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Biannual Research Report

November 2015 — April 2016

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C4T

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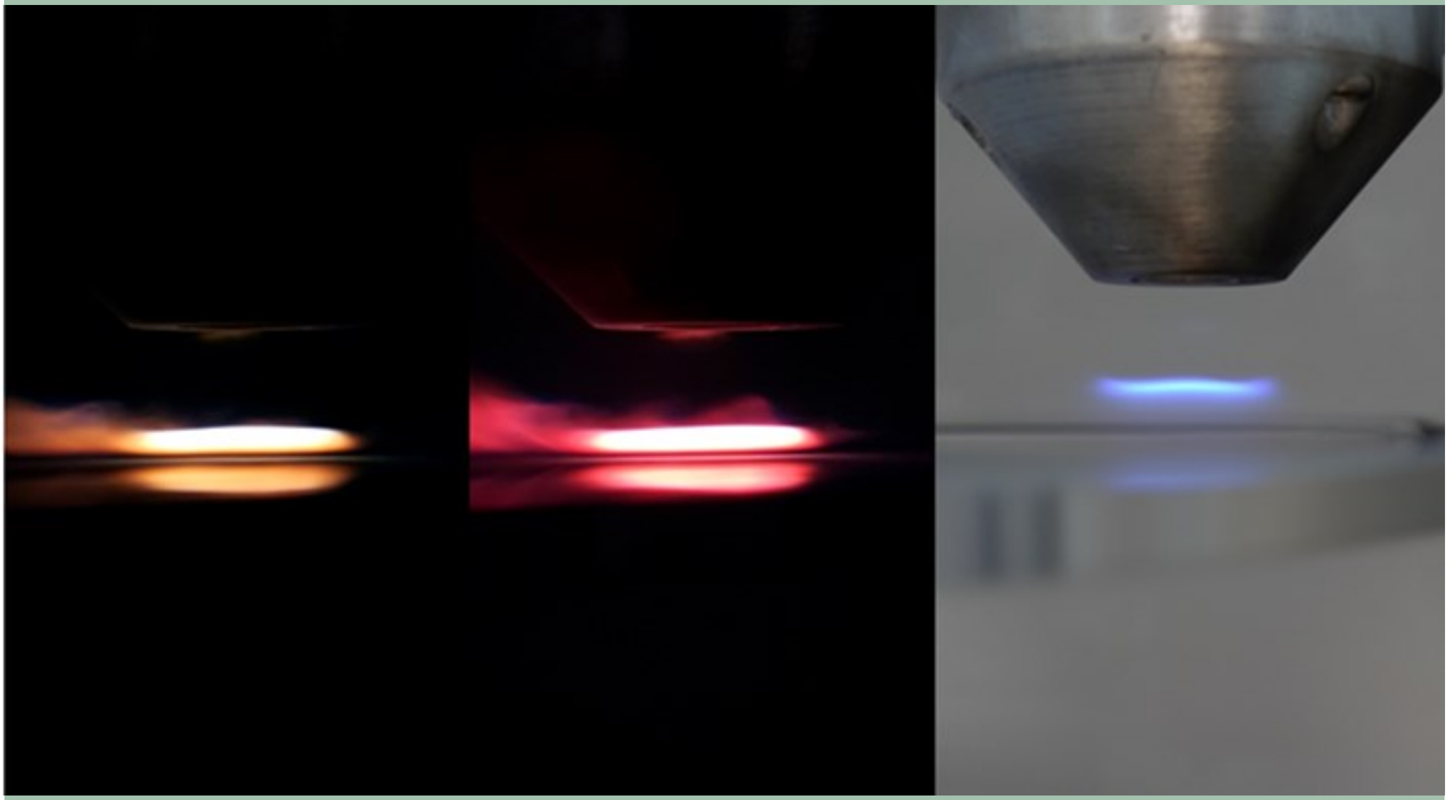
Carbon Reduction in
Chemical Technology



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University of Cambridge
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National University of Singapore

Cover figure: WANG Weijing, Research Fellow, IRP3, NTU. FSRS flames with different conditions (From left to right: Undoped fuel rich flame, f=2.14; TTIP doped fuel rich flame, f=2.14; undoped fuel lean flame, f=0.45):

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Foreword

Prof. Markus Kraft,

CARES Director.

