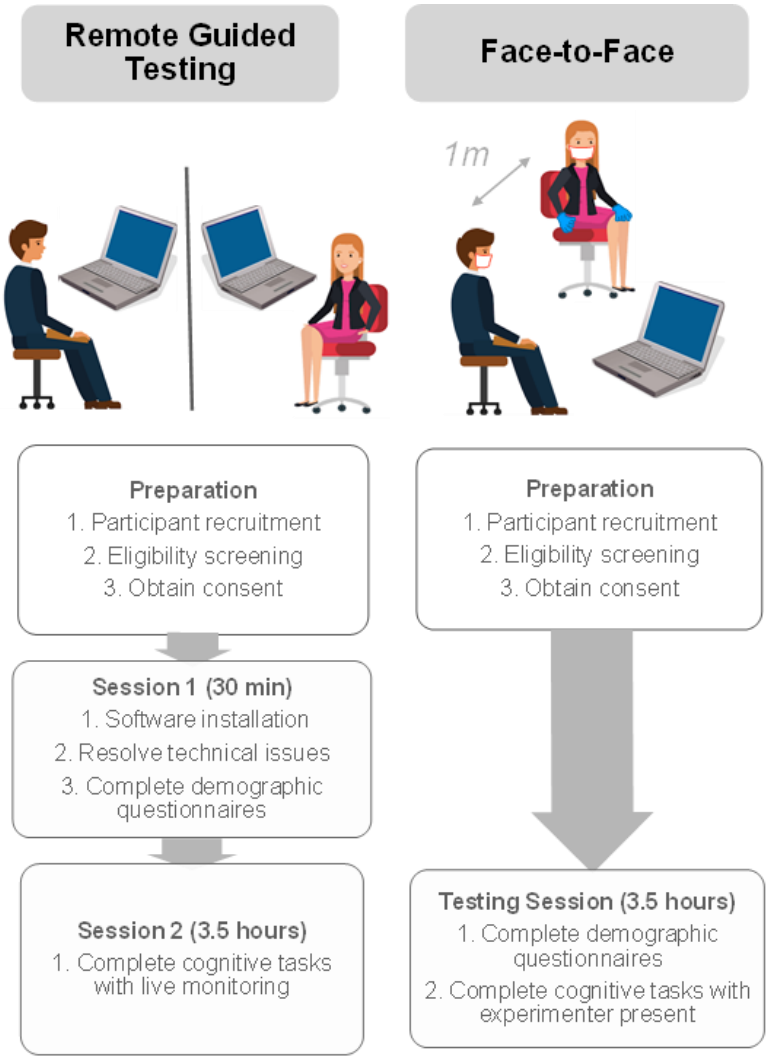


Figure 7.1: Overview of remote guided and face-to-face testing processes.

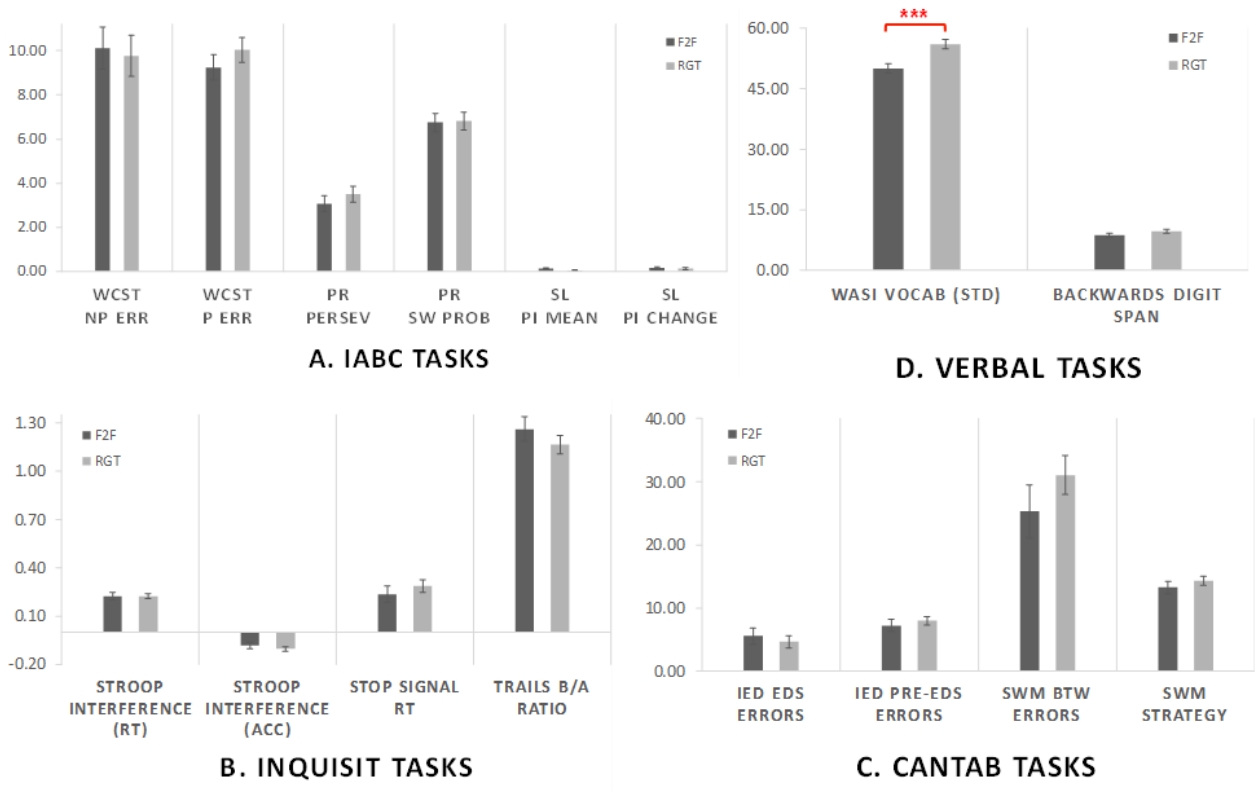


*Figure 7.2: Plot of performance indices for (a) i-ABC; (b) Inquisit; (c) CANTAB and (d) Verbally delivered tasks. Face-to-face participants are shown in dark grey bars, remote guided participants are shown in light grey bars. Errors bars indicate the standard error of the mean. Significant group differences in performance were only observed for WASI Vocabulary (***P<.001), where remote guided participants scored more highly on the task. Performance was statistically equivalent across groups for all other tasks.*

Update on work package 2

Social influences on flexible learning

Over the past six months, the Social work package has largely been focused preparing research materials/tools, obtaining Institutional Review Board (IRB) approvals, collecting pilot data and recruiting/hiring research staff.

For preparation of research materials/tools, the work group has discussed, reviewed and finalised the battery of measures that will be administered in this work package, as well as the procedure for dividing and administering this approximately three hours long battery across multiple sessions to minimise participant burden. Other CLIC investigators **Assoc. Prof. Bobby CHEON (PI, NTU)**, **Dr TEO Chew Lee (Co-I, NTU)**, **Asst Prof. Victoria LEONG (PI, NTU)** and **Prof. Trevor ROBBINS (PI, CAM)** from other work packages have also expanded the scope of the measures in the social work package to include dedicated measures of creativity. Administration licenses and hard copies have been purchased for tests as required. **Prof. Henriette HENDRIKS (PI, CAM)**, in collaboration with **Assoc. Prof. Peipei SETOH (Co-I, NTU)**, **Ms Mandy WIGDOROWITZ** and **Ms Lina VASSILIU (in-kind PhD students, CAM)**, has been involved in particular with the development and adaptation of the questionnaires measuring levels of multilingualism.

The study has received an IRB approval. This part of the study is, at the moment, fully online, thus allowing flexible delivery regardless of the COVID-19 situation. The data is being evaluated to further decide the feasibility of this delivery method.

For collecting pilot data, the work group (headed by **Assoc. Prof. George CHRISTOPOULOS, Co-I, NTU** for this effort) has collected responses from N=58 young adult participants for the battery of social workgroup measures. The group has collected two rounds of data in order to evaluate time required for completion of the questionnaires/tasks. Additional pilot data for social measures have been collected by the Education work package on adolescent participants. The workgroup has also met with other workgroups to review and update logistics and procedures for administering social tasks based on these pilot studies. Assoc. Prof. Cheon held workshops with research staff for training and standardising scoring procedures for creativity tasks (Test of Creative Thinking—Drawing Production).

Update on work package 3

Real-world translation to education

Prof. David HUNG (PI, NTU) and **Dr Peter SEOW (Co-I, NTU)** provided insightful comments to the design of the pilot studies that will lead to the actual characterisation study of cognitive flexibility (CF) in adolescents. **Dr TEO Chew Lee (Co-I, NTU)** then led a team of researchers to implement the pilot studies in secondary schools.

In the past few months, three pilot studies involving 96 Secondary 1 and 2 students from three Singapore secondary schools were conducted. The pilot studies aim to implement small-scale testing of the methods and procedures to be used in the larger-scale characterisation study. Each pilot study implemented a combination of cognition tasks, social measures and creativity tasks that lasted for six hours. Prior to the pilot study, Dr Teo recruited schools for the study through the Knowledge Building Community Network Learning for school leaders held in January 2019. In the months leading up to the pilot studies, the research team worked closely with IT departments from the participating schools to conduct trial runs on the platforms used for data collection. With complications associated with the COVID-19 pandemic, the research team had to coordinate with the participating schools to conduct pilot studies within the parameters of schools' social distancing regulations.

Unlike laboratory-based CF studies, data collection in this study was conducted in a classroom setting. Thus, the research team made a conscious effort to assess the data collection process to determine its feasibility for subsequent implementations. In the first and second pilot studies, the research team encountered difficulties during the implementation as participants struggled to complete the rigorous tasks over an extended duration. The pilot studies also revealed the need to explore the possible relationships between affect (emotion) and CF as overt displays of affect from the participants were observed during the study. This observation presented the possibility that the participants might be going through the battery with significant influences from their affect. To address the difficulties faced in the first two pilot studies, the research team created deliberate designs in the form of pedagogical moves and tools to facilitate the study's implementation. Figure 7.3 shows an example of pedagogical designs created to prepare the participants for the cognitive tasks. These pedagogical designs created to adapt laboratory-based tests for the classroom environment received positive responses when implemented in the third pilot study.

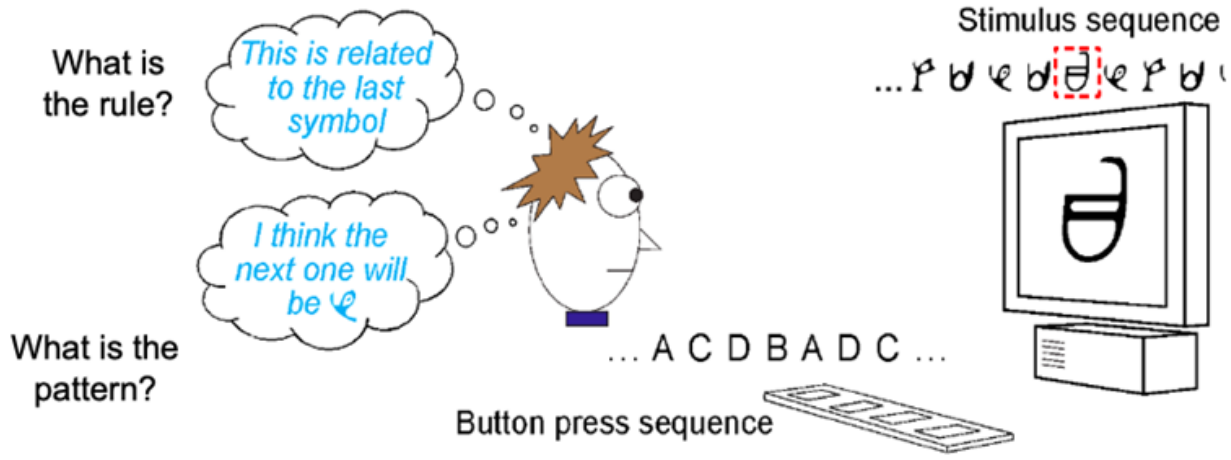


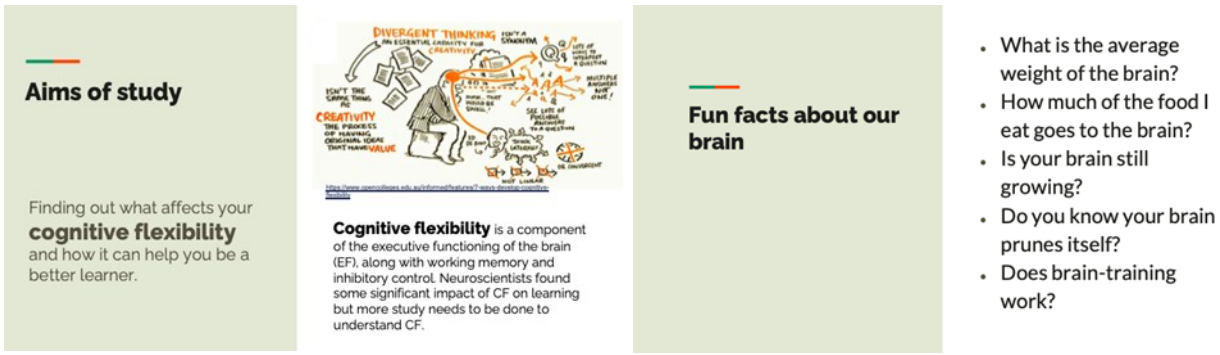
Figure 7.3: A Structure Learning game is one of the cognition tasks implemented in the study. In the game, students attempt to seek patterns in stochastic presentation of stimuli with no feedback.

Throughout the three pilot studies, **Dr Michelle ELLEFSON (PI, CAM)** was consulted on the data collection protocol using the different cognitive tasks, specifically on the set-switching tasks and the Structure Learning Protocol. **Prof. Zoe KOURTZI (PI, CAM)** and team supported the fine-tuning of the Structure Learning protocol to adapt to the authentic school setting in which 20 students were engaged with the tasks concurrently.

Two students' projects based on the pilot data were completed during this time:

Ms CHUI Yingqi's (final year undergraduate in-kind student, NTU) main research interest lies in the implicit theories of intelligence, non-academic abilities and creativity. Recently, she examined the relationships between intelligence, non-academic capabilities and creativity alongside reactive and spontaneous flexibility to investigate the associations between implicit beliefs and cognitive flexibility and creativity. Under the guidance of **Prof. Annabel CHEN Shen-Hsing (PI, NTU)** and Dr Teo, she completed her final year research project on comparing two differently-achieving adolescent groups, the Normal Technical stream and the Express stream, to determine the presence of any differences in these areas.

Ms Nur Hanisah Binte GHAZALI's (final year undergraduate in-kind student, NTU) research topic lies in bilingual students' creativity. Over the past few months, she examined the relationship between creativity and bilingualism by examining its underlying cognitive processes. Her study for the URECA project investigates the relationship between students' bilingual experiences, divergent thinking and selective attention. With guidance from Dr Teo, she completed the project which involves forty secondary school students in the Normal Technical stream using tools such as the language background questionnaire, the Test for Creative Drawing and Production (shown in Figure 7.5) and the Stroop Task.



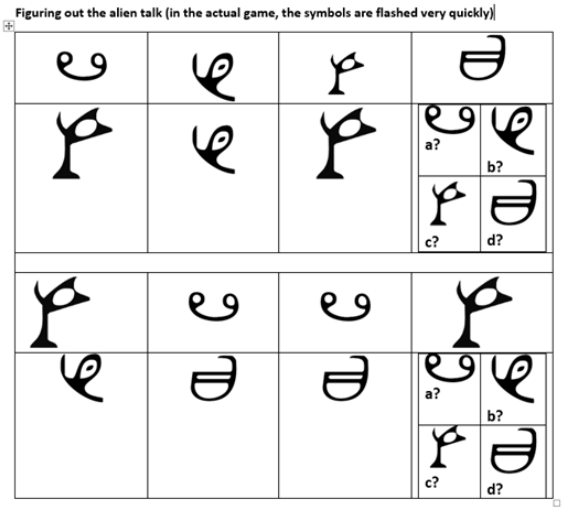


Figure 7.4: Examples of Powerpoint slides and activity sheet used to guide participants to understand the purpose of the study and increase their interest in the tasks conducted.

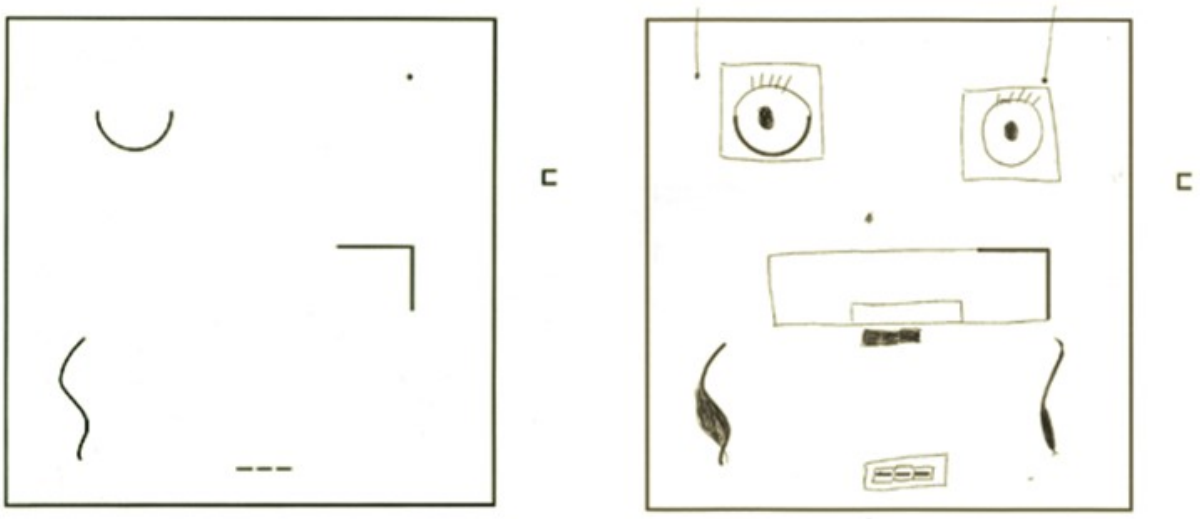


Figure 7.5: A sample of a student's creativity task using TCT–DP.

Update on work package 4

Neuroimaging

The neuroimaging work package aims to investigate the effects of structure learning training on cognitive flexibility, relative to training in working memory and no training. The multimodal approach, which includes neuroimaging data and a comprehensive battery of cognitive-behavioural measures, will be adopted to allow the identification of neural and cognitive-behavioural factors relating to cognitive flexibility. The neuroimaging workgroup is currently amid preparatory works for the project. These include the setting up of recruitment and testing procedures, ethics protocol and neuroimaging protocol. Additionally, the team is starting preparations for two pilot studies. The first study aims to develop a working memory training for the active control group. The working memory training will be designed with a similar structure and format to the structure learning training but will not tap on any cognitive flexibility. The second study aims to test out pulse sequences which will be used in the main study.

The data management plan for the CLIC project has been submitted, and **Prof. John SUCKLING (PI, CAM)** is currently helping to set up the data transfer between Nanyang Technological University and University of Cambridge. Additionally, the neuroimaging team is building up the server infrastructure and REDCap data management system in preparation for data collection.

Other activities and achievements

The CLIC Launch Event was held on 23 February 2021; a virtual celebration of the official launch of the interdisciplinary and collaborative programme between NTU and University of Cambridge and hosted by Cambridge CARES.