April 2016

I am very pleased to present the 4th Biannual Research Report of the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T), the first programme managed by the Cambridge Centre for Advanced Research and Education in Singapore (CARES). Observant readers may have noticed the slight change in meaning of the CARES acronym since our last report ('Energy Efficiency in Singapore' has changed to 'Education in Singapore') – this is to ready us for a possible second Cambridge CREATE programme in a non-energy related field!

The first part of 2016 has been an exciting time for CARES C4T. In November 2015, we moved to our dedicated offices in the CREATE Tower. This allowed all members of the programme to sit together for the first time and has already had highly significant positive benefits for our collaborative efforts. These efforts were further supported in March 2016 when we took handover of our new 850m^2 laboratories in the CREATE Research Wing. As I write, equipment is being unboxed, the first gas deliveries are arriving and our researchers are trying on their new lab coats. At the beginning of April, we had a very enjoyable visit from Prof. Sir Leszek Borysiewicz, Vice-Chancellor of the University of Cambridge, who was delighted to be one of the first visitors to the programme's impressive new home. We are all looking forward very much to the increased scientific output that will now be possible for the programme. A number of IRP4 members continue to be housed at NTU and to work on the micro-grid facility; we remain grateful for this valuable support.

Despite lots of packing boxes and removal vans, our team has continued to make good progress towards our overarching programmatic goal of investigating technologies and techniques for the reduction of the carbon footprint of chemical industrial parks such as Jurong Island in Singapore. Across our four Interdisciplinary Research Programmes (IRPs) we have now published 143 papers in peer-reviewed journals and conference proceedings. The programme has produced eight technology disclosures and, with the kind help of NTUitive, has made patent applications for four of these. A Singapore-based start-up company has been formed to commercialise one of the patents, a solution for energy recovery from biomass waste streams.

At the time of our last report, Prof. John Dennis (the first Cambridge PI of IRP1) had just stepped down due to increased commitments in Cambridge. His successor, Prof. Alexei Lapkin, was appointed in October 2015 and has already made two highly successful visits to Singapore to meet with the IRP1 team. Prof Lapkin presents some thoughts on the future work of IRP1 later in this report; I am very much looking forward to seeing the results of these workstreams in the months to come.

In February 2015, we were delighted to welcome Prof. Christof Schulz (University of Duisburg-Essen) as the first visitor under the C4T Visiting Scientists Programme. During his visit, Prof Schulz gave a well-attended public talk on 'scalable gas phase synthesis of functional nanoparticles' and had productive and generative conversations with members of IRP1, 2 and 3.

The centrepiece product of CARES C4T, the J-Park Simulator or JPS, a virtual world industrial park in which we can model and further investigate the macro- and systemic effects of our emerging technologies and solutions for carbon footprint reduction, has also made significant progress since our

last report. I was very pleased to be invited to present it to the World Economic Forum meeting in Davos in January 2016, where it received some keen interest from industry and public sector delegates from around the world.

Looking forward, we are preparing for a busy and exciting few months. In July 2016 we will be joined in Singapore by our International Scientific Advisory Committee, who will conduct a mid-term review of the programme's progress. In parallel with preparations for that review, the CARES C4T team is also currently beginning to craft a proposal for a Phase 2 of the programme (2018 onwards). I look forward to sharing further details of our plans (and the world-class science I anticipate they will generate) in future reports. For now, I am certain you will find plenty of interest in our current outputs; I warmly encourage you to contact us for further details of any of our workstreams.