The Launch Event was graced by the honourable presence of Prof. Subra Suresh (President of NTU), Prof. Stephen Toope (Vice-Chancellor of University of Cambridge), Prof. Anne Ferguson-Smith (Acting Pro-Vice-Chancellor (Research) of University of Cambridge), Prof. Lam Khin Yong (Senior Vice President (Research) of NTU), Her Excellency Ms Kara Owen CMG CVO (British High Commissioner to Singapore) and Professor Markus Kraft (Director of CARES) and attended by 183 people across the globe.

eCO$_2$EP

CARBON CAPTURE AND UTILISATION USING A TABLE-TOP CHEMICAL FACTORY

This is CARES' first large Intra-CREATE project and is aimed at developing a "table-top chemical factory" that uses electrochemical processes to convert CO_2 into ethylene or to 1-propanol – two molecular products widely used in the chemical industry. Earlier research carried out at CREATE had demonstrated that CO_2 molecules can be transformed into hydrocarbons through the application of electro-catalysis. eCO$_2$EP's research studies the viability of scaling CO_2 reduction processes, including techno-economic evaluation of the use of off-peak renewable electricity in areas with excess capacity, with the goal of developing new energy-chemistry solutions for a more sustainable future.

eCO$_2$EP Principal Investigators:

Professor Alexei LAPKIN
University of Cambridge

Professor Joel AGER
University of California, Berkeley

OVERVIEW

The current report covers the penultimate six months of the project. Over this period the project team has converged on the materials for large scale cathode and anode, developed a new design of the scaled-up cell, generated promising results on products separations and identified several new commercialisable outputs. The final stage of the project is promising to be very busy and very exciting, gearing towards demonstration of the scaled mini-plant operation and generating data for detailed technoeconomic evaluation of the process.

Professor Alexei Lapkin, PI
University of Cambridge

Professor Joel Ager, PI
University of California, Berkeley

Update on work package 1

New catalyst discovery and characterisation

Dr CHEN Yubo (Research Fellow, NTU) that perovskite oxides based on earth-abundant transition metals have been extensively explored as promising oxygen evolution reaction (OER) catalysts in alkaline media. The (electro)chemically induced transformation of their 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 the amorphised surface from that of the 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 Fe ions absorbed from the electrolyte, on the OER activity of $SrCoO_{3-\delta}$ model perovskite to identify the active phase. Transmission electron microscopy and X-ray photoelectron spectroscopy confirmed the surface amorphisation of $SrCoO_{3-\delta}$ as well as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ after potential cycling in Fe-free KOH solution. By further cycling in Fe-spiked electrolyte, Fe was incorporated into the amorphised surface of $SrCoO_{3-\delta}$ ($SrCoO_{3-\delta}$ + Fe^{3+}), yielding approximately sixfold increase in activity. Despite the difference in remaining perovskites, $SrCoO_{3-\delta}$ + Fe^{3+} and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ exhibited remarkably similar activity. These results reflect that the *in situ* developed surface species are directly responsible for the measured OER activity, whereas the remaining bulk phases have little impact.

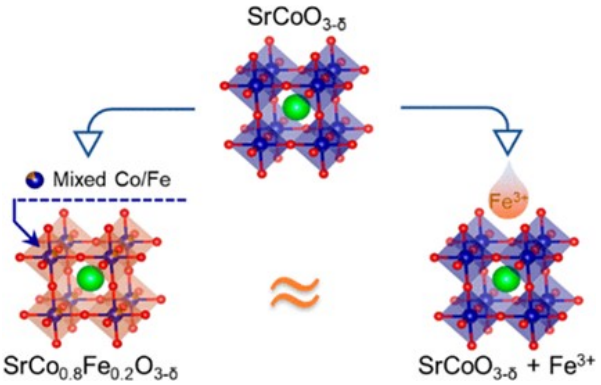


Figure 8.1.

Dr CHEN Yubo

Dr LIU Guanyu (Research Fellow, NTU) has developed a facile solvent-free synthesis method for a copper-based metal-organic framework (MOF) as an electrocatalyst for the carbon dioxide reduction reaction (CO_2RR). This Cu-based MOF can selectively catalyse CO_2RR towards methane production with a Faradaic efficiency of up to 60%. An *in situ* dissolution-redeposition process of the initial MOF was observed during CO_2RR to form Cu nanoparticles as the actual catalysts. In addition, he completed writing a review paper about wetting-regulated gas-involving (photo) electrocatalysis. This review was dedicated to bridging the fields of wetting and catalysis by reviewing cutting-edge design methodologies of both gas-evolving and gas-consuming (photo) electrocatalytic systems. In the review, the fundamentals of various in-air/underwater wetting states and their corresponding bioinspired structural properties were first introduced. The relationship amongst bubble transport behaviours, wettability and porosity/tortuosity were also discussed. Subsequently, the latest implementations of wetting-related design principles for gas-evolving reactions (i.e. hydrogen evolution reaction and oxygen evolution reaction) and gas-consuming reactions (i.e. oxygen reduction reaction and CO_2 reduction reaction) were summarised.

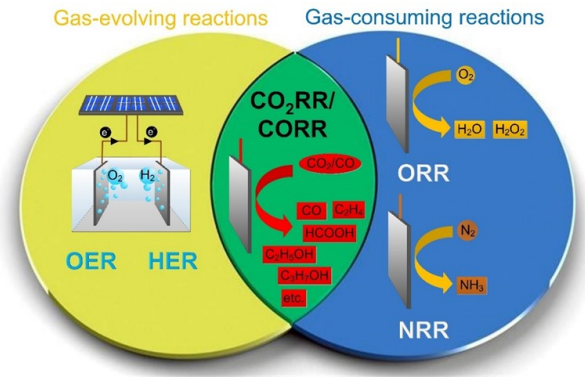


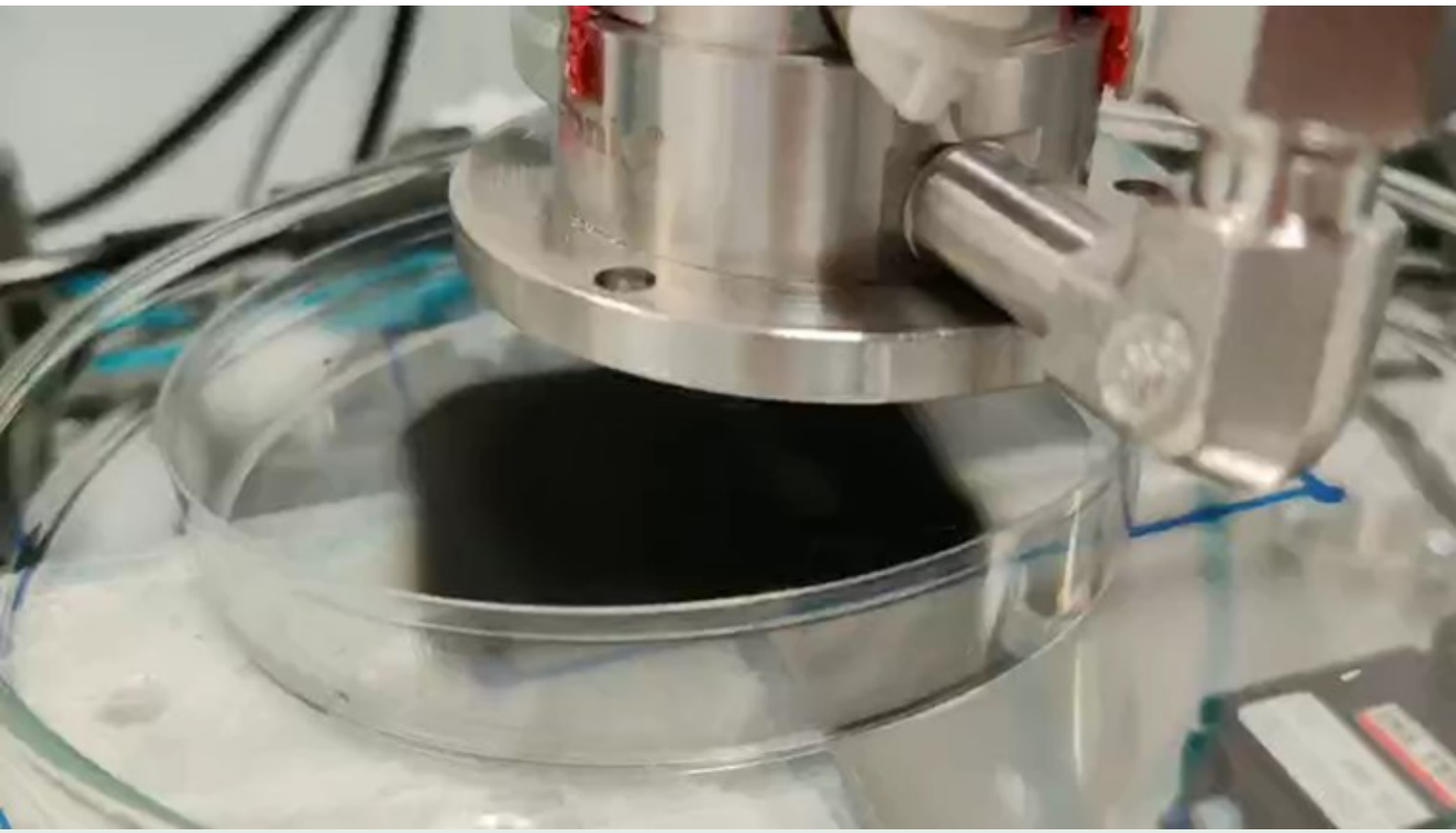
Figure 8.2: Review of wetting-regulated (photo) electrocatalytic gas-involving reactions.

Dr LIU Guanyu

Dr REN Hangjuan (Research Fellow, CARES) is working on electrochemical CO_2 reduction (eCO_2 reduction), which can transfer the greenhouse gas CO_2 to constructive organic chemicals, such as ethylene and other C_{2+} products. However, there are too many by-products and thus driving the reaction towards any single product is very difficult. Additionally, the reaction mechanism is complex and unclear, especially in gas diffusion cells. Hangjuan prepared a Cu-based gas diffusion electrode using an ultrasonic spray system. The present work demonstrates a world-leading current density of ethylene (more than 1A/cm^2) at a low potential in a same cell (1 cm^2). This electrode is easily scaled up to 100 cm^2, which is going to be used in a large cell. Besides this, Hangjuan worked with Dr Mikhail KOVALEV (Senior Research Fellow) on the mechanism of eCO_2 reduction using *in situ* Proton Transfer Reaction – Mass Spectrometry (PTR-MS). Many findings that overturn traditional perceptions have been discovered. These discoveries can direct other researchers to synthesise better electrodes.

WANG JingJing (Research Associate, NUS) reports that the electrochemical reduction of CO_2 into high-value carbonaceous products using renewable electricity is a promising way to transit towards global carbon neutrality. The selectivity for multi-carbon products can be enhanced by facets engineering and modification of the electrocatalysts used. Herein, we report that by coating amino silanes in a thin layer onto exposed (100) facets of Cu nanocubes, we could improve the latter's activity, stability and selectivity to C_{2+} products for CO_2 reduction. In particular, the Faradaic efficiency (*FE*) and partial current density for C_{2+} can increase to 73.8% and 550.2 mA cm^{-2} at -0.55 V vs RHE. This is significantly larger than the FE of 51.0% and partial current density of 180.8 mA cm^{-2} for C_{2+} using only pristine Cu nanocubes under the same conditions.

Figure 8.3: Ultrasonic spray coating of gas diffusion electrode. *Dr REN Hangjuan*



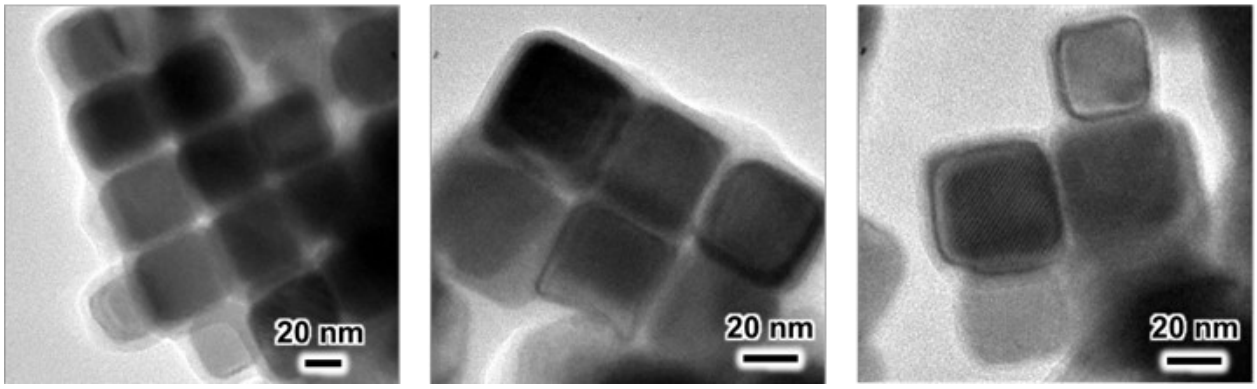


Figure 8.4: TEM images of amino silane coated Cu nanocubes.

Dr WANG JingJing

SHEN JingJing (Research Assistant, NTU) and **Prof. Jason XU Zhichuan (PI, NTU)** employ the strategy of introducing lithium into Co_3O_4 in various quantities to realise the enhancement of Co-O bond covalency in octahedral sites to promote OER activity. XRD patterns in Figure 8.5 have confirmed the spinel oxide structures of the synthesised materials. In addition, as more lithium is being introduced into Co_3O_4, the (111)/(220) peak ratio increased accordingly. The intensity ratio of these two peaks reflects the lithium vacancy, whereby a higher ratio indicates more vacancies. This shows that more lithium in the tetrahedral position can be removed to induce higher Co-O bond covalency. XPS spectra of Co 2p demonstrates that as more lithium is being introduced, the Co^{2+}/Co^{3+} ratio decreases, suggesting that the oxidation state of cobalt is becoming higher. Electrochemical measurements in Figure 8.7 reflect that the sample whereby its tetrahedral site is entirely replaced by lithium ($LiCo_2O_4$) has the highest current density and smallest overpotential among the $Li_xCo_{3-x}O_4$ catalysts, and it is also superior to CoOOH and IrO_2. Furthermore, by comparing the 2nd and 500th cycle of $LiCo_2O_4$, there is a significant increase in the OER current after further cycling, which may be ascribed to surface reconstruction.

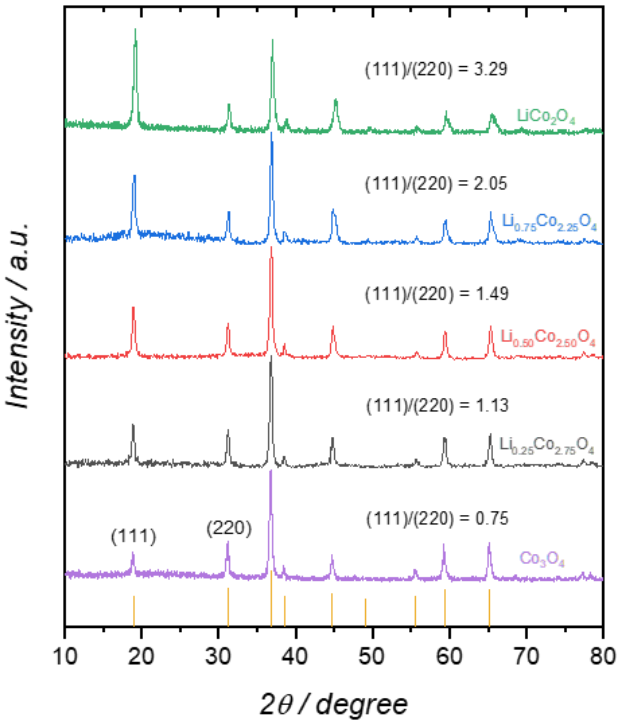


Figure 8.5: XRD patterns of as-synthesised $Li_xCo_{3-x}O_4$ samples.

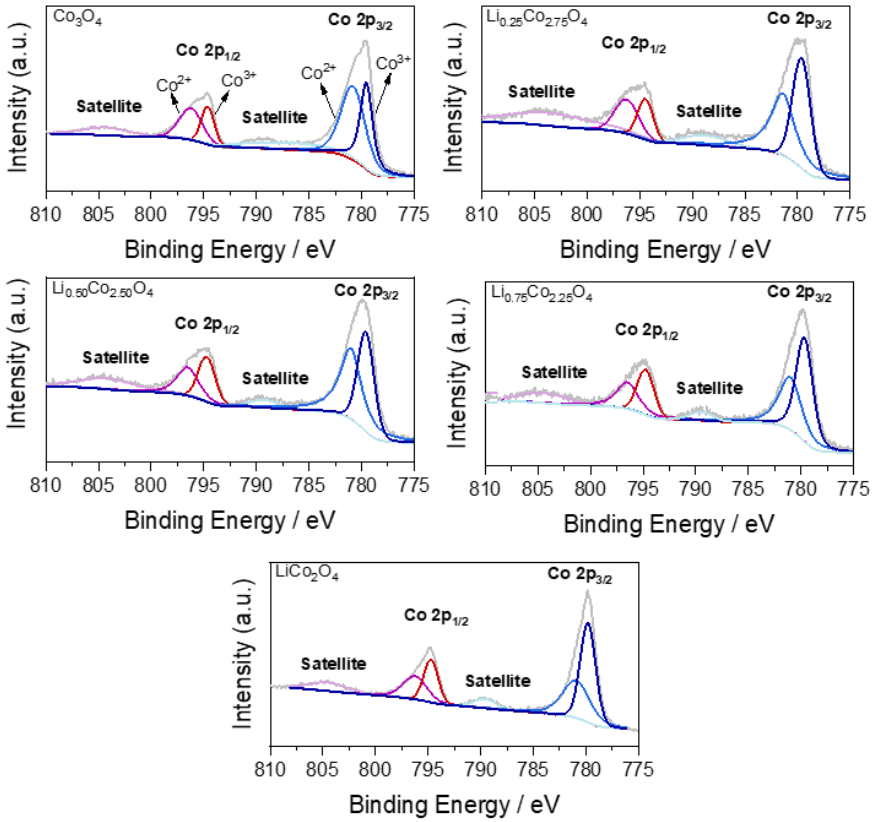


Figure 8.6: XPS spectra of Co 2p of the $Li_xCo_{3-x}O_4$ samples.

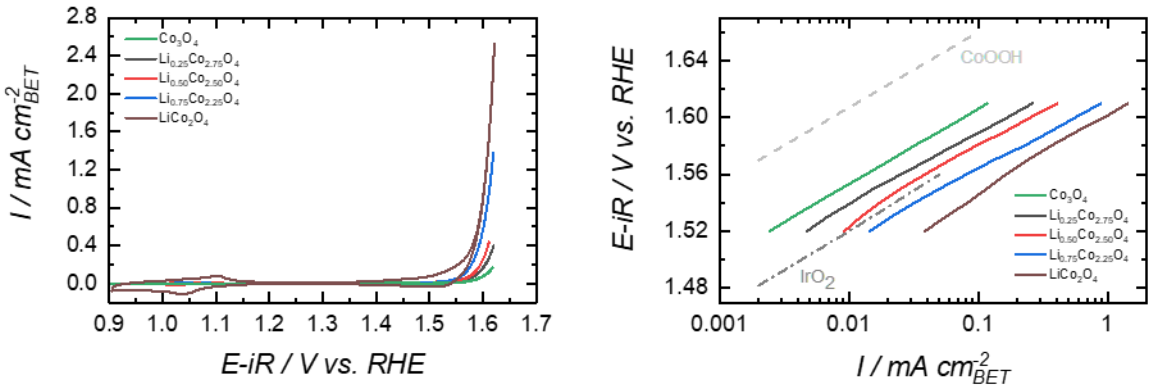


Figure 8.7: (left) The 2nd cycle of OER CV curves performed in 1 M KOH (scan rate: 10 mV/s) after background correction and iR correction. (right) Tafel plots of the $Li_xCo_{3-x}O_4$ samples with current densities normalised by BET surface areas, in comparison with IrO_2 and CoOOH.

SHEN JingJing

Update on work package 2

Modelling and data informatics

Simon RIHM (Researcher, CARES) joined CARES in August 2020 and has been working on kinetic modelling of the CO_2 Reduction Reaction (CO_2RR) as well as building an automated pipeline for the processing of measurement and modelling data.

He created a microkinetic model and verified its inner workings by comparing a simple electrocatalytic mechanism with its analytical solution. Subsequently, he implemented more complex mechanisms and deployed a full mechanism from CO_2 to C1 and C2 products with automated generation of input files and post-processing.

For parametrisation of the model, Simon generated an interlinked database of reaction steps, intermediates and kinetic data that are reported in the literature. This serves as a foundation for mechanism analysis and automated model generation. Furthermore, he proposed a framework for investigation and evaluation of C3+ reaction mechanisms based on experimental findings.

Simon was working with Dr Magda BARECKA, Dr REN Hangjuan and Dr Mikhail KOVALEV (Research Fellows, CARES) to automate and standardise analysis of experimental data. Within a newly defined template, measurements can now be shared more efficiently. Based on the available data, he was able to formulate several hypotheses regarding the reaction mechanism and propose experiments to test them.

Currently, Simon is calibrating the microkinetic model with measurement data and was able to reproduce several experimentally observed qualitative trends. He started integration of the model with a higher-dimensional meso-scale model of Peace ADESINA (PhD student, CAM).

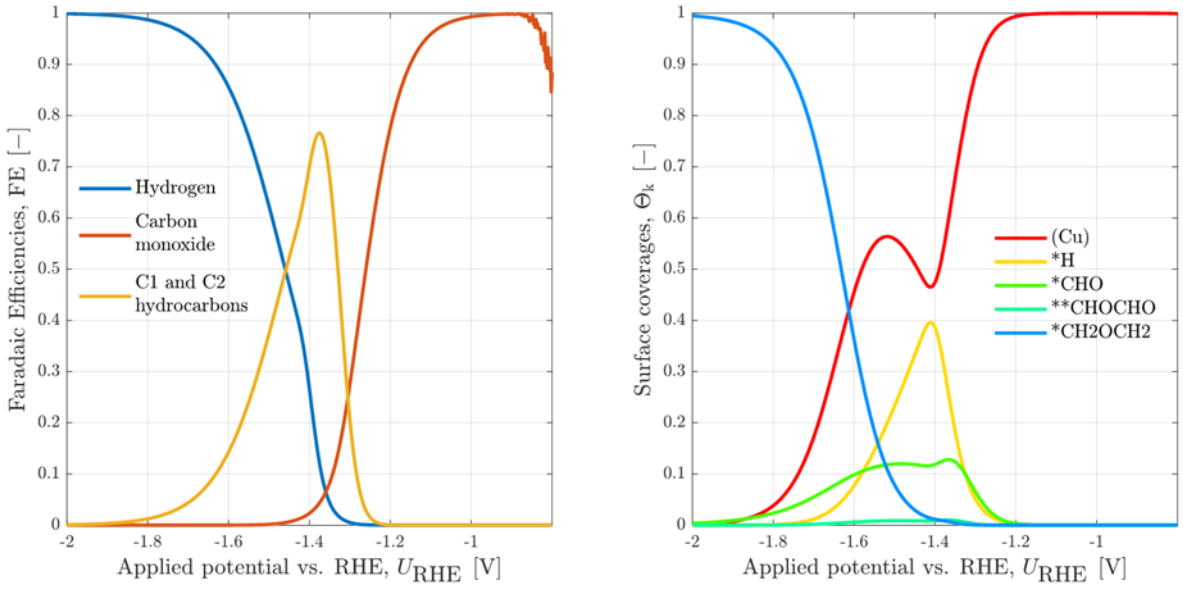


Figure 8.8: First results from the microkinetic model of CO_2RR. The Faradaic efficiencies of each product can be compared to experimental data while surface coverages of the copper catalyst provide additional insights that are experimentally unavailable.

Simon RIHM

Update on work package 3

Chemical factory on a table

Dr Magda BARECKA's (Research Fellow, CARES) main research interest lies in the development of CO_2-based manufacturing concepts that can be viable on the current market and scalable to the size of technologies that can meaningfully contribute to achievement of carbon neutrality goals. Within the eCO_2EP project, Magda is involved in the plant design/integration and process optimisation for the table-top factory converting carbon dioxide to ethylene. Recently, she has been focusing on further research on energy efficient approaches for liquid products separation. She has been supervising an intern (under the NTU Professional Internship programme) twho is testing a wide variety of membranes and performing long-term separation runs. The data collected will enable detailed process modelling and faster integration of the separation techniques into the eCO_2EP plant once the core of the plant, a scaled-up electrolyser, is ready for operation.

Magda has been also working on the optimisation of the overall process design and purchasing some of the equipment necessary for the plant operation. Together with other colleagues working under the eCO_2EP project, she has been developing a new application for CO_2 electrolysis, which resulted in a patent application. Furthermore, Magda has been continuing to work on the industrial implementation of CO_2 recycling and a forward-looking perspective on the potential of this technology is currently under review in *iScience*.

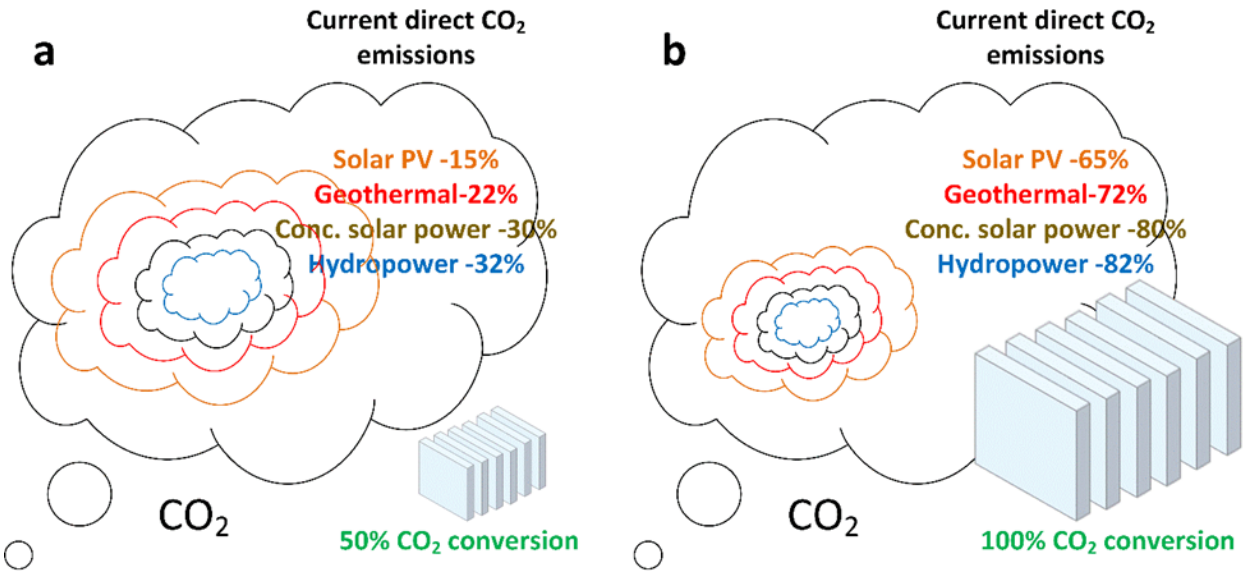


Figure 8.9: Potential for CO_2 emissions reduction from ethylene oxide manufacturing by means of a dedicated retrofit based on CO_2 electrolysis and powered by different sources of electricity. This figure is part of a recent article published in Energy & Environmental Science.

Dr Magda BARECKA

Dr Mikhail KOVALEV's (Senior Research Fellow, CARES) research interests are in the area of gas diffusion electrode (GDE) preparation and analytical studies of its performance. Typically, GDEs consist of several layers where each one has its particular function. The optimisation of the layers' structure and formulation may significantly improve the GDE's performance and long-term stability. Following optimised structure and preparation methods for small size electrodes is important to achieve repeatability and scalability to meet industrial flow cell standards. Currently, developed GDEs have a size of 16 cm^2 while the future focus is to increase size to over 100 cm^2 with preserved efficiency and stability similar to the lab size.

Another of Dr Kovalev's activities is to set up analytical methods for reaction products analysis. The CARES lab is well equipped with modern analytical tools like Gas Chromatography (GC), High Pressure Liquid Chromatography (HPLC), Quadrupole (QMS) and Proton-Transfer-Reaction Time-of-Flight Mass Spectrometers (PTR-TOF-MS). With the combination of electrochemical reduction flow cell and the above equipment, the CARES team is able to reveal details of CO_2 electroreduction process. The example of the electrochemical flow cell setup combined with GC and PTR-TOF-MS is shown in Figure 8.10.

The combination of products separation on GC and outstanding resolution and sensitivity of PTR -MS allow detection and characterisation of intermediates and by-products formed during the reduction of CO_2. These species are the key element in understanding the mechanism and performance of various GDEs. The example of the resolution of PTR-MS is shown in Figure 8.11.

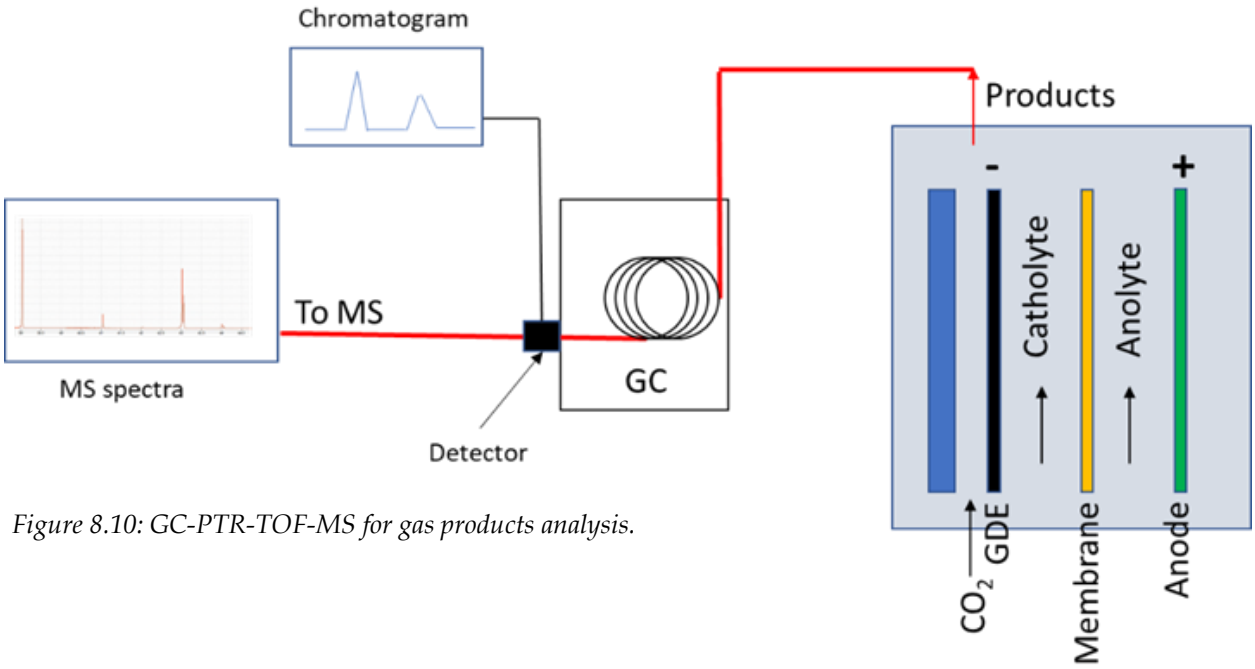


Figure 8.10: GC-PTR-TOF-MS for gas products analysis.

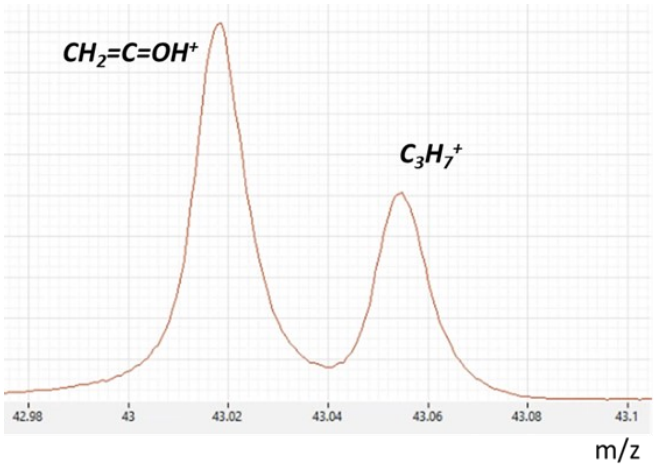


Figure 8.11: PTR-TOF-MS resolution on the example of protonated Ketene ($C_2H_3O^+$, m/z = 43.018) and Propene ($C_3H_7^+$, m/z = 43.054) where Δm = 0.036 amu.

Dr Mikhail KOVALEV

Dr Alexandr KHUDOROZHKOV (Research Fellow, CARES) reports that modified 4Å molecular sieves were obtained via ion exchange with Ag, Cu and Co in order to test their efficiency in separation of C_2H_4 and CO_2. It was found that Ag -modified molecular sieves are the most selective, with ethylene:carbon dioxide adsorption selectivity as high as 77 for 5% C_2H_4 in CO_2 mixtures. Co-modified molecular sieves in turn demonstrate much higher selectivity toward CO_2 adsoprtion. Cu-modified samples are highly selective to CO_2, almost no adsorption of ethylene was observed.

Selectivity is calculated as

$$\frac{q_{C_2H_4}}{q_{CO_2}} \div \frac{\omega_{C_2H_4}}{\omega_{CO_2}},$$

where q_i - adsorption capacity for the i^{th}-component, mmol/g; ω – volumetric concentration of the i^{th}-component, %.

4Å-Ag sample, due to its high stability and performance, was selected as the most suitable material for further breakthrough and selective adsorption experiments with more a complex mixture modelling the real composition of the products of CO_2 electrocatalytic reduction.

Sample	C_2H_4 adsorption, mmol/g	CO_2 adsorption, mmol/g	Selectivity toward C_2H_4
4Å-Ag	0.370	0.091	77.2
4Å-Co	0.017	0.350	0.9
4Å-Cu	0.005	0.115	0.8

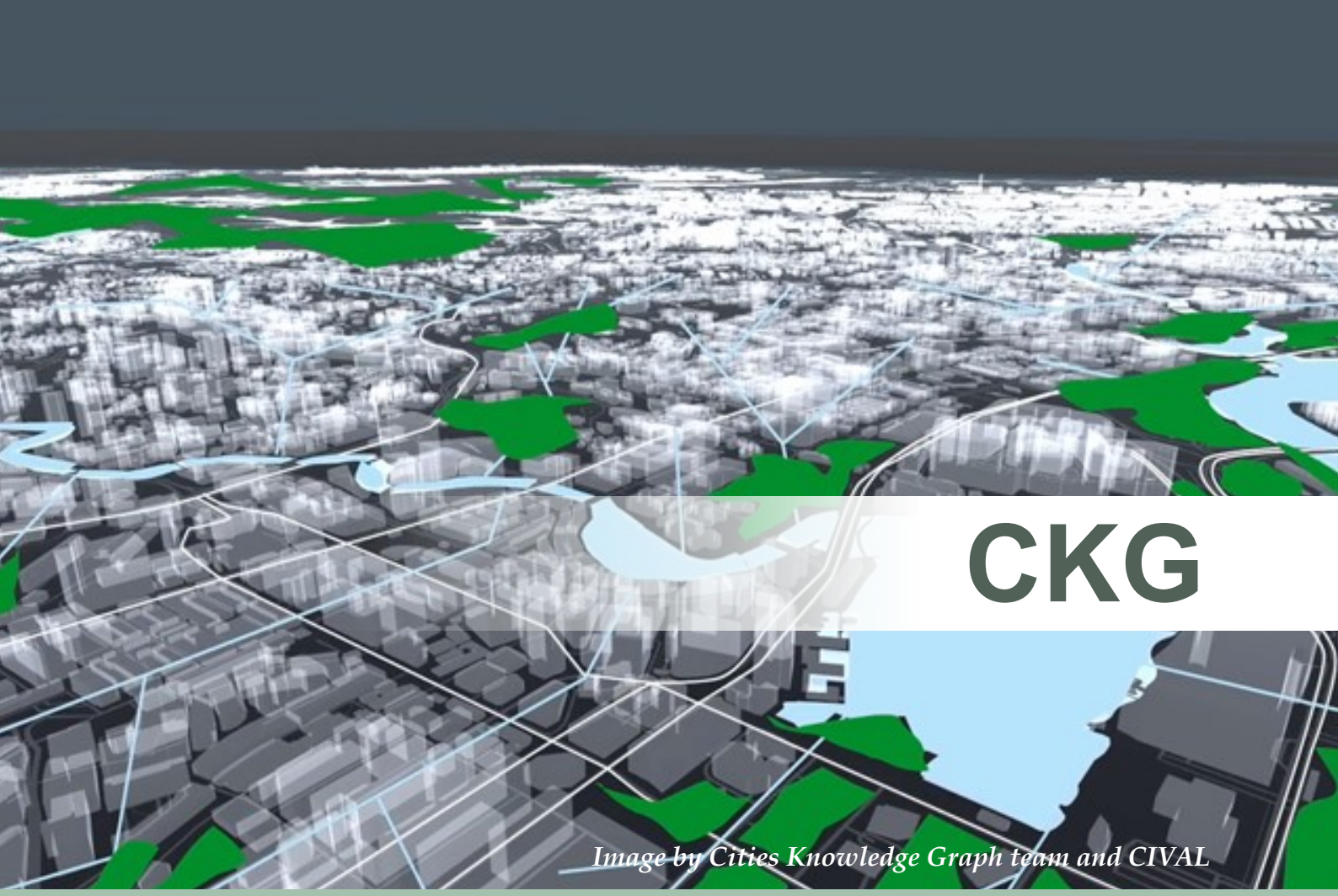
Table 8.1: C_2H_4 and CO_2 adsorption for C_2H_4:CO_2 5:95 mixture at 30 °C and 45 sccm flowrate.

Dr Alexandr KHUDOROZHKOV

Other activities and achievements

Dr Magda BARECKA (Research Fellow, CARES) presented a virtual booth on CO_2 recycling technology during the 2020 Singapore Week of Innovation and Technology (SWITCH).

Simon RIHM (Researcher, CARES) was admitted for PhD studies at the University of Cambridge where he will continue to work on the development and integration of novel computational models under the supervision of Prof. Markus KRAFT.



CKG

Image by Cities Knowledge Graph team and CIVAL

CITIES KNOWLEDGE GRAPH

Cities Knowledge Graph (CKG) aims to transform master-planning related data, information and knowledge into a semantic and extensible platform – a knowledge graph. The proposed CKG would be similar to a knowledge management system for urban planning, integrating information from various sources and domains, evaluating planning proposals against visions and targets set for future urban development, and supporting policy makers and planners by mapping interesting planning directions. It further ties together existing 3D geo-databases, such as URA Space, as well as novel analysis, simulation and visualisation tools developed by CARES and SEC, creating an unprecedented knowledge graph for master-planning.

CKG Principal Investigators:

Professor Markus KRAFT
University of Cambridge

Professor Stephen Cairns
ETH Zürich

OVERVIEW

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). Dr Aurel von Richthofen (Senior Researcher, SEC) and Dr Pieter Herthogs (Senior Researcher, SEC) are Co-Investigators of the project.

Over the past six months, we have completed the extension work of an existing importer-exporter tool to the extent required for a proof of concept that demonstrates the import of publicly available Charlottenburg-Wilmersdorf LOD2 (Level of Detail 2) building data, as well as providing geospatial search capabilities over such data in the context of a dynamic geospatial knowledge graph. Using the extended importer-exporter tool, we have successfully processed and imported over 22,000 buildings found in the native CityGML data source, which have been subsequently converted into semantic triples described in terms of the OntoCityGML ontology. The tool also permits the automatic detection and construction of datatype configurations for over 2,000 different geometrical shape types found in the Charlottenburg-Wilmersdorf LOD2 building data.

Furthermore, we have utilised the Feature Manipulation Engine (FME) Workbench to convert data for buildings, Singapore Land Authority (SLA) land parcel and Singapore Urban Redevelopment Authority (URA) land use information into CityGML format. These transformed data will be instantiated into the Blazegraph using the OntoCityGML ontology and the aforementioned importer-exporter tool. We have also continued our work on integrating the City Energy Analyst, as an energy simulation engine, into the CKG. This involves developing a new ontology, OntoUBEM, to describe the concepts relevant for urban building energy modelling.