M. Kraft

Prof. Markus Kraft, CARES Director

April 2016

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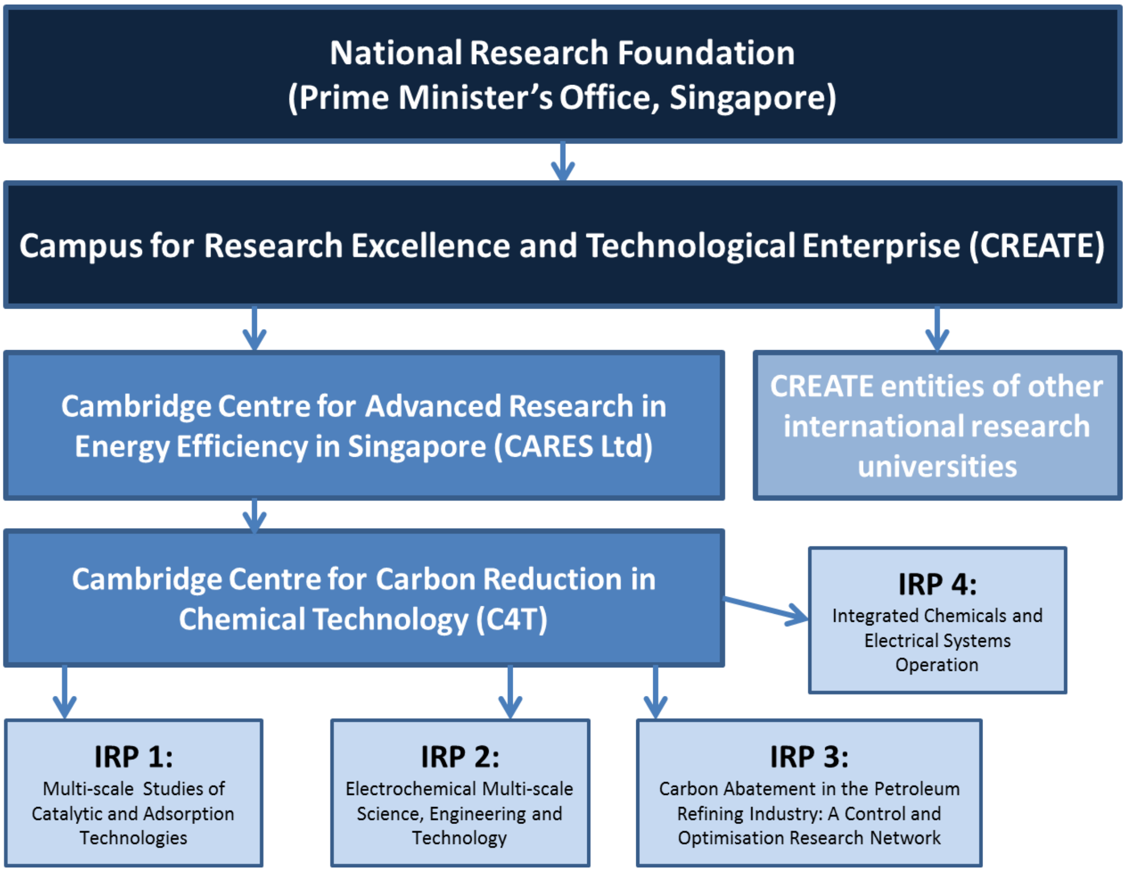
A Facts and Figures

1.1 Structure and Organisation

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

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

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



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

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

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

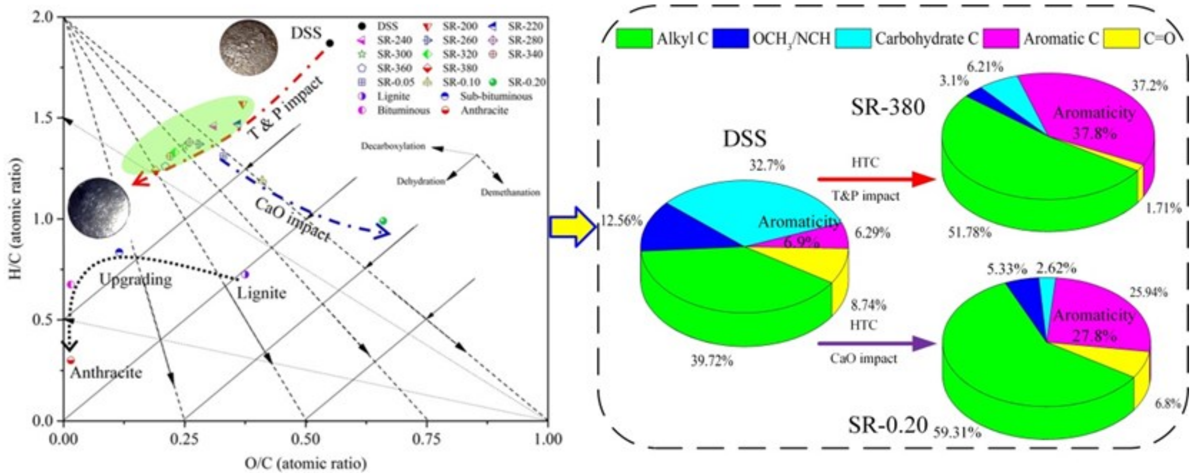
2.1 IRP1: ‘Multiscale Characteristics Dynamics of Hydrochar from Hydrothermal Conversion of Sewage Sludge under Sub- and near-Critical Water’.