As part of the stakeholder engagement strategy, we have conducted a wide range of outreach activities towards academia including Swiss, German, UK and Israeli universities; industry including urban project consultants and developers in Japan and Europe as well as software companies in Switzerland and Singapore; and government agencies such as the public works in Germany and Bulgaria, the Urban Redevelopment Authority in Singapore, and the Asian Development Bank in Manila.

Professor Markus Kraft, PI
University of Cambridge

Professor Stephen Cairns, PI
ETH Zürich

Update on work package 1

Developing master-planning ontologies

This work package aims at developing the master -planning ontologies for the Singapore Master Plan. This will be carried out by reviewing and assessing relevant existing master-planning data, software, practice and ontologies.

Dr Aurel von RICHTHOFEN (Senior Researcher, SEC) and **Dr Pieter HERTHOGS (Senior Researcher, SEC)** have prepared and submitted a literature review paper on semantic city planning systems (under review), titled "Semantic City Planning Systems (SCPS): A Literature Review", which explores the intersection of two core concepts defined in this project: "City Planning" and core levels of the "Semantic Web".

Dr von Richthofen, Dr Herthogs, **Ms Shiying LI (Software Engineer, SEC)**, **Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES)** and **Dr Nenad B. KRDZAVAC (Senior Software Developer, CARES)** have adapted a subset of CityGML (an open data model and XML-based format for the storage and exchange of virtual 3D city models) concepts into an OWL format for the OntoCityGML ontology. This new subset of the ontology has been checked for consistency and new ontology unit test cases have been incorporated. As the existing master-planning datasets are available in numerous formats, Dr von Richthofen and **Ms Ayda GRIŠIŪTĖ (Researcher, SEC)** have utilised the Feature Manipulation Engine (FME) Workbench to convert data for buildings, Singapore Land Authority (SLA) land parcel and Singapore Urban Redevelopment Authority (URA) land use information into CityGML format. Figure 9.3 illustrates an example of the data conversion workflow in FME. These transformed data (in CityGML format) will be instantiated into the Blazegraph (an open-source ultra high-performance graph database) using the OntoCityGML ontology and an importer-exporter tool (described in Work Package 2). Dr von Richthofen will also be leading the preparation of a journal manuscript on the topic of visualising urban data types.

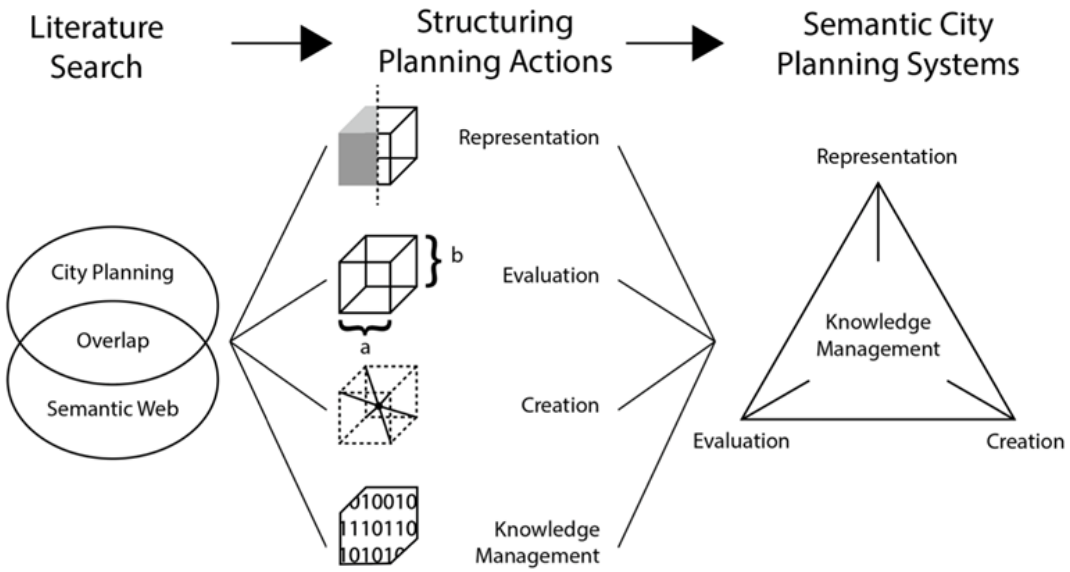


Figure 9.1: Graphical abstract of "Semantic City Planning Systems (SCPS): A Literature Review". Each of these four core actions supports the main action of a City Planning process: Decision-making (the act of making decisions).

Dr Herthogs, **Dr Zhongming SHI (Postdoctoral Researcher, SEC)** and **Ms Heidi SILVENNOINEN (Researcher, SEC)**, in close collaboration with Mr Chadzynski, have been exploring the concepts and functionalities present in the URA Space and open government datasets (the URA Singapore Master Plan and SLA's land parcel data in particular). The URA Space is an online portal developed by the Singapore URA to deliver location-based services and information. It comprises a variety of data – including structured data on the Singapore Master Plan. This activity is a prerequisite for applying and extending the OntoCityGML ontology to Singapore's context, and loading various datasets into a knowledge graph for Singapore city planning.

Dr Shi, Ms Silvennoinen and Dr Herthogs are developing planning libraries that link land use and zoning types with building uses to produce occupancy profiles for each land parcel type. As a starting point, Google Map API data will be utilised in this work. Dr Shi is also leading the preparation of the related journal manuscript, titled "Linking master plan's zoning types and urban building energy modelling's use types". The aim of this journal manuscript is to bridge the gaps between the land use and zoning concepts in the domain of master-planning and the building use concepts in the domain of urban building energy modelling.

In addition, Dr Shi has continued his work on integrating the City Energy Analyst (CEA), as an energy simulation engine, into the CKG. This involves developing a new ontology, OntoUBEM, to describe the concepts relevant for urban building energy modelling.

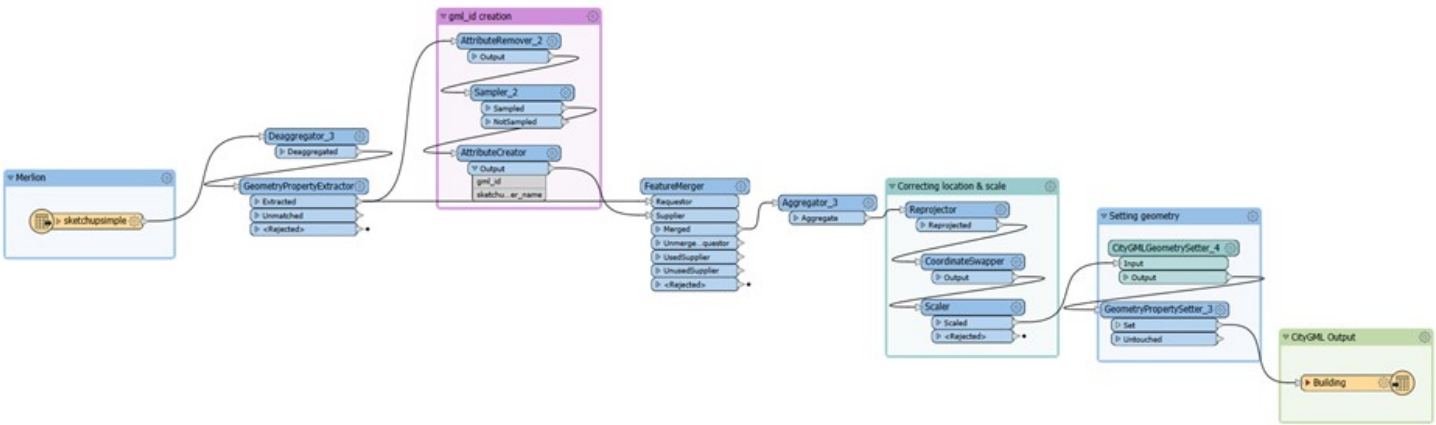


Figure 9.3: An example of the data conversion workflow in FME for converting building geometries into CityGML format.

Update on work package 2

Developing the knowledge graph's architecture

This work package aims at developing the knowledge graph's architecture in order to make use of the full potential of Semantic Web technologies. We will approach this by developing 1) agent ontology to describe the agents' functionalities and characteristics to enable agent discovery and composition; 2) semantic agent composition framework to facilitate automatic agent discovery and composition, to dynamically generate cross-domain applications and to provide information for decision-making; 3) "Parallel world" functionalities to facilitate design space exploration and 4) decentralised architecture to facilitate the integration of data repositories.

Mr Arkadiusz CHADZYNSKI (Senior Research Fellow, CARES) has completed the extension work of an existing importer-exporter tool to the extent required for a proof of concept that demonstrates the import of publicly available Charlottenburg-Wilmersdorf LOD2 (Level of Detail 2) building data, as well as providing geospatial search capabilities over such data in the context of a dynamic geospatial knowledge graph. This involves, amongst others, the modification of 13 classes corresponding to CityGML features such as CityObject, Building, SurfaceGeometry, GenericAttribute, etc. The original importer-exporter tool, developed at the TU Munich, was augmented in order to make it capable of executing SPARQL queries against triple store endpoints for importing data. **Ms Shiying LI (Software Engineer, SEC)** is also working on similar modifications in order to make the tool capable of exporting the Keyhole Markup Language (KML) models from the triple stores. The equivalents of appropriate SQL prepared statements have been included in the tool. Mr Chadzynski, together with Ms Li, has developed unit tests for the new functionalities. Ms Li is also in the process of extending the tool for extracting 3D geospatial models from the triple stores. By preserving the structure of the original TU Munich 3D City database, the extended tool is able to leverage the previous TU Munich research efforts. Figure 9.4 presents a high-level overview of how this has been achieved.

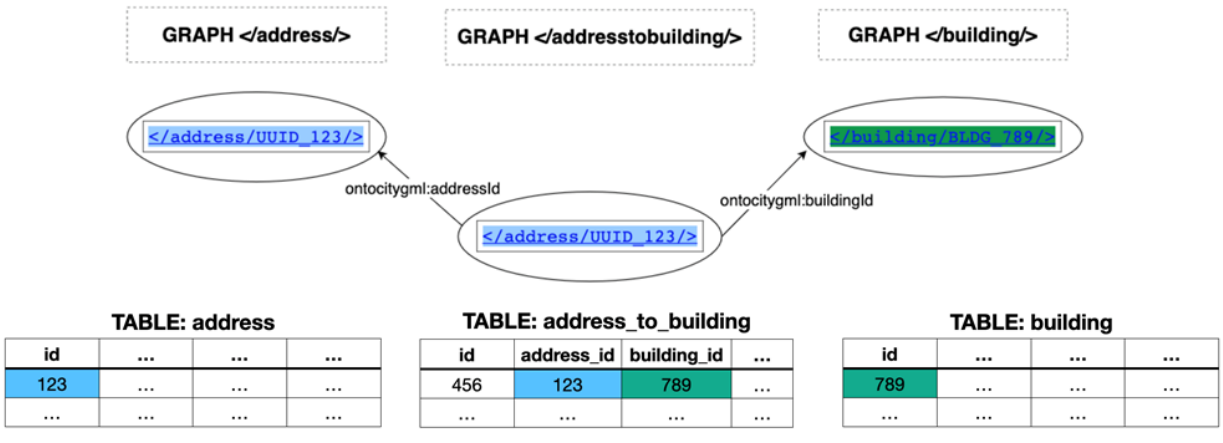


Figure 9.4: An example of structural isomorphism illustrating equivalence of city model representations within the original TU Munich 3D City database and its semantic twin. The named graphs for addresses and buildings correspond to the tables with the same names in the relational database. The IRIs help in identifying entities in a similar manner as unique and sequential IDs does (primary keys) in the original table records of the database. Instead of using records containing appropriate foreign keys in the original binding table, addresses are associated to buildings through data linking with their IRIs in the named graphs.

Mr Chadzynski and Ms Li have successfully processed and imported over 22,000 buildings found in the native CityGML data source using the extended importer-exporter tool, which have been subsequently converted into semantic triples described in terms of the revised OntoCityGML ontology. The triples have been organised into eight different named graphs in Blazegraph to maximise optimal data storage and query performance. Blazegraph was selected for this proof of concept because of its scalability and in-built geospatial search algorithms.

To take advantage of Blazegraph's in-built geospatial search functionality, it was necessary to develop a custom vocabulary class as well as datatype configuration properties file. However, due to the diverse types of geometrical shape found in the data, it was not feasible to create the vocabulary class and configuration files manually. Consequently, Mr Chadzynski created a functionality to automate the construction of such datatype configurations along with the corresponding vocabulary items. This functionality has been added to the tool's

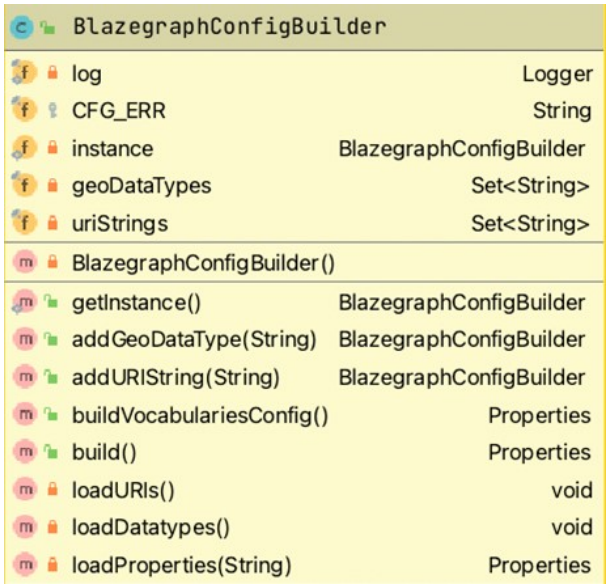


Figure 9.5: Class diagram for geospatial datatype and vocabulary item configuration builder.

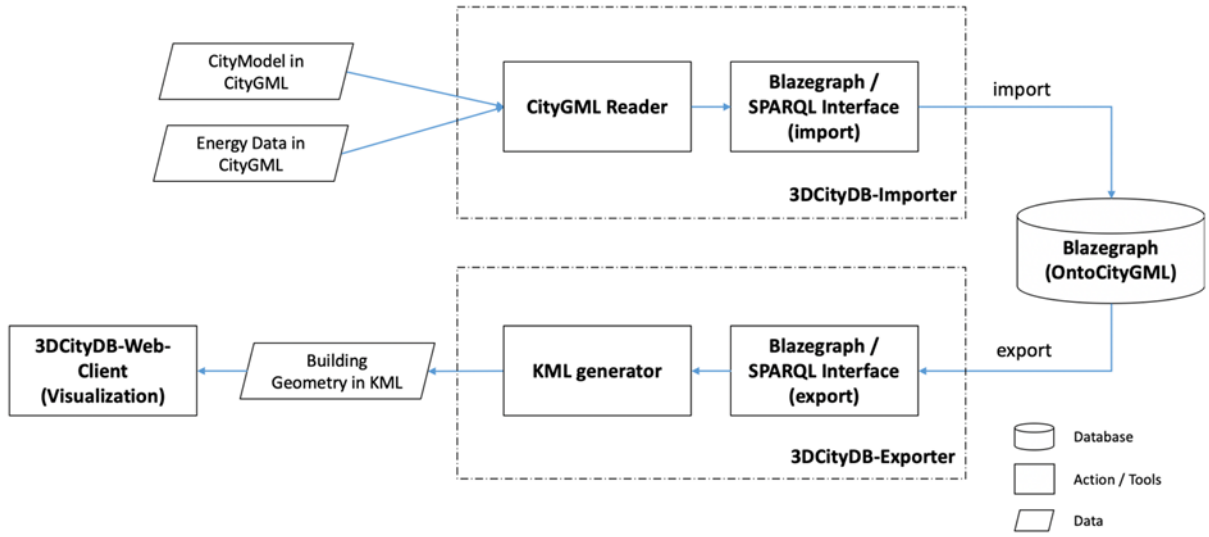


Figure 9.6: Flowchart diagram illustrating the intermediate software architecture design for the use case of master-planning informed by urban building energy performance.

"GeometryConverterAdapter" class. In conjunction with the newly introduced "BlazegraphConfigBuilder" class (as shown in Figure 9.4), the extended importer-exporter tool – based on a thread safe singleton design pattern, detects any new shape type and automatically creates appropriate configurations depending on its geometrical properties. The geometrical properties are also encoded in the vocabulary item names in order to facilitate the classification of data into their underlying geometries. This classification allows users to query for coordinates stored under a certain datatype. For example, an instance with a datatype IRI ending with "SOLID-3-15-15-15-15-15-15" is associated with a cube. The first number, e.g., 3 in the above example, describes the dimensionality of the stored geometry type. The remaining numbers, e.g., 15 in the above example, indicate that the stored data consists of 6 parts (six "15") of a cube and that each part is represented as a polygon in terms of the 5 points (5 sets of x, y and z coordinates) encoded in a coordinate system. This design permits the automatic detection and construction of datatype configurations for over 2,000 different geometrical shape types found in the Charlottenburg-Wilmersdorf LOD2 building data. The team is in the process of preparing a journal manuscript titled "Semantic 3D City Database – an enabler for dynamic geospatial knowledge graph" which describes the main ideas and findings of this work.

Update on work package 3

Developing agents to operate software and integrate data

This work package aims at developing agents to operate software and integrate data in order to populate the knowledge graph. We will approach this by developing agents for data pre-processing, packaging existing and new planning libraries as agents and incorporate them into CKG using ontologies and developing reasoning and inference capabilities to facilitate design space exploration and scenario analysis.

This work package has not yet started in its entirety as the project is in the process of recruiting post-doctoral researchers for this work package.

Update on work package 4

Developing interfaces and planning libraries for the CKG

This work package aims at developing interfaces and planning libraries in order to allow stakeholders to interact easily with an interface to, e.g., receive information about a planning area, ask "smart queries", or input a range of planning scenarios they would like the CKG to explore and analyse. We will approach this by developing planning libraries (agents) that can perform certain planning actions (master-planning tasks) based on user input.

Dr Pieter HERTHOGS (Senior Researcher, SEC) has developed the first mapping of the CKG platform functionalities and features, including a development prioritisation map. This map informed the development of an interface mock-up for the CKG platform by **Ms Ayda GRIŠIŪTĖ (Researcher, SEC)** and **Dr Aurel von RICHTHOFEN (Senior Researcher, SEC)**. Figure 9.7 illustrates an interface mock-up for Gross Plot Ratio related queries and visualisation sketches.

Ms Shiying LI (Software Engineer, SEC) has reviewed the geo-visualisation pipeline requirement and researched on the different proposed frameworks to identify the limitation of the existing solutions. Ms Li is also extending an existing static web-based visualisation tool, which utilises Cesium Virtual Globe as an underlying 3D geo-visualisation engine, to visualise the Keyhole Markup Language (KML) models exported from the Blazegraph using the extended importer-exporter tool mentioned in Work Package 2. The web-based visualisation tool is an open-source project that allows continuous development and adaptation for the CKG project's needs. In addition, she is in the process of creating a dynamic interactive web-based visualisation tool that loads information based on the user queries.

Figure 9.7: A mock-up for Gross Plot Ratio related queries and visualisation sketches.

Update on work package 5

Developing design informatics functions

This work package aims at developing models and algorithms to analyse planning capacities and potentials, and visualisation modes for the models to inform stakeholders. We will approach this by developing specific models or algorithms, integrating existing metrics where possible, and developing several metrics to inform the outcomes of particular planning actions in order to compare or evaluate different planning proposals or scenarios.

This work package has not yet started in its entirety, as it strongly relates to the types of functionalities and analysis modes to be added to the CKG platform. In preparation, **Dr Pieter HERTHOGS (Senior Researcher, SEC)** has been developing an ontological framework for design evaluation and design decisions, which supports the inherently goal-seeking activity of planning by hierarchically mapping goal types and linking complex planning goals (e.g., liveability) to measurable properties in an urban environment. In addition, **Dr Zhongming SHI (Postdoctoral Researcher, SEC)** and Dr Herthogs have started exploring methods to parametrically define the boundaries of a planning site for analysis (i.e., mathematical, goal-driven definitions of a site context).

Update on work package 6

Demonstrators: horizontal and vertical use cases

This work package aims at developing two use cases: one horizontal and one vertical use case, in order to demonstrate the potential applications and extensibility of the CKG approach. The vertical use case examines gross plot ratio planning in a key development area, while the horizontal use case looks at land use planning from concept plan to master plan.

Dr Zhongming SHI (Postdoctoral Researcher, SEC) has prepared a paper, titled "Land Use Type Allocation Informed by Urban Energy Performance: a use case for a semantic-web approach to master planning" and presented it at the 2021 annual conference for the Computer-Aided Architectural Design Research in Asia (CAADRIA). The use case described in the paper serves as a pilot demonstrator for the CKG project, which is a much broader research scope. Figure 9.8 illustrates some aspects of this use case. In addition, Dr Shi is in the process of creating other potential use cases, e.g., building floor area allocation.

Complementary to this, **Dr Aurel von RICHTHOFEN (Senior Researcher, SEC)**, **Dr Pieter HERTHOGS (Senior Researcher, SEC)** and Dr Shi co-supervised a master thesis on "Energy-driven urban design", which explored use cases of energy-related planning questions more broadly. The student, **Ms Ekaterina VITITNEVA** (Bauhaus University Weimar; main supervisor Prof. Dr Reinhard KOENIG) has successfully completed her thesis in March 2021. The research outcome will lead to conference publications; two abstracts have been accepted for CISBAT 2021 (Carbon Neutral Cities - Energy Efficiency & Renewables in the Digital Era) and ISUF 2021 (International Seminar on Urban Form).

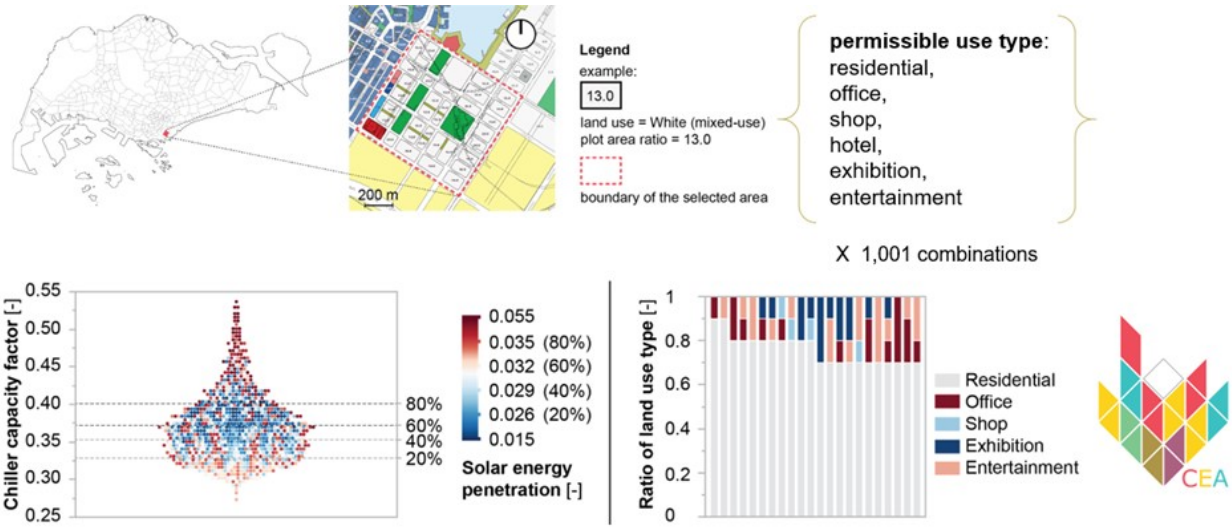
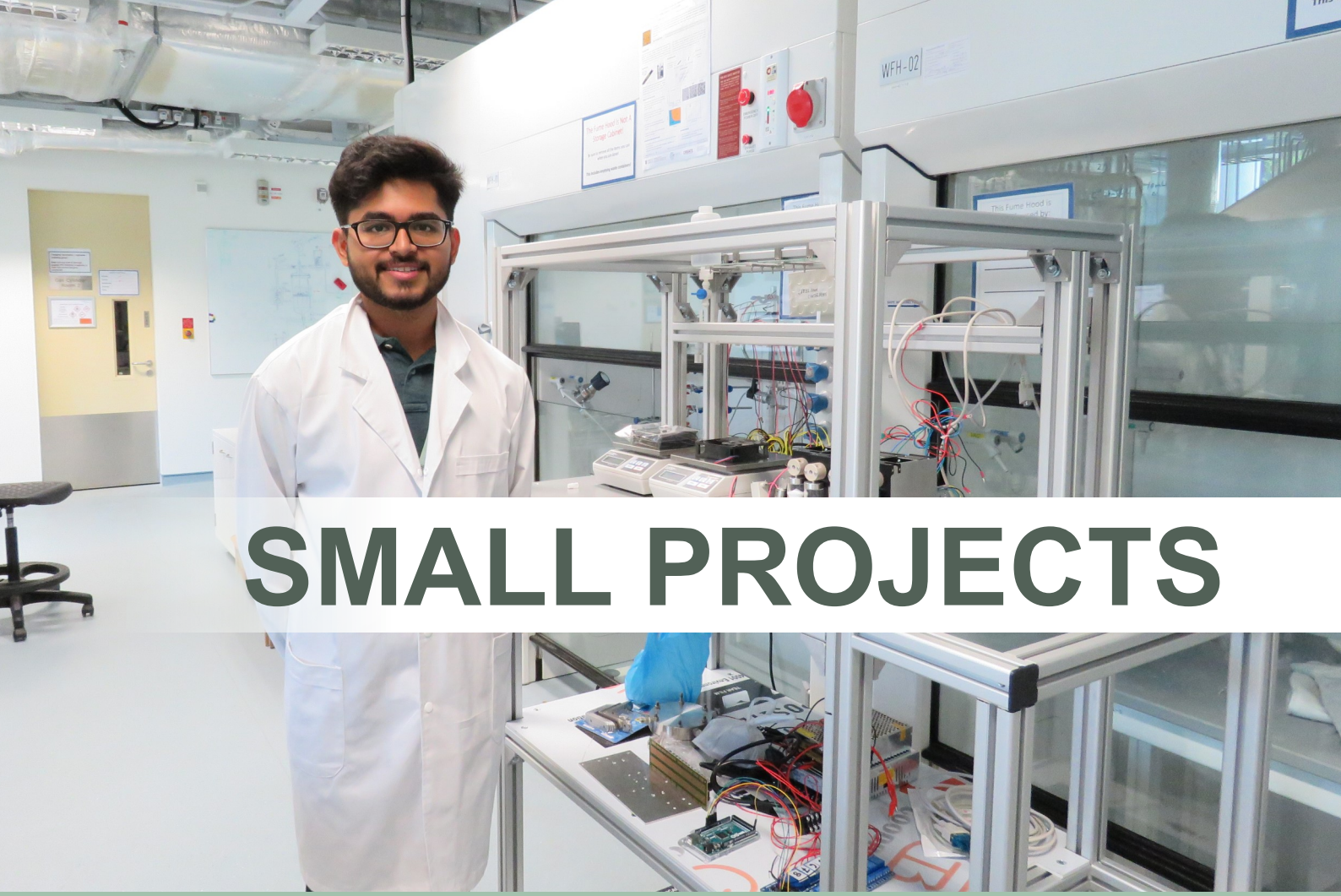


Figure 9.8: The use case of land use allocation informed by urban energy performance. This work has been submitted to CAADRIA 2021.


UOB
OCBC Bank



SMALL PROJECTS

OTHER CARES-FUNDED PROJECTS

In addition to C4T and eCO_2EP, CARES hosts a number of other projects. 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 in 2019) to have a novel experience of research and technology development not easily available during their undergraduate degrees.

The current CARES small projects include three funded by the private-public partnership Pharmaceutical Innovation Programme Singapore (PIPS) and Consumer Energy Usage Data in Smart City Development (CEUS, an Intra-CREATE seed grant project).

The Smart Innovation Centre-funded project Rapid Industrialization of Next Generation Nanomaterials (RINGs) has now come to an end and its final report can be found on page 124.

This section also includes updates on the ten projects under the C4T Emerging Opportunities Fund, which was created to support exciting new ideas that have arisen since the start of C4T Phase 2.

Consumer Energy Usage Data in Smart City Development (CEUS)

Intra-CREATE seed grant

CEUS commenced in October 2020 and is a seed funded Intra-CREATE collaborative project between Cambridge CARES and the Singapore-ETH Centre which will run for 18 months. CEUS will lay the groundwork for Singapore consumers to manage their energy usage and cost. It will also outline ways for local government to make informed decisions based on real-time energy use for smarter city planning. The project is led by Principal Investigators **Dr Franziska SIELKER (CAM)** and **Dr VSK Murthy BALIJEPALLI (SEC)** and supported by other researchers at Cambridge CARES, the Singapore-ETH Centre, NTU and ETH Zürich. At CARES, **Mr Gourab KARMAKAR (Research Associate)** is the lead researcher.

The project aims to develop data standardisation and information for the end consumer domain using the Common Information Model (CIM). It will allow customers to analyse their energy usage information for active participation in the retail energy market and make better-informed decisions. CEUS will also link up with the existing data platform already developed by CARES, the J-Park Simulator, to enable seamless and effective exchange of consumer energy usage data with third party services, and to test the potential use of this data in GIS and BIM software. Here the project has already started to coordinate with the Cities Knowledge Graph project (page 105), with **Dr Aravind DEVANAND (Research Fellow, CARES)** working on both projects. Singapore's energy policies as well as the planning and governance systems will be taken into account to ensure that the project's outputs can be easily adopted for widespread use.

The information provided by the common data platform opens the path towards a consumer digital-twin. This project therefore lays the foundation for the integration of consumer usage real-time data into city information modelling. The project is a testbed for improving interoperability among many different digital technological systems and provides information to city planning authorities while respecting consumer privacy. Further, this project questions which policies need to be set in place to protect consumer data and at the same time to provide information on how the platform's data can be used in smart city planning in Singapore.

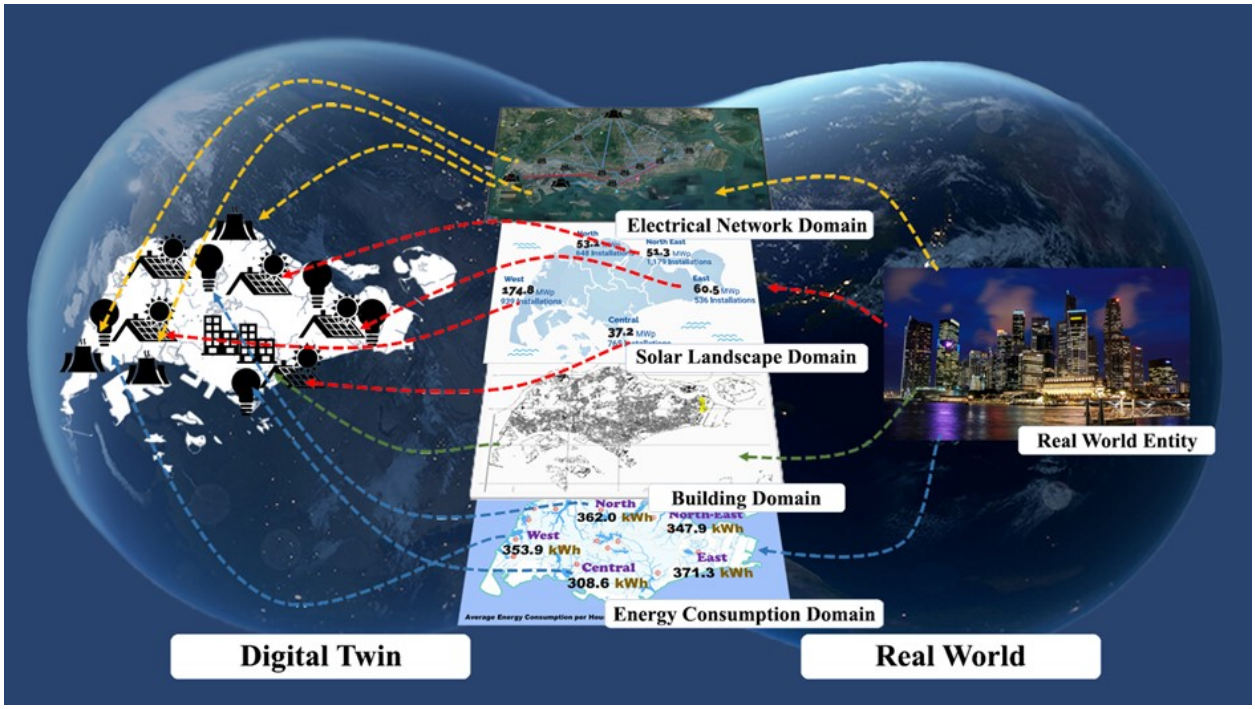


Figure 10.1: An image showing the interface between the digital and real world in the CEUS model.

The aims of the CEUS project are:

A common language—New forms of consumer semantics will be provided to expand the smart city planning of the future. A Singapore-specific Common Information Model will allow consumers to make better decisions around their energy use.

More effective data sharing—An autonomous agent framework will be developed in the CARES J-Park Simulator that enables a seamless and effective consumer energy usage data exchange with third party services.

Smart city energy policies—Amendments to the existing energy policy framework will be suggested to implement the proposed technical solution in a smart city environment.

Work package 1: Development of a common information model

WP1 is led by SEC and developed in close cooperation with the other entities. Dr Balijepalli conducted a literature survey focusing on the development of Common Information Modelling (CIM), complemented by information on BIM and knowledge graphs through the CARES team. CIM is a well-established open standard in the power systems domain due to its common semantics used to construct communication messages between the applications. It is considered an enabler of smart grids due to its robust framework for accurate data sharing, merging and transformation into reusable information. An indicative assessment of CIM compliant software has been carried out and the results have been presented. It involves a comparison of various CIM tools on defined attributes and highlighting key strengths and weaknesses (see Figure 10.2). Under the lead of SEC, the project team submitted the literature review as a paper titled "Evolution of Power System CIM to Digital Twins - A Comprehensive Review and Analysis" to *IEEE PES ISGT Europe 2021*.

✓ - Supported; × - Not Supported; • - Not Provided by the Authors

Name of the Tool	Year[1]	Type of the Tool (License)	CIM Application Schema/ Profile Generation	UML/ Equipment Visualization	RDF XML import/ export (Merging Models)	Class Searching Strategies	Schema Driven Model Validations	CIM Oriented Database	Managing Extensions	Send/ Receive CIM messages	User custom applications
CimConteXtor [77]	2011	Desktop: Add-on	✓	•	×	×	✓	×	✓	×	✓
Cimphony [78]	2008	Desktop (Commercial)	✓	✓	✓	✓	✓	✓	•	✓	•
CIMSpy EE [79]	2005	Web Based/ Desktop (Commercial)	✓	✓	✓	×	✓	•	×	✓	•
DIgSILENT PowerFactory [80]	2011	Desktop (Commercial)	×	•	✓	×	•	•	×	✓	×
EUROSTAG® [81]	2011	Desktop (Commercial)	×	✓	✓	×	✓	✓	×	×	×
NEPLAN® [82]	2013	Web Based/ Desktop (Commercial)	•	•	✓	•	•	•	×	×	×
Ventyx NM EMS [83]	2011	Desktop (Commercial)	✓	✓	✓	•	•	✓	×	×	•
CIMTool [84]	2007	Desktop (Free)	✓	×	✓	•	✓	•	✓	•	•
PSS/ODMS [85]	2007	Desktop (Commercial)	✓	✓	✓	✓	✓	✓	✓	✓	✓
SPIRA [86]	2010	Desktop (Commercial)	•	✓	•	•	•	•	×	×	×
TNA [87]	2011	Desktop (Commercial)	✓	✓	✓	✓	✓	✓	•	•	•
CIMvian [88]	2007	Desktop (Free)	×	×	✓	×	✓	×	×	×	×
InterPSS [89]	2010	Desktop (Commercial)	•	✓	✓	×	✓	•	✓	×	•
UIB SISCO Model Store [90]	2007	Web Based Commercial	✓	✓	✓	✓	✓	✓	✓	✓	✓

[1] *year from which CIM support provided*

Figure 10.2: Indicative assessment of the features of various tools which support CIM in the power system domain.

Work package 2: Knowledge graph ontology development

The CARES team is working actively with **Dr VSK Murthy BALIJEPALLI (PI, SEC)** to develop the ontologies needed to link the Consumer Information Modelling prepared in WP1 with the J-Park Simulator (JPS) framework. As a first step, the xml file provided by SEC that includes the CIM grammar was validated and put into a consistent format with the JPS grammar. A first version of the ontology schema in the OWL/RDF format was developed by Dr Devanand. In order to integrate the xml CIM to the JPS system the next step is for Dr Murthy to provide further contextual information. Moving ahead, Dr Devanand and Mr Karmakar will work closely with Dr Murthy to understand more about the way information is modelled in the xml file to develop a schema in xmltds (xml transformation language) and map that schema to the elements in the RDF schema. At the time of writing the project team was also working on providing clarity on what information exists in the common information model or needs to be included so that it can be used for planning purposes. At the same time the team analysed data privacy requirements. The project team expects the work on WP2 to be finalised on schedule.

Work package 3: Implementation of digital-twin use case

This work package deals with the implementation of the use case and is led by SEC. The development of the use case has been finalised and will utilise the consumer ontology developed under WP2. Real-time consumer energy data will be integrated with the developed ontology to showcase the advantage of Common Information Modelling, which will be a part of JPS.

Work package 4: Planning and energy consumption information for policy-making

To start the work package, the team conducted regular meetings to understand each others' disciplines. As a first step in WP4, an overview of relevant policies and institutions in Singapore was created. As a second step, Mr Karmakar, with guidance from Dr Sielker, conducted a comprehensive literature review on the application of knowledge graphs and semantic web technology in the domains of architecture, engineering and construction (AEC). The goal of this literature review is to identify what other approaches exist to make use of knowledge graph technology and link it to building information modelling, city information modelling and GIS. The findings from the literature review were classified into the following topics:

Interoperability—Knowledge graphs and semantic web technology will help to enable vendor-neutral model exchange ensuring interoperability between Industry Foundation Class (IFC) expressed using various standards such EXPRESS and STEP standards. Semantic web technology will also help to combine different information representations and support use case based information exchange.

Linking across domains—Semantic web and knowledge graph technologies provide the option to link information stemming from diverse domains (e.g. BIM, GIS, heritage, sensor data, simulation data, smart cities) into one web of linked building data. The key research question is often related to the creation of domain ontologies, which aim at providing a shared representation for the concepts within a domain of knowledge, and how they should be linked together and still remain useful.

Logical inference and proofs—The topic that is often used in arguing for the adoption of semantic web technologies in the architectural design and construction industry relates to the logical foundations available in semantic web technologies. Using generic inference engines, extra information can be inferred from the information in RDF and OWL through simple deep learning principles. Moreover, it is possible to represent IF-THEN rules, for example using SWRL, thus allowing reasoning within First Order Logic (FOL). When integrating these rules and combining them with original building data and a reasoning engine, a considerably powerful inference process can be realised.

The researchers are also involved in preparing a paper titled "Knowledge Graphs for Urban Planning: A Literature Review" which summarises the current research being done on the application of semantic web technology in urban planning, key research challenges and future research directions focusing on efficient knowledge and data management in the AEC domains. Further more, in collaboration with other institutes Dr Sielker submitted a session proposal to the Data for Policy Conference 2021 entitled "Knowledge graphs and smart city developments – better public policies through parallel worlds?". The panel will host five short presentations that address various fragmented operating models drawn from the Singapore and the UK context.

- The first presentation, led by Radboud University Groningen, will present the use of digital twins for communication between smart cities and urban systems.
- The second presentation, led by University of Cambridge, will present the use of digital twins and discuss the challenges of digital twins in support of decision-making and planning.
- The third presentation, led by Cambridge-based CMCL Innovations, will present the knowledge graph technology and examples for its applications in (urban) planning.
- The fourth presentation, led by the Singapore-ETH Centre, will present the Cities Knowledge Graph and its potential to support policy making.
- The fifth presentation, led by CARES, will present an attempt to use the knowledge graph technology as an interlocutor between BIM, CIM and GIS software using the example of energy.