He, Chao, Jun Zhao, Yanhui Yang, and Jing-Yuan Wang.

Bioresource Technology 211 (July 2016): 486–93. doi:10.1016/j.biortech.2016.03.110.

Highlights

- Sewage sludge was upgraded to hydrochar via three characteristic regimes in HTC.
- Aliphatic C was mainly transformed to aromatic C−C/C−H in subcritical water.
- More N than C−(C,H) was decomposed below 300 °C.
- Considerable aromatic C−(C,H) was transformed to C−(O,N) and C−H at 380 °C.
- CaO favored intense destruction of aromatic C-C/C-H, anomeric O−C−O, C−H, C−(O,N).



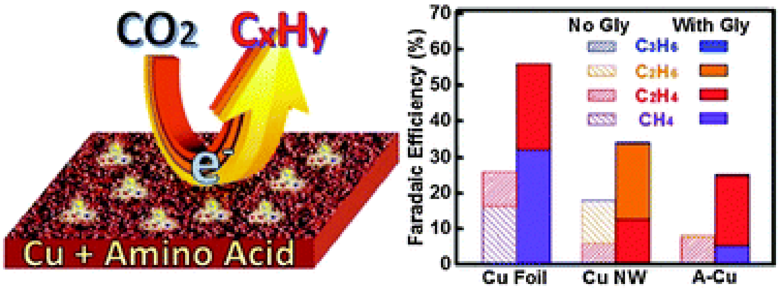
Dewatered sewage sludge was upgraded to hydrochar using hydrothermal conversion in sub- and near-critical water. Three characteristic temperature regimes responsible for the upgrading were identified. Drastic hydrolysis of carbohydrates, amide II or secondary amines occurred at 200 °C while noticeable decarboxylation initiated above 260 °C. Elevated temperature improved porosity but did not induce higher surface area. Aliphatic C was mainly transformed to aromatic hydrocarbon rather than aromatic C−O in subcritical water, whereas COO/N−C=O and aromatic C−O were decomposed to carbohydrate C at 380 °C. Below 300 °C, carbon functionalities in hydrochars were thermally stable and faster decomposition of N than C−(C,H) resulted in dramatic decline of N/C. Above 300 °C, C−H was gradually polymerized to aromatic C−(C,H) which was considerably transformed to C−(O,N) and C−H at 380 °C. CaO favored intense destruction of aromatic C−C/C−H, anomeric O−C−O, C−H and C−(O,N) functionalities but introduced more aromatic C−O and O=C−O.

In addition, a group from IRP1 (Prof YANG Yanhui et al) continued work on the commercialisation of the patent ‘Efficient Energy Recovery from Wet Biomass Waste Streams Using a Two-Stage Hydrothermal Conversion System’, including carrying out consultancy work for a potential licensee.

2.2 IRP2: Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons

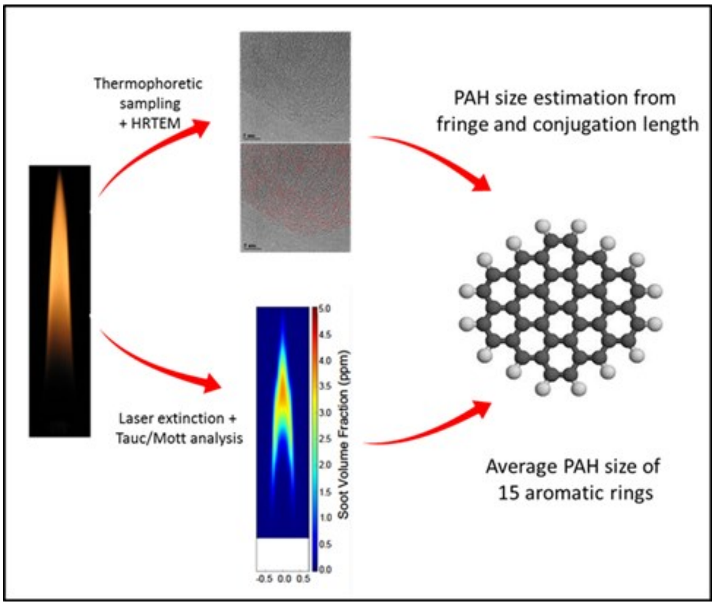
Xie, Ming Shi; Xia, Bao Yu; Li, Yawei; Yan, Ya; Yang, Yanhui; Sun, Qiang; Chan, Siew Hwa; Fisher, Adrian; Wang, Xin