The corresponding paper to the conference "Towards smart city planning – digital twins and parallel world scenarios to support better public policies?" is drafted, and will now be revised before submission to the *Data & Policy* journal.

Data2Knowledge in the Digital Manufacture of Pharmaceuticals

With funding from Pharma Innovation Programme Singapore (PIPS), via A*STAR

Data2Knowledge in the Digital Manufacture of Pharmaceuticals is a project funded under the Pharma Innovation Programme Singapore (PIPS) programme and led by **Professors Alexei LAPKIN** and **Markus KRAFT (PIs, CAM)**. This is a 15-month project and commenced in December 2020.

The digitalisation of chemical manufacturing is one of the critical technology paths towards a more sustainable society, as it promises to deliver a significant level of decarbonisation of industry. It focuses on creating a digital twin of the physical entities that bridges the gap between the cyber - and the real-world, shortening the time span from design to the delivery of the target product to the end-users. Data2Knowledge is a project that aims to develop a fully automated data exchange and knowledge management within a closed-loop self-optimisation experiment.

As a pre-requisite condition, the absence of standards in data representation and communication protocols is seen as one of the critical challenges faced by the chemical manufacturing community. Despite several competing standards for representing molecules co-exists, there is no standard method of representing results or reci-

Figure 10.3: Dr Mohammed JERAAL and Dr Simon SUNG with the automated flow chemistry system.

pes for chemical experiments, not to mention the communications between the equipment employed. We hypothesise that the knowledge graph technology, along with utilisation of ontological data representation and autonomous agents' interaction, would improve the interoperability between the different data standards, hence enabling rapid implementation of AI tools for data manipulation, knowledge generation, sharing and exploitation.

To reach a consensus of all partners on the approaches to developing the overall data and knowledge exchange framework, **Mr Jiaru BAI (in-kind PhD student, CAM)** and **Ms Liwei CAO (in-kind Research Associate, CAM)** have conducted a literature review on the state-of-the-art studies of the experiment automation. The common practice towards experiment automation can be summarised as a platform-based approach where the entire setup is separated into function components with ad-hoc data representation and different data communication protocols based on their utilities. The data storage ranges from variables stored in programming languages to a CSV file, or even to a proprietary database. These data are transferred in various ways, e.g., assigning values stored in the computer memory, file transfer protocol, HTTP request/response, etc. However, these systems usually face scalability issue as a considerable amount of time is often required when new hardware or software is to be integrated. The heterogeneous data format also lacks interoperability that precludes the full utilisation of the embedded information. Mr Bai and Ms Cao are in the process of preparing a paper which describes their findings.

As the project will utilise the existing automated flow chemistry system, Mr Bai has been working on extending the OntoChemExp ontology, which was originally developed for combustion experiments, to further support the flow chemistry experiment by providing semantic descriptions for the experiment process. In addition, Mr Bai and Ms Cao, together with **Dr Mohammed JERAAL (Research Associate, CARES)**, are refactoring the existing codes such that they can be packaged as agents in the next step.

Development of Multi-Step Processes in Pharma

With funding from Pharma Innovation Programme Singapore (PIPS), via A*STAR

Development of Multi-Step Processes in Pharma is funded under the Pharma Innovation Programme Singapore (PIPS) programme and led by Prof. Alexei LAPKIN. This is a three-year project which commenced in June 2019.

For a given active pharmaceutical ingredient (API), the complexity of the multi-step chemical synthesis and purification, and the enormous number of possible reagent and reaction condition combinations are significant bottlenecks for rapid large-scale manufacturing. The work conducted by **Dr Simon SUNG** and **Dr Mohammed JERAAL (Research Fellows, CARES)** is focused on developing a novel automated self-optimising system that can rapidly identify sustainable and high yielding multi-step chemistry and purification routes in tandem. This will be achieved by combining programmable chemical handling equipment, analytical tools and machine learning (ML).

With greater experience in chemistry, Dr Sung has led the development of parameters that describe the chemistry properties (chemical descriptors) of the solvents and reagents used in the first chemical reaction step in the multi-step synthetic path (Figure 10.4). The choice and quality of the chemical descriptors are crucial to allow the ML algorithm to effectively learn their effects on the chemical reaction and select solvents and reagents during the reaction optimisation. These were produced using computational chemistry based around Density Functional Theory (DFT) and the COSMO (COnductor-like Screening Model) solvation model.

In combination with extensive optimisation of the self-optimisation equipment and ML algorithm by Dr Jeraal, the set-up was finally utilised for automated training set development and self-optimisation of the first reaction step. Current efforts are being focussed on ensuring the process optimisation parameters selected are optimum and planning for the second reaction step.

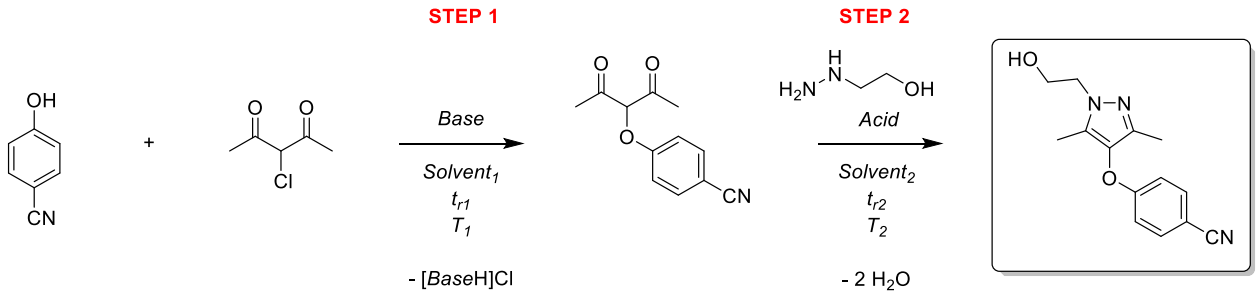


Figure 10.4: Reaction scheme for a multi-step reaction to form an analogue of the antiviral drug Lersivirine. Case study intended to test the automated continuous and discrete variable multi-objective reaction ML optimisation platform. Temperature = T, residence time = t_r.

Digital Workflow and Continuous Processing in Pharmaceuticals Manufacturing

With funding from Pfizer as part of the Pharma Innovation Programme Singapore (PIPS)

Digital Workflow and Continuous Processing in Pharmaceuticals Manufacturing is funded under the Pharma Innovation Programme Singapore (PIPS) programme and led by Prof. Alexei LAPKIN. This is a two-year project which commenced in January 2021.

Transformation of manufacturing in the pharmaceutical industry to new emerging business models (on demand, customisation, sustainable manufacturing, etc.) is heavily dependent on the development of supporting technologies, such as a novel manufacturing paradigm of fully continuous processes and digital tools for support of R&D and manufacturing.

A number of current challenges in the supporting technologies are interlinked. Thus, development of effective flow processes and the use of continuous flow technology in manufacturing requires innovation in process modelling, reactor technology/reactor manufacturing, process data monitoring and knowledge management. This requirement spans the areas of synthesis, process engineering, process control, data science and artificial intelligence.

The objectives of this project are:

- To develop a technical solution for exploration of a maximally diverse range of operating conditions using a minimal set of reactor components.
- To explore a multi-modal analytics approach for rapid generation of data from experimental systems.
- To demonstrate the application of rational design of a continuous flow process to industrially relevant case studies.

A new Research Fellow, Dr CHEN Guoying, started on the project in March.

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) was 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 were combined as a platform for materials development and scale-up. The proof-of-concept project is the rapid development of antibacterial nano-ZnO coatings.

Over the past six months, samples of material for potential customers (including Dow Chemical and HDB) were produced. Research findings on the synthesis of ZnO materials, machine learning and 2D metal organic frameworks were presented at the *AIChE Annual Meeting* and *Singapore Week of Innovation and Technology (SWITCH)* conferences.

On the technological side, a new method for creating high rate 2D layered double hydroxide electrodes was conceived and is being disclosed to NTUitive. New strategies were developed for highly robust flow distributors. This is the subject of a new disclosure to NTUitive, which is being prepared. Further work will include the investigation of LDH electrode fabrication methods and scale-up strategies. New methods will continue to be developed for scaling the annular microreactor developed in CARES. The project has now been successfully completed with all milestones met.

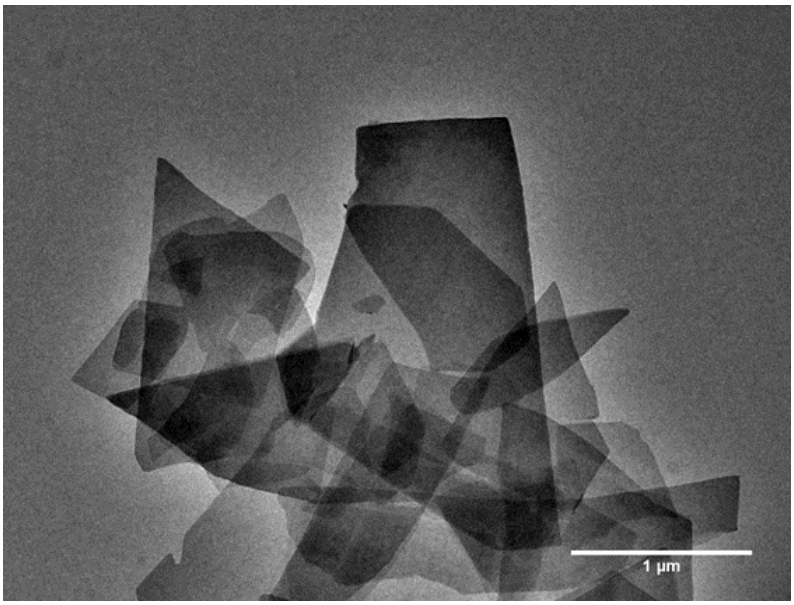


Figure 10.5: A "nano-cubist" image of ZnO flakes captured using a transmission electron microscope.

Ms Kencha SATYA (Research Engineer, CARES) worked primarily worked on RINGs, focusing on rapid optimisation of nanomaterial production.

Ms Satya's main research interest lies in the studying the anti-bacterial properties of zinc oxide (ZnO) nanocrystals embedded in a polymer (latex) matrix coated on different substrates of interest. Currently she is working on optimisation and establishing characterisation procedures for studying the nanoparticle zinc oxide. She has documented the preliminary results-based on qualitative/quantitative analysis of anti-bacterial (e.g. *E. Coli*) and anti-fungal (e.g. a real-life fungus sample) performance of ZnO/latex coated substrates in comparison with control blank substrates. ZnO/latex coated substrates shows excellent (~ 4 log) anti-bacterial/anti-fungal performance compared to control blank substrates.

As RINGs has ended, Ms Satya has now shifted to eCO_2EP and is currently refining methods for controlling nanoparticle synthesis in the annular flow microreactor.

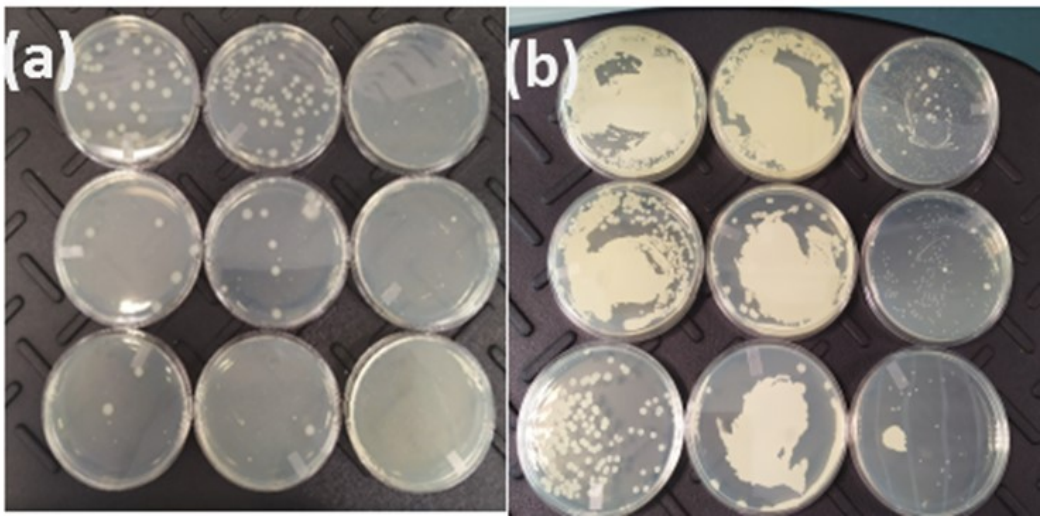


*Figure 10.6: (a) Anti-bacterial (*E. Coli*), (b) Anti-fungal (fungal sample cultured from neighborhood surface) testing of blank, latex and ZnO/latex (left to right columns) at different dilutions of inoculum.*

Cooling Singapore 2.0

In collaboration with the Singapore-ETH Centre

Cooling Singapore was launched in 2017 and is hosted by the Singapore-ETH Centre. The first phase of the project – Cooling Singapore 1.0 – focused on assessing Singapore's urban heat island effect and outdoor thermal comfort in order to identify potential heat mitigation measures. This work allowed identification of knowledge and technology gaps and several ideas for future work were proposed. CARES is partnering with Cooling Singapore as it enters its second research phase, which aims to construct a Digital Urban Climate Twin for Singapore. This platform will bring together several computational models (environmental, land surface, industrial, traffic, building and energy) as well as climate models to investigate ways to reduce Singapore's urban heat and mitigate its effects. The Digital Urban Climate Twin will also allow researchers to trial various scenarios and predict the impact they may have on urban heating.

CARES' contribution to Cooling Singapore 2.0 will be evaluating the anthropogenic heat emissions from Industry in Singapore by developing computational energy models using The World Avatar Knowledge Graph. Ultimately, these energy models will be fed into the Digital Urban Climate Twin. We will also be developing models to simulate the effect of potential mitigation solutions on the anthropogenic heat emissions from Industry in Singapore.

Singapore's high building density increases urban heating.

Dr Vishvak KANNAN (Research Fellow, CARES) joined the project in February 2021 to work on developing ontology frameworks and computational models to map and quantify the anthropogenic heat emissions from Jurong Island, the core of Singapore's energy and chemicals industry.

Dr Kannan has prepared a survey for obtaining data to identify the major industry heat emitters, as well as to calibrate and validate the computational energy models that will be developed. In addition, Dr Kannan is in the process of creating preliminary spatial-temporal distribution profiles of heat fluxes across Jurong Island for different scenarios. These profiles will be fed into the Weather Research and Forecasting (WRF) model to investigate the impact of the anthropogenic heat emissions from Jurong Island on the Singapore mainland. Dr Kannan, in close collaboration with **Dr Aravind DEVANAND (Research Fellow, CARES)**, is in the midst of developing ontologies for describing the concepts relevant to the legacy information from an ArcGIS model.

Cambridge Alternative Finance Collaboration Network

University of Cambridge Judge Business School

Since January 2021, the CAFCN has been active in the Asia-Pacific region through the establishment of a research collaboration with Cambridge CARES alongside a bi-lateral programmatic relationship between the Asian Development Bank Institute and the Cambridge Centre for Alternative Finance (CCAF), with the aim of accelerating tech-enabled financial innovation and knowledge sharing across the region.

CCAF is an interdisciplinary academic research institute at the University of Cambridge Judge Business School, dedicated to the study of alternative finance, which includes technology-enabled financial instruments, channels and systems that emerge outside of the traditional financial system. The CCAF is leading the establishment of a global knowledge network that accelerates the creation and transfer of knowledge relating to FinTech: the Cambridge Alternative Finance Collaboration Network (CAFCN). Earlier this year, the CAFCN launched operations in Sub -Saharan Africa and in the Middle East, North Africa and the Mediterranean. As a cross-sectoral and cross-regional network, the CAFCN can facilitate FinTech market development and effect evidence-based regulatory changes in economies seeking to promote the sustainable growth of FinTech industries. This programme has established the CAFCN in Singapore for coverage across the Asia Pacific region (APAC), starting in January 2021.

C4T Emerging Opportunities Fund

1) Brown carbon laser characterisation and light-absorbing property

Prof. Markus KRAFT and Dr Yichen ZONG

Brown carbon (BrC, light-absorbing organic carbonaceous species) has attracted strong concern as a possible cause of climate change and a major air pollution source in Southeast Asia. In this study, we will investigate the characterisation of combustion emissions from diesel, biomass and peat by measuring the chemical composition, number concentration and size distribution. An optical method (multi-wavelength light absorption) will be used to distinguish brown carbon from all other organics and black carbon emission. An estimation of absorption properties will be performed to evaluate the role of brown carbon in atmospheric radiation balance.

The experimental work of the project is conducted under the collaboration of CARES researchers and Assoc. Prof. YU Liya (Department of Civil and Environmental Engineering, NUS). With the use of a soot particle-aerosol mass spectrometer (SP-AMS) and a seven-wavelength aethalometer (model AE33), the researchers are able to directly detect brown carbon as well as other organics from engine emissions. These organic species show a complicated relationship with engine conditions and blending ratio; the conventional soot reduction measures may not work on BrC. Now that pandemic restrictions are beginning to ease in Singapore, the next round of joint engine experiment will be carried out in late April.

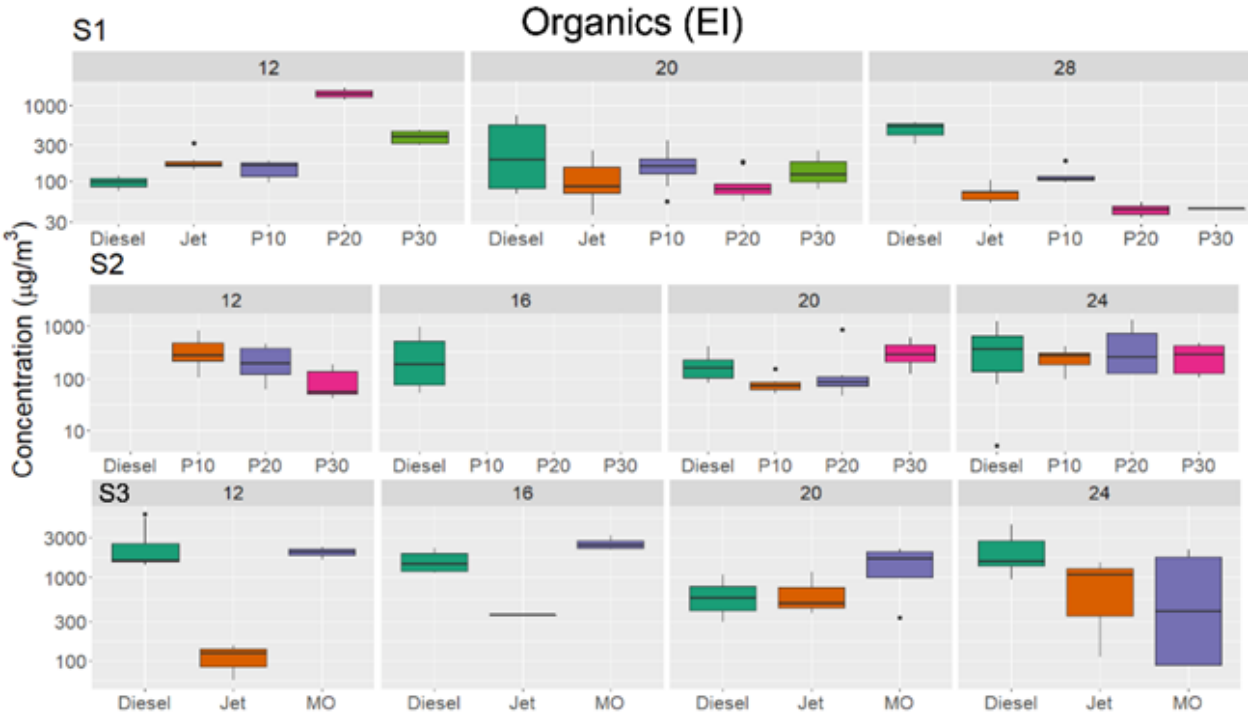


Figure 10.7: Organic species detected from engine emissions with various fuel blends.