DOI: 10.1039/C5EE03694A



For the first time, we report an efficient method for the synthesis of highly monodispersed surfactant-free, composition segregated octahedral PtNi alloy nanoparticles with an average edge length of 4 nm. The pristine octahedral PtNi nanoparticles showed Pt-rich corners/edges and slighly concave Ni-rich (111) facets. After thermal annealing at high temperature under H2 atomosphere, the Pt-rich surface atoms at the corners/edges diffused onto and subsequently covered the concave Ni-rich (111) surfaces, leading to perfectly flat Pt-rich (111) surfaces with Ni-rich subsurface layers. More importantly, by using the same method, well-defined Pd@PtNi core-shell composites were also obtained. We demonstrated that the Pd@PtNi composites exhibited an improvement factor of more than 1 order of magnitude in activity versus octahedral PtNi nanoparticles and 2 order of magnitude more active than the current state-of-the-art conventional Pt/C catalysts for PEMFC.

2.3 IRP3: PAH structure analysis of soot in a non-premixed flame using high-resolution transmission electron microscopy and optical band gap analysis



Botero, Maria L.; Adkins, Erin M.; González-Calera, Silvia; Miller, Houston; Kraft, Markus

DOI: 10.1016/j.combustflame.2015.11.022

Highlights:

- Soot particles were characterised by laser extinction and HRTEM. Extinction measurements were used to calculate the soot volume fraction and optical band gap (OBG).
- Optical measurements in three flames yield conjugation lengths between 0.98-1.02 nm; corresponding to an average size PAH with 15 aromatic rings.

Soot particles formed in a system of non-premixed liquid fuel flames supported on a wick-fed, smoke point test burner (ASTM D1322-08) were characterized by in-situ visible light extinction and thermophoretically-sampled high-resolution transmission electron microscopy measurements, HRTEM. The fuels studied were heptane, toluene and their iso-volumetric mixture (H50T50), given their relevance as surrogate fuels. Extinction measurements were used to calculate the soot volume fraction, Fv, and determine the optical band gap (OBG) as a function of flame position. The OBG was derived from the near-edge absorption feature using Tauc/Davis-Mott analysis. A direct band gap (r = 0.5) was selected for this analysis assuming that the electronic properties of soot are dominated by the molecular structure of the PAHs. For the HRTEM analysis, soot samples were collected at different locations in the flame using thermophoretic sampling and a fast-insertion technique. The images were then analyzed using a 'lattice-fringe' algorithm, to determine important parameters such as the fringe length. Polycyclic aromatic hydrocarbon (PAH) sizes were estimated from conjugation lengths obtained from OBG measurements and fringe lengths from HRTEM measurements. Across all studied flames, the peak Fv ranged from 3.4 ppm in the heptane flame to 17.6 ppm in the toluene flame. Despite this wide range, the average OBG across the different flames only varied from 2.05 eV in the H50T50 to 2.10 eV in the toluene flames, which is consistent with molecule lengths of between 0.96 nm and 0.99 nm. Lattice fringe analysis yielded slightly lower average fringe lengths between 0.91 and 0.99 nm throughout the different flames. Results of in-situ and ex-situ characterization of soot suggests that flames of different fuel nature and sooting stage undergo the transition from chemical to physical growth at a similar size, about the size of circumpyrene.

2.4 IRP4: The Bernstein branch-and-prune constrained global optimization algorithm for MINLPs

Bhagyesh V. Patil.

Proceedings of the 6th International Conference on Mathematical Aspects of Computer and Information Sciences (MACIS'15). Berlin, Germany, 2015.

This paper address the global optimization problem of polynomial mixed-integer nonlinear programs (MINLPs). A improved branch-and-prune algorithm based on the Bernstein form is proposed to solve such MINLPs. The algorithm use a new pruning feature based on the Bernstein form, called the Bernstein box and Bernstein hull consistency. The proposed algorithm is tested on a set of 16 MINLPs chosen from the literature. The efficacy of the proposed algorithm is brought out via numerical studies with the previously reported Bernstein algorithms and several state-of-the-art MINLP solvers.

2.5 Focus on Impact: Doing More With Less

In the first of a CARES C4T series of short articles focusing on the potential real world impact of the programme's research, Dr Joymala MOIRANGTHEM (Research Fellow, IRP4, NUS), explores the implications of smarter power extraction techniques on chemical industrial parks.

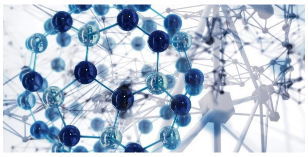
What could help reduce the carbon footprint of any physical process which consumes large electrical power? The simplest answer to this would be switching to power generation methods which have low carbon footprint. Fossil-fuelled generation of electrical energy has the largest carbon footprint (up to 1000g CO_2e/kWh). Low carbon or carbon neutral technologies have low life-cycle greenhouse emissions (less than 100g CO_2e/kWh). Running processes efficiently using low carbon energy sources is but easier said than done.

Chemical processes involve power-hungry loads such as variable frequency drives which also collectively draw harmonic currents. It is a well-known idea to extract useful energy from photovoltaic panels, or even batteries for local consumption using power-electronic converters. But there could be dumb extraction and there could be smart extraction. The questions here are – "can extraction be made better such that it can also mitigate the harmonic disturbances apart from supplying fundamental power? Can we thus further lessen the requirement of power drawn from the utility grid?". The answer is — yes, we can have better extraction of useful energy through better techniques of converter switching & network management. A technique, Selective Harmonic Optimization, is proposed to optimally switch the inverter to attain the desired waveform of injected current. It works by electrical waveform shaping through intelligent algorithms that then regulate the quantity of power and maintain the quality of power at the Point-of-Common-Coupling (PCC). In combination with electrical storage and management, the benefits could be multifarious. For example, 1) uninterrupted power supply to all plants thus preventing the halt of plants, even when renewable energy is intermittent 2) reducing the carbon footprint will lessen the damage to the environment 3) economic benefit since lesser power needs to be drawn from the grid.

The idea of having better extraction is inspired from "Ephemeralization", a term coined by Richard Buckminster Fuller which implies that the ability of technological advancement is to "do more and more with less and less until eventually you can do everything with (almost) nothing". Techniques that can provide better power and resolve power quality issues using local renewable sources would lead to even lesser requirement of power from fossil-fuel based thermal plants, thereby reducing the overall CO_2e contribution from the operation of chemical industrial parks. Smarter management of the electrical network would also enable sharing of renewable resources, more fluid business models and higher sustainability for lesser installation of renewables. Thus world will change incrementally as the technologies related to smart-grids evolve. We can certainly do more with less.

Dr. Joymala Moirangthem received her Bachelor of Engineering in Electrical and Electronics Engineering from Anna University, India in the year 2006. She completed her Masters in Power System Engineering in the year 2008 from Anna University and also has been awarded Michael Faraday Gold Medal for securing first rank in the university. She finished her Ph.D. in 2013 from SRM University, India and worked as Assistant Professor in two universities – Siksha 'O' Anusandhan University, Bhubaneswar and National Institute of Technology, Manipur, India. She is currently a Research Fellow at National University of Singapore, supervised by Prof. Sanjib Kumar Panda under the CARES C4T program. Dr. Joymala has research interests in power system protection, power flow studies, islanding conditions, graph-theoretical network analysis, relay coordination and evolutionary computation. She is currently involved in electrical network modelling, steady-state analyses and dynamic simulations of the same. She is also working with harmonic mitigation in microgrids using local power generation from the renewables.