2) Chemical farming

Assoc. Prof. YAN Ning, Prof. Alexei LAPKIN, Dr Zhen GUO Dr SONG Song and Dr DING Shipeng

Organonitrogen chemicals such as amino acids, amines and nitriles are essential in many aspects of modern life. However, the prevailing industrial processes for the manufacturing of nitrogen-containing chemicals rely heavily on non-renewable fossil resources. The aim of the project is to develop new chemical pathways and identify efficient catalytic systems for the synthesis of organonitrogen chemicals from renewable biomass. The production of α-amino acids from biomass-derived α-hydroxyl acids and glucose was achieved in previous research.

Recently, a single-step conversion of biomass-derived furfural to pyrrole was developed, pyrrole being an important primary nitrogen-containing chemical extensively used as a precursor for fine chemicals, drugs, catalysts and materials. A 75% yield was achieved via tandem decarbonylation–amination reactions over tailor-designed Pd@S-1 and H-beta zeolite catalytic system. Pyrrole was further transformed into DL-proline in two steps following carboxylation with CO_2 and hydrogenation over Rh/C catalyst. After treating with Escherichia coli, valuable D-proline was obtained in theoretically maximum yield (50%) bearing 99% ee. This study establishes a route bridging commercial commodity feedstock from biomass with high-value organonitrogen chemicals through pyrrole as a hub molecule.

Progress has also been made on the search tools on the basis of Reaxys to identify possible routes to link raw biomass with proline. The product yields were then experimentally verified and improved. In two steps, proline has been obtained from chitin monomer glucosamine.

Aside from this, the researchers are actively working on the reductive amination to produce amine using single-atom alloy catalysts. Single-atom alloy Ru_1Co showed the best activity among the studied Ru_1Co, Ru_1Cu and Ru_1Fe catalysts. In the next step, the structure of catalysts will be characterised using techniques such X-ray absorption spectroscopy and high resolution TEM to correlate the catalytic performance with the structure.

3) Impact of Singapore's shipping activities on urban air quality

Prof. Markus KRAFT, Mei Qi LIM and Jiaru BAI

This project began with the development of a framework to evaluate the impact of emissions from shipping activities on air quality in Singapore by combining a physical-based model with a data-driven model based on morphology and real-time data such as marine traffic and weather conditions. In the course of this work, low interoperability between the multiple domains involved has been observed as a challenge to generalising the potential outcome to any location in the world. Consequently, knowledge graph technology was applied in the context of digital twins, in order to link and query for data from different domains in a highly flexible manner.

Previously, agents (software, methods and models etc. that utilise semantic web technologies and operate on the knowledge graph) were constructed to simulate the atmospheric dispersion of pollutants emitted from ships around Singapore and Hong Kong using the Eulerian urban dispersion model "EPISODE-CityChem" – jointly developed with IRPs 4 and JPS. We are in the process of generalising the agents to permit their application to any location in the world. The goal of this activity is to enable users to place virtual sensors at any location and if applicable, automatically trigger the associated agents to generate new dispersion data within its vicinity.

As part of the generalisation, a new ontology (OntoDispersionSim) was developed to describe dispersion simulations in order to allow the co-existence and monitoring of multiple simulations in the knowledge graph. OntoDispersionSim stores the key parameters of each dispersion simulation – including the coordinates of the simulated locations and its local coordinate reference system. In addition, OntoDispersionSim allows ship and weather data to be linked semantically with a particular simulation. Therefore, each simulation within the knowledge graph can be tracked systematically. We are also in the process of developing a web interface to allow users to place the virtual sensors on the world map and visualising the simulation results by querying data from OntoDispersionSim.

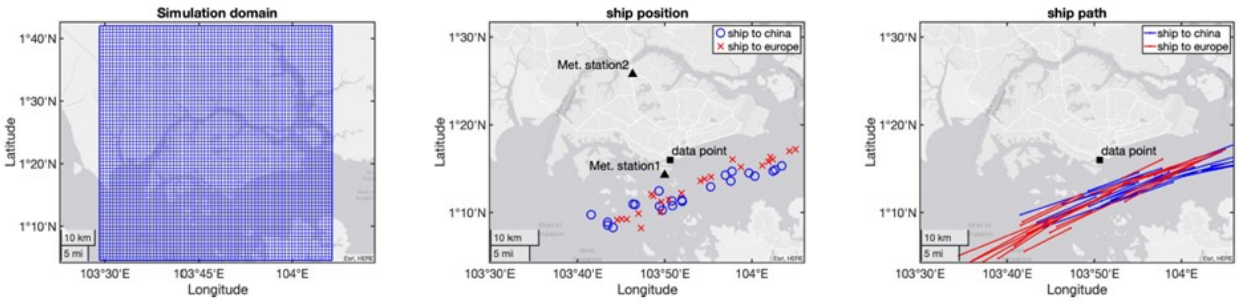


Figure 10.8: Configuration of the simulation domain in Singapore used in the simplified simulation.

4) Ignition systems and methane slip in marine natural gas engines

Prof. Epaminondas MASTORAKOS

The project involves modelling of methane slip and ignition systems (pilot, jet) with Large-Eddy Simulation and finite-rate kinetic sub-grid combustion models. Work on the theoretical and code development front has already started at University of Cambridge by Savvas GKANTONAS (Researcher, CAM) and simulations of engines and test cells will be performed by a new post-doc who has been appointed and should start soon.

5) Future marine economy

Prof. Epaminondas MASTORAKOS, Prof. Steve EVANS, LAW Li Chin

As a continuation of the previous research done by Beatrice FOSCOLI (visiting Masters student, CAM), the main focus of the current phase is on data acquisition for the energy, operating cost, and greenhouse gas emission for various marine fuels. This will allow a quantitative comparison of the energy consumption, economy and environmental benefits of alternative bunkering fuels to be carried out. Current work is focusing on constructing commercial-based models for various marine fuels including LNG, hydrogen, ammonia, methanol and electricity derived from both natural gas (fossil-based fuels) and renewable energy (e-fuels) as well as biofuels. For alternative fuels with greenhouse gas emission, integration of carbon capture technology is included as part of the model to allow the assessment on the potential of carbon capture. The modelling and analysis are grouped into two parts which are fuel production and fuel consumption. Energy and economics analysis of these models would provide a clear picture of the energy requirement

and potential environmental benefits of transitioning into these alternative fuels. This output will provide a new understanding of the advantages and weaknesses of various proposed energy vectors for shipping. At a later stage, scenario-based dynamic energy models with considerations of Singapore's future energy transition trend, technology readiness and developments, and availability of the energy feedstock can be developed for a more sophisticated analysis. This would allow us to predict the technology pathways which may emerge in Singapore towards a sustainable and zero carbon marine sector.

6) Carbon reduction strategies of top chemical companies

Prof. S. VISWANATHAN, Dr Abhiruchi GADGIL, K. R. Preethi

The research question that is being addressed for this project is twofold: How should big multi-unit firms design the internal carbon tax and how can their carbon reduction strategies be represented most holistically?

For these multi-unit firms, an internal carbon tax should be set high enough that it materially affects the investment/operational decisions. At the same time, it should be low enough that the firm stays competitive. Game-theoretic modelling and optimisation methods were used to model and game the optimal action of the firm and the Strategic Business Units (SBUs) in the firm. It was observed that when the firm uses a uniform internal carbon tax, the SBUs that operate in emission-intensive or trade-exposed sectors are at a disadvantage and may lose significant business. Therefore, it is suggested that a firm operating in multiple sectors implement non-uniform internal carbon taxes. Although non-uniform taxes might affect short-term profits, such a design would ensure that the trade-exposed SBUs are protected from competition effects and performs better in the future when all the firms in the market are subject to emission regulations. It was shown that the results hold for different abatement cost structures.

Work is also being extended to include a two-period model in which the decisions made in the first period affect the cost parameters for the second period. This model incorporates the benefits of the learning effect from implementing an internal carbon tax. It can help to demonstrate the advantage of a non-uniform carbon tax design by keeping the SBU in business.

Figure 10.9 shows that the appropriate design mechanism should be in place to ensure that the carbon is economically and environmentally efficient and at the same time protects the firm against competitive pressure.

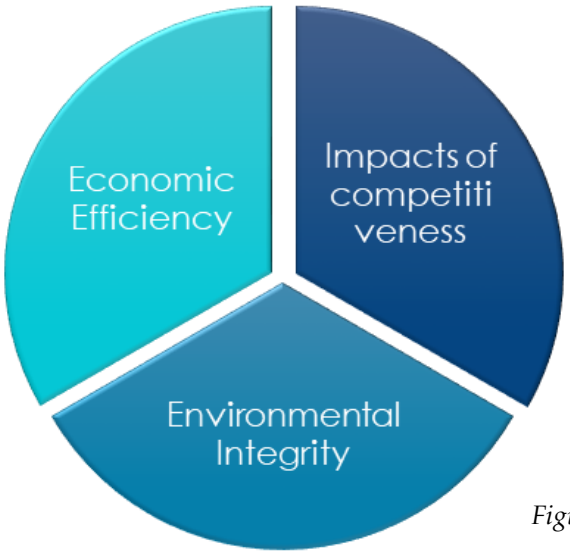


Figure 10.9: Three pillars in designing carbon internal price.

For the holistic representation of carbon reduction efforts, data was obtained from publicly available datasets, sustainability reports, and several consultancy analyses. The data is classified into four categories: emissions *impact* (in terms of temporal data), *financial transition* (in terms of investments, divestments, mergers, and acquisitions), *CO_2 abatement technological efforts* (in terms of R&D expenditure, patent landscape, publications), and *price on carbon* (in terms of carbon tax and internal carbon pricing) as shown in Figure 10.10. The temporal data in these categories will indicate pathways taken by specific companies, and will underscore the geopolitical diversity in the process too. All the categories are being worked on concurrently. The data has several inconsistencies in terms of absence of common base lines, non-reporting of absolute data (for emissions), disparities in different datasets, or in some cases, unavailability of data, etc. The BB team is in the process of consolidating the data, removing inconsistencies and finding the best ways to represent it. In parallel, they are also working on a short study on how the oil and gas companies are pivoting because of the pandemic as there has been a clear-cut shift in the industry due to the large economic impacts in the COVID period.

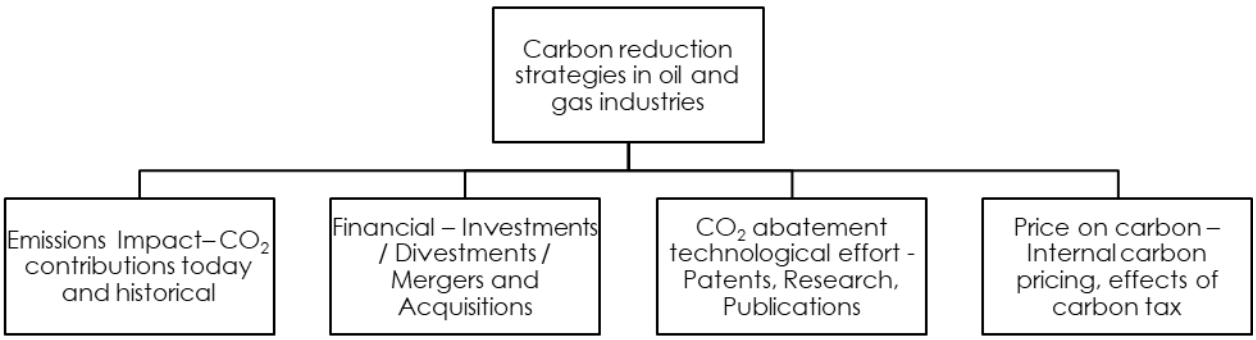


Figure 10.10: Factors to represent the carbon reduction strategies and efforts in the oil and gas industries.

7) Carbon capture, storage and utilisation roadmap 2050

Asst Prof. Paul LIU, Prof. Markus KRAFT

In this roadmap study, a retrosynthetic approach will be taken to identify the research intensity and the scaling-up milestones required to achieve the 2030 and 2050 emission reduction targets by carbon capture, storage and utilisation (CCSU). The former is linked to Singapore's pledge following the Paris Agreement whilst the latter will be addressed by this project's analysis. Firstly, the decarbonisation potential of the various emission reduction approaches, including improved power plant efficiencies (e.g. combined cycle gas power plants, co-gen and waste-to-energy plants), improved grid efficiencies and improved user efficiencies (e.g. building efficiency, green manufacturing, etc.), circular economy, renewable power generation (primarily by photovoltaics, in the Singapore context) and CCSU will be evaluated. Secondly, the major point-sources of emission will be paired with the market demand for purified CO_2, carbonaceous fuels, solidified carbon (e.g. carbonates and biochars), and downstream chemical products (e.g. olefins and liquid fuels), to develop a carbon circular supply chain. Then, by developing process models and financial models for the various key CCSU plants (e.g. CO_2 to methanol, power to liquid, carbon aggregate production), the levelised cost of manufacturing products via CCSU can be estimated. Overall, the multi-scale model will enable the evaluation the cost-effectiveness of the proposed carbon circular economy, which will be compared against the fossil-fuel driven economy. The modelling results are anticipated to show that the carbon circular economy, as the current technologies stand, compares unfavourably to the fossil-fuel based economy from a financial point of view.

Pandemic-related hiring delays have slowed progress on this project, but a suitable candidate at the Senior Research Fellow level has been identified and a job offer is being prepared. If this goes smoothly, this project can commence in the second quarter of 2021.

8) Designing the structure and composition of active site motifs in CO_2 hydrogenation catalysts with atomic-level specificity

Asst Prof. Paul LIU, Prof. Alexei LAPKIN, Asst Prof. Tej CHOKSI

The overall objective of this project is to build operando-computational models for bifunctional Cu/CeO_2 interfaces by closely integrating theory with precisely targeted characterisation and kinetic experiments. Successes in this effort will establish quantitative capabilities for determining both structures of bifunctional interfaces under reaction conditions, and CO_2 hydrogenation kinetics with atomic level specificity. These models will then be deployed for the high-throughput design and validation of thermodynamically feasible active sites of physically and chemically modified Cu/CeO_2 interfaces that demonstrate superior rates and selectivity towards methanol. The central hypothesis of this proposal is that bifunctional gains observed in the rates and selectivity of CO_2 hydrogenation are induced by electronic interactions between the metal and the oxide support.

Direct evidence was recently found of strong metal-support interaction (SMSI) between noble metal nanoparticles (viz. Pt, Pd, Ag and Au) and 2D titanium boride (TiB_2) and their catalytic consequences for aqueous phase formic acid dehydrogenation (Fig. 1). Upon thermal treatment, the TiB_2 overlayers migrate over the noble metal nanoclusters, encapsulating them to form core-shell nanostructures that are sintering-resistant even at metal loadings as high as 12.0 wt%. In contrast to the trade-off between stability and activity observed during conventional SMSI, TiB_2 -based SMSI concurrently increases stability while promoting catalytic turnovers of formic acid dehydrogenation. The thickness and coverage of the TiB_2 overlayer was optimised by changing the pre-treatment temperature. It was shown that Pt covered by a monolayer of TiB_2 displays an outstanding hydrogen productivity

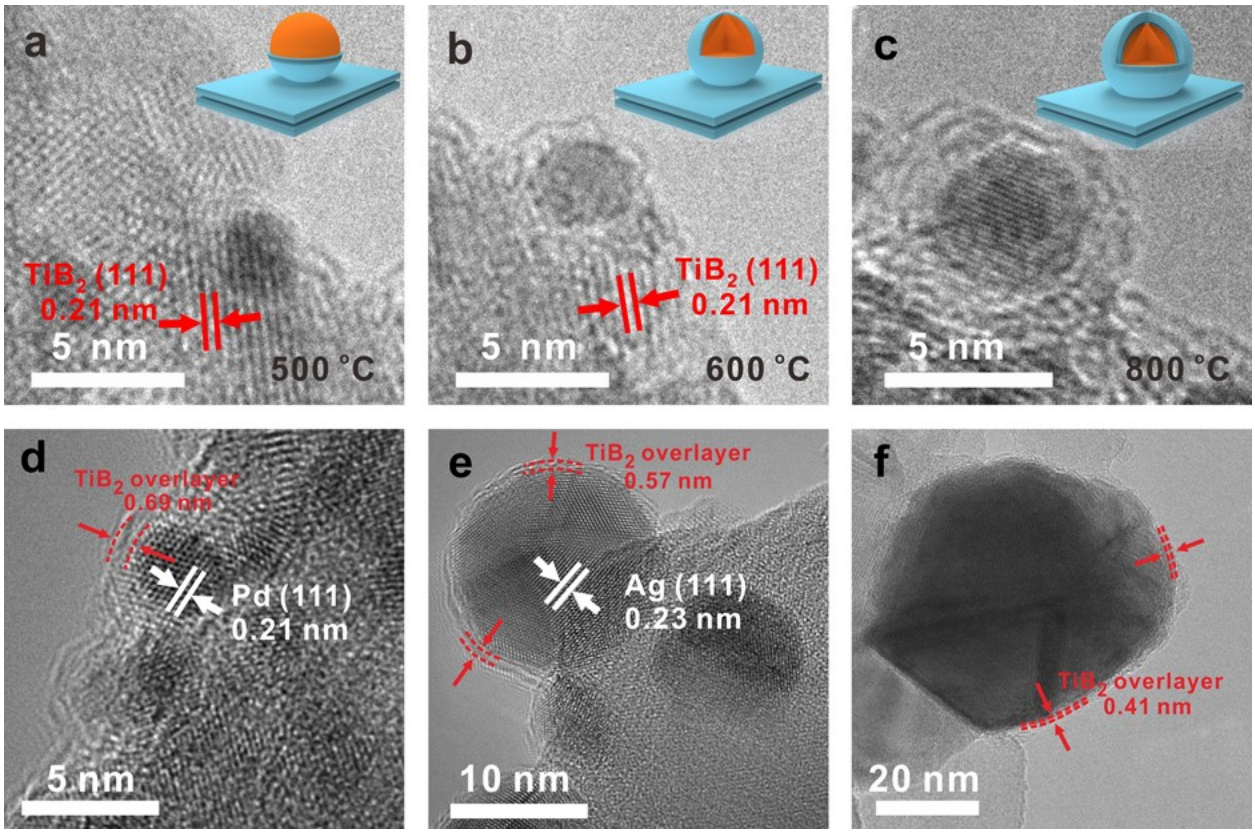


Figure 10.11: HRTEM images of (a) Pt/TiB_2-500 (the inset models show TiB_2 partly covers a Pt particle), (b) Pt/TiB_2-600 (the inset shows a monolayer of TiB_2 encapsulating a Pt particle), (c) Pt/TiB_2-800 (the inset shows the core-shell heterostructures of a TiB_2 tri-layer covering a Pt particle), (d) Pd nanoparticles encapsulated by TiB_2 overlayers, (e) Ag nanoparticles encapsulated by TiB_2 overlayers, and (f) Au nanoparticles having grown into large particles despite the initial encapsulation by TiB_2.

solution without any additive or pH adjustment, with >99.9% selectivity towards CO_2 and H_2 (Figure 10.12a). The origin of the SMSI-induced improvements in catalytic activity is systematically investigated by complementary experiments and DFT calculations. Theoretical studies also suggest that the TiB_2 overlayers are stabilised on different transition metals through an interplay between covalent and electrostatic interactions (Figure 10.12b). Overall, the computationally determined trends are wholly consistent with the experimental results. The present research introduces an entirely new means to create thermally stable and catalytically active metal/support interfaces for scalable chemical and energy applications. The work is currently under revision with a journal.

Furthermore, steady progress was made with regard to Aims 1 and 2 of this project. Aim 1 develops rational design principles unique to synergistic active sites at interfaces. In Aim 2, operando computational models of supported metal nanoparticles are constructed. Aims 3 and 4 will develop microkinetic modelling and catalyst screening capabilities to design novel bimetallic nanoparticles on oxides, carbidses, and nitride supports. Two principle advances have been made in this regard:

Aim 1: Using density functional theory and electronic structure analysis an intuitive workflow was developed to predict catalytic descriptors like CO* and OH* with atomic level resolution at bifunctional interfaces. It was rigorously shown that the interfacial effect is confined to the first two metal layers proximal to the interface. Furthermore, using a data-driven approach, it was revealed that the bifunctional perturbation caused by synergistic active sites depends strongly on the coordination number of the active site. Interfacial metal atoms having low (high) coordination numbers have larger (smaller) bifunctional perturbations. It was also shown that structure sensitivity for supported metal catalysts can be exquisitely tuned by modulating the electrostatic and covalent interactions. These fundamental advances will create new design paradigms leading to interfaces having a higher density of catalytically active sites. The predictive power of the scheme is indicated in the parity plot below. This work is being prepared for submission in the next two months.

Aim 2: In collaboration with experimental researchers within CARES (Prof. Paul LIU and Prof. XU Zhichuan), electronic structure calculations were employed to understand the bifunctional properties of supported metal catalysts. In collab-

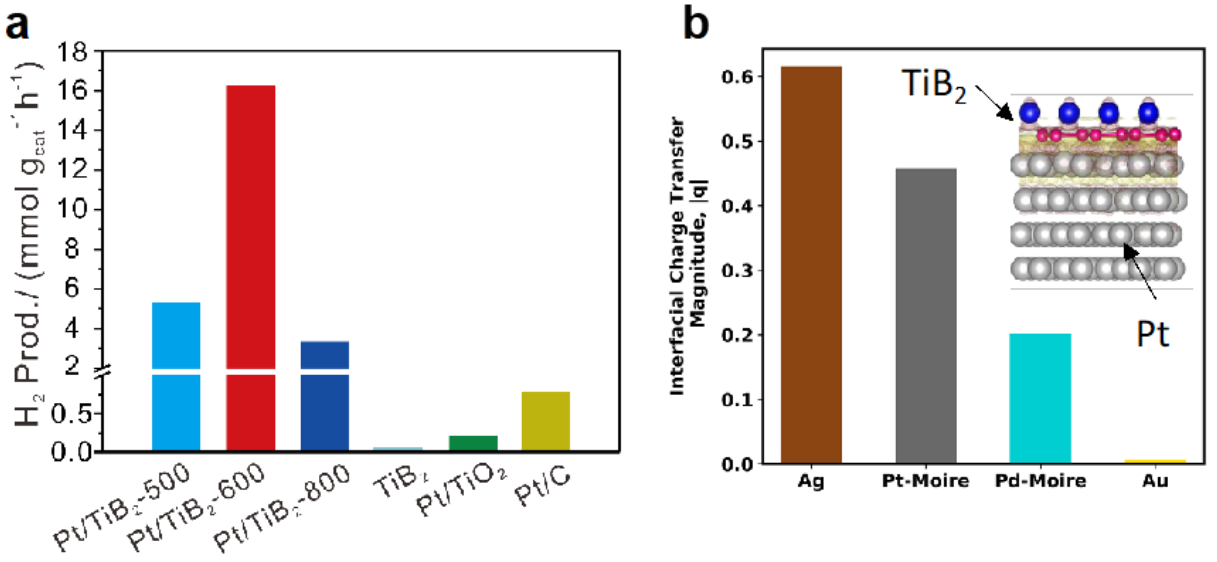


Figure 10.12: (a) Comparison of the rate of H_2 production from HCOOH (10.0 M aqueous solution) dehydrogenation over different Pt-based catalysts carried at room temperature. (b) DFT-calculated charge transfer (electrostatic contribution to adhesion energies) across different metal/TiB_2 interfaces.

oration with Prof. Liu's group the surprising strong metal support interaction seen in metal/TiB2 systems were explained and atomistic models of interfaces which are cognisant with experimental characterisation were created. Similar operando-computational approaches were also employed to study Au/TiO_2 interfaces for CO_2 photo-electro-reduction in collaboration with Prof. Xu. The collaboration with Prof. Liu is currently in revision, while the collaboration with Prof. Xu has been submitted for review.

In summary, within the past six months, a workflow was established to compute catalytic descriptors, and capabilities were built to construct atomistic models of interfaces using operando computational principles within Aims 1 and 2 of the project. Building on this foundation, work will commence on determining site-specific reactivity trends at interfaces for Water Gas Shift and Oxygen Reduction Reaction within the next six months.

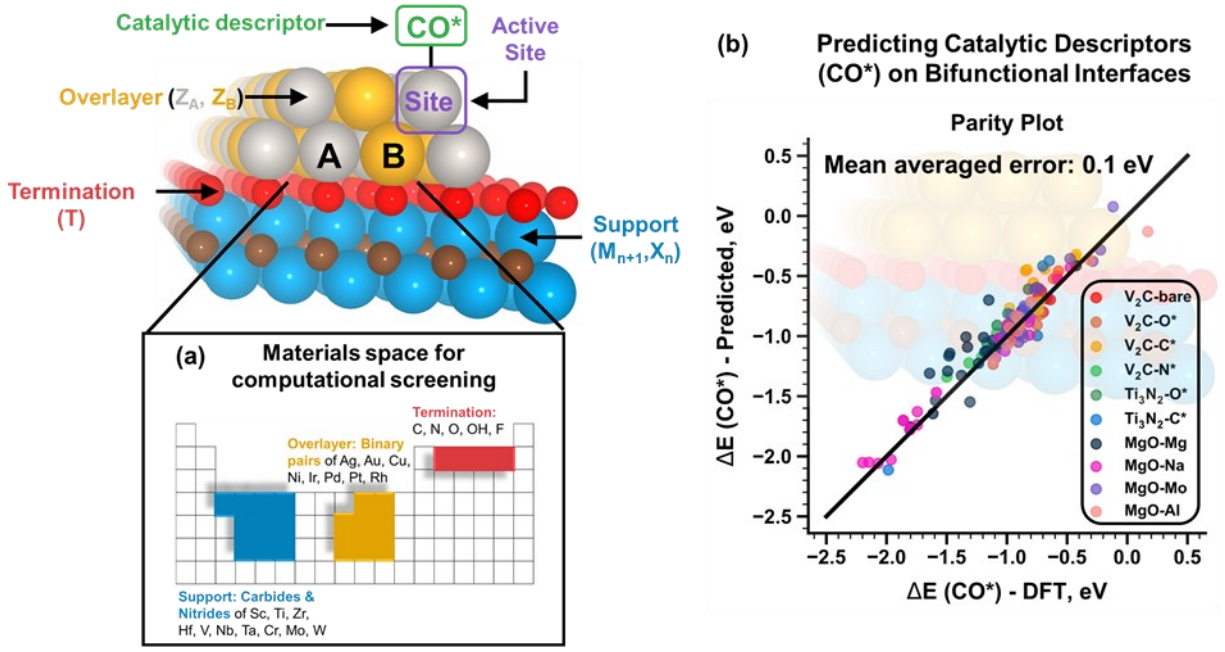


Figure 10.13: (a) The space of bifunctional interfaces across which we can predict catalytic descriptors like the binding energy of CO with site-specific precision. (b) Parity plot comparing model predictions and density functional theory calculations on the test set. We achieve a mean averaged error of 0.1 eV, well within the ballpark of a computational screening paradigm.*

9) Electrified chemical production: AI strategies for accelerated intelligent design of disruptive technologies and electrochemical processes

Prof. Jason XU Zhichuan, Dr Adrian FISHER, Dr CHEN Gao

This project aims to develop machine learning methods for electrocatalysis and longer term reactor engineering design. First, a database of various catalyst materials and their related catalytic performance will be built for training purposes. The machine learning models will be built on the basis of the fundamentals discovered. The models will be further optimised by incorporating more data sets, such as materials' physical and chemical parameters. DFT simulation will be employed for experimental data mining as well as the validation of machine screened catalysts. Finally, the machine designed catalysts will be synthesised and tested to confirm the successful design. A computational strategy will be developed and used for proof of concept for target reactions in the area of small molecule transformations. Targets would include hydrogen production (water oxidation), C1-C4 molecule transformation, high value chemicals, and high energy consuming products such as nitrogen oxide, etc.

Dr CHEN Gao and colleagues proposed that attention should be paid to the possible existence of singlet oxygen in oxygen electrocatalysis. The dioxygen molecule has two bound states, singlet and triplet, which are different in energy, lifetime, and reactivity. In the context of oxygen electrocatalysis as applied to fuel cells and water splitting the involved O_2 is typically considered to be exclusively in its triplet ground state. However, applying spin-conservation rules for the transformation between triplet O_2 and singlet OH^-/H_2O reaction intermediates predicts an additional free energy barrier associated with the required spin flip. As a result, for conditions under which both can form, the formation of triplet dioxygen from the singlet $OH^-/H2O$ might be slower than the formation of singlet O_2. Correspondingly, singlet O_2 might be more active than triplet O_2 in the oxygen reduction reaction. Therefore, they discussed the possible existence and influence of singlet oxygen in oxygen electrocatalysis. The possible mechanisms involving the singlet oxygen in oxygen electrocatalysis are presented below and over the page.

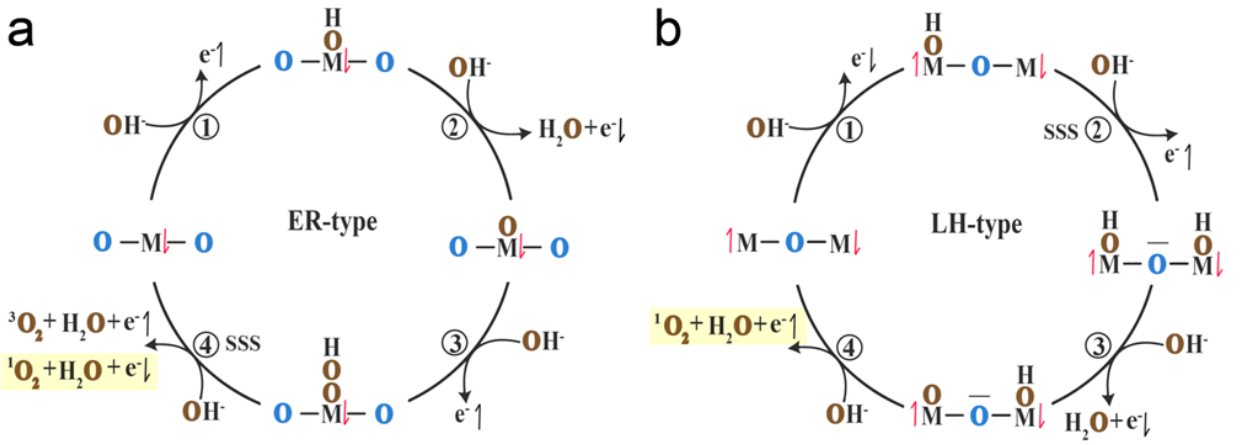


Figure 10.14: The adsorbate evolution mechanism (AEM) mechanisms of oxygen evolution reaction (OER) by considering the spin of transferred electrons. (a) The ER-type route and (b) LH-type route. M means the metal site and the arrow beside M represents the spin direction of unpaired t_{2g} electrons; the blue O and brown O represent the lattice oxygen and adsorbed oxygen species, respectively. SSS refers to the spin selective step. The singlet oxygen formation is highlighted in yellow.

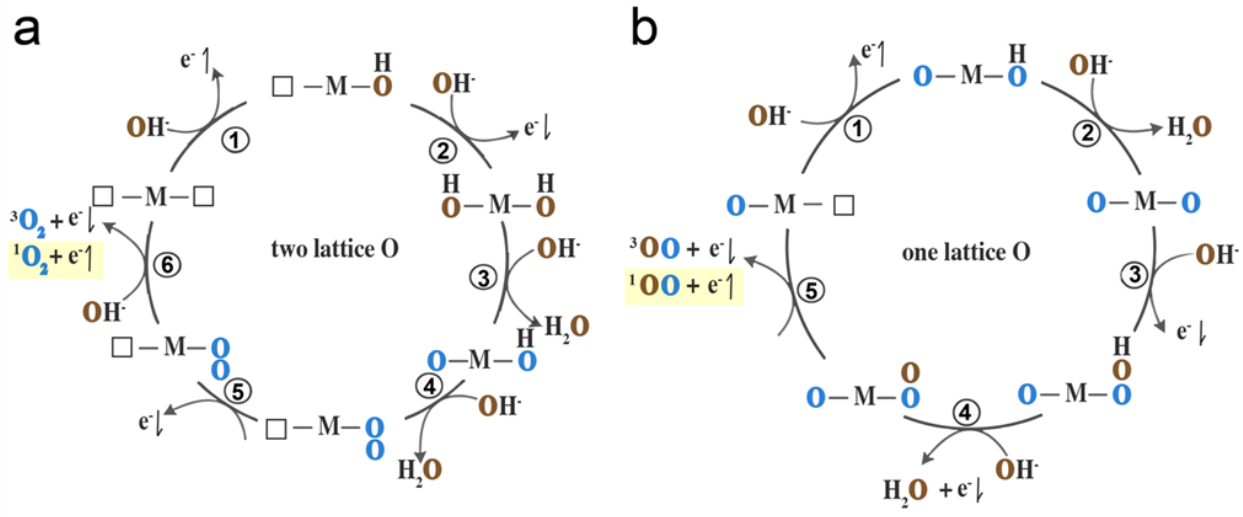


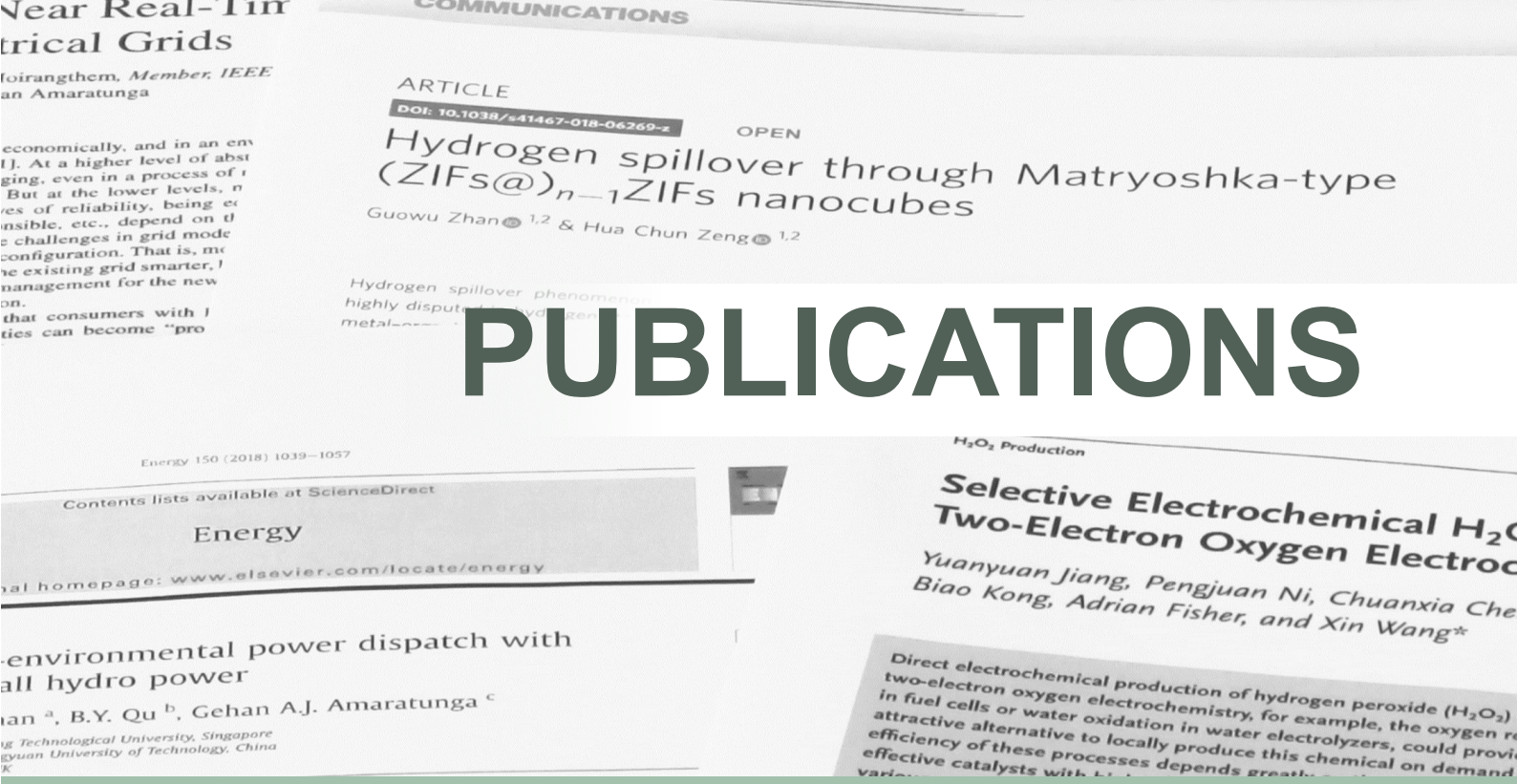
Figure 10.14: Lattice oxygen mechanism (LOM) mechanisms of OER by considering the spin of transferred electrons. (a) Both two oxygen atoms of the produced dioxygen molecule are from the oxide lattice; (b) One from lattice oxygen while the other from the electrolyte. M refers the metal site; the blue O and wine O represent the lattice oxygen and adsorbed oxygen species, respectively. The singlet oxygen formation is highlighted in yellow.

10) Construction of isolated metal sites for selective electrocatalytic production of H_2O_2

Prof. WANG Xin

Hydrogen peroxide (H_2O_2) is one of the most important chemicals, being widely used in almost all industrial areas with an annual demand of 4 million tons. $H_2O_2$is currently produced almost exclusively with the anthraquinone oxidation process. However, the anthraquinone technology involves multistep reactions and separations, which require significant energy input and generate substantial waste. Electrochemical strategy via the oxygen reduction reaction (ORR) process provides a promising approach to achieve the low-cost, green, continuous and on-site production of H_2O_2, making it a simpler and safer method compared with the conventional anthraquinone process. This research aims to develop a novel and low cost catalyst and reactor system to efficiently produce H_2O_2.

Due to work visa limitations, the two candidates previously identified were unable to join the project and a search for new candidates is underway. Dr LI Xiaogang is instead working on the project full time and another candidate will join the team in July 2021. Regarding the research progress, a molecular strategy was designed to confine anthraquinone-based molecules on the single-atom NiN_4/C catalyst and the catalytic activity of the above molecule modulated catalyst was systematically investigated for electrocatalytic H_2O_2 production. DFT calculation is ongoing in collaboration with Asst Prof. Tej CHOKSI. A manuscript has been prepared and is ready for submission. In another research project, hetero-atom modified MN_x sites were explored for their activity for H_2O_2 production. The key for improving the H_2O_2 selectivity is to optimise the binding energy of OOH* on MN_x sites. It is believed that substituting the coordinated N in MN_x sites with exotic element or introduction of exotic element near the MN_x sites could serve this purpose. The introduction of S into CuN_x sites was realised and preliminary results showed it can greatly improve the selectivity for H_2O_2 production. The maximum selectivity improved from 25% for CuN_x/C to about 70% for CuN_x/C-50 S. Nevertheless, the S modulated NiN_x and CuN_x sites present low catalytic current. Therefore, optimisation of the S doped amount and other S doped approaches will be explored to try to achieve both high selectivity and selectivity.



PUBLICATIONS

ALL C4T PUBLICATIONS WITH CREATE ACKNOWLEDGEMENT

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

C4T joint IRP publications

IRP 1 and IRP 3

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

IRP 3 and IRP JPS

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- **Cao, Liwei, Danilo Russo, Kobi Felton, Daniel Salley, Abhishek Sharma, Graham Keenan, Werner Mauer, Huanhuan Gao, Leroy Cronin, and Alexei A. Lapkin. 2021. 'Optimization of Formulations Using Robotic Experiments Driven by Machine Learning DoE'. *Cell Reports Physical Science*, January, 100295. https://doi.org/10.1016/j.xcrp.2020.100295.**
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