3 Interdisciplinary Research Programme Updates



3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

Electrochemical Multi-scale Science, Engineering and Technology

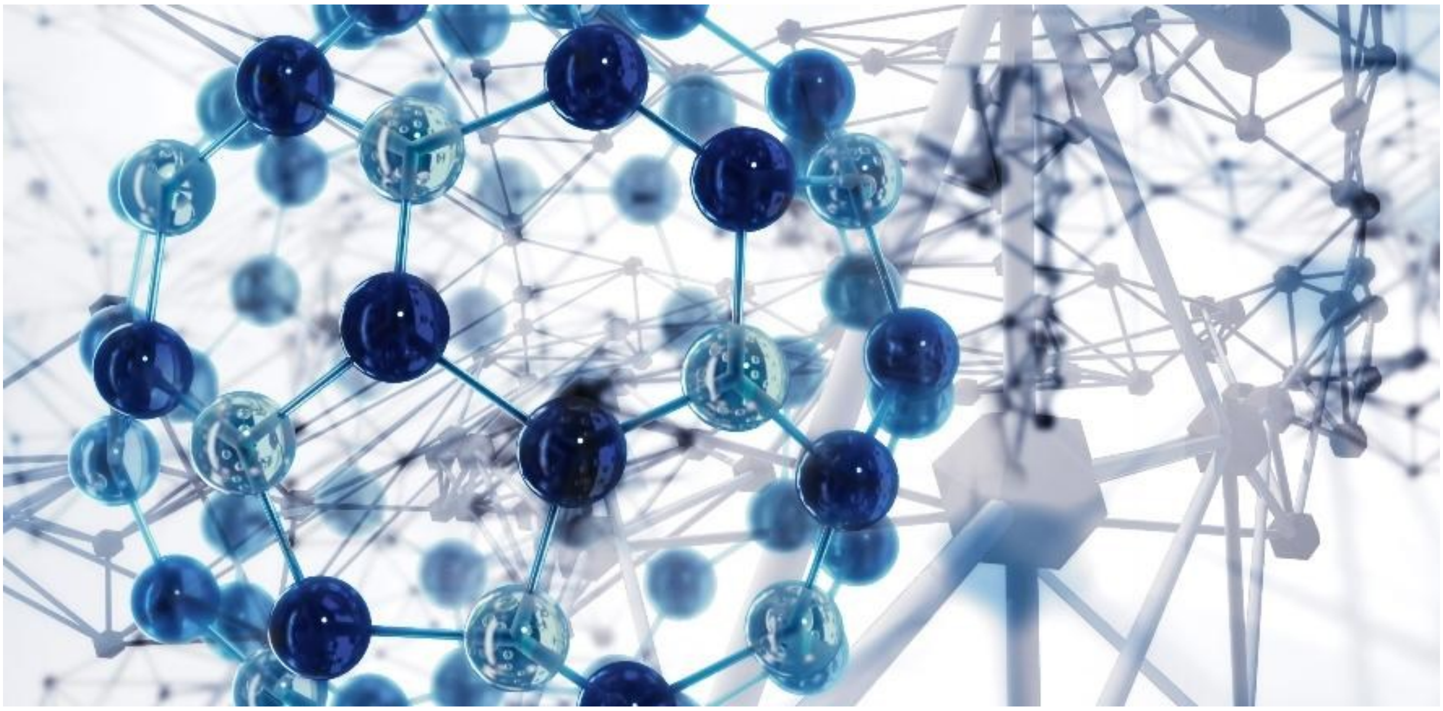
3.3 IRP3 — CAPRICORN

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

3.4 IRP4 — ICESO

Integrated Chemicals and Electrical Systems Operation

3.1 IRP1 — MUSCAT



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

MUSCAT is led by PIs:

Prof Alexei LAPKIN (Cambridge) - appointed October 2015

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

Prof. Alexei Lapkin,

University of Cambridge

PI, IRP1,

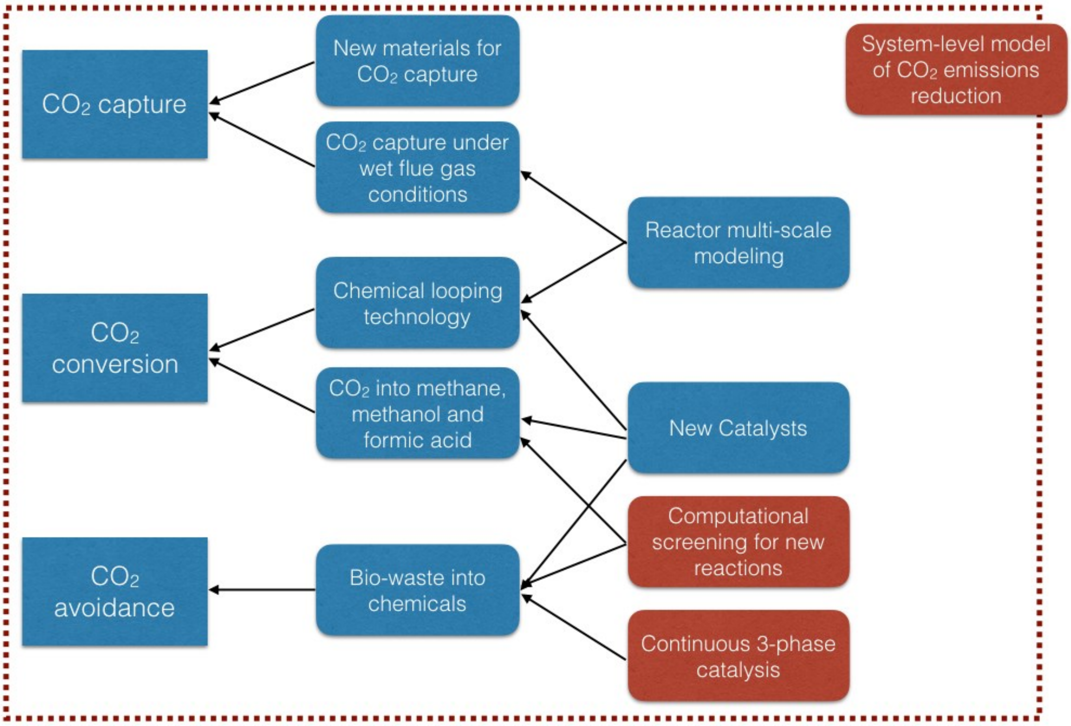
April 2016

3.1.1 IRP1 Research Overview

The overall objective of IRP1 is to establish a world-class, enduring collaboration in Multi-Scale Low-Carbon Reaction Engineering, to deliver immediate and longer-term benefit to both Singapore and the UK (e.g., through new catalytic approaches, improved multi-scale modelling for improved reactors and processes, and carbon capture and use of green-house gas emissions). The work-packages currently in progress:

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

Up to the end of the current reporting period IRP1 develop a coherent set of projects, with multiple interrelationships and collaborations across CARES programme. The overall programme consists of projects aimed at reducing industrial CO_2 emissions, as well as avoiding them, and is underpinned by research into advanced materials and novel reactor concepts. IRP1 has developed new active projects with IRP2 and IRP3.

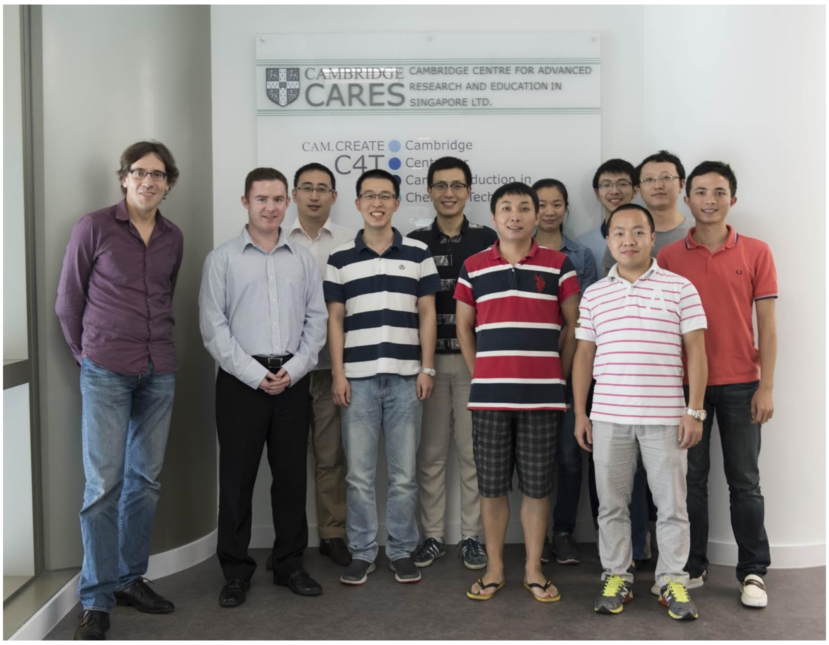


During this period new Cambridge PI, Alexei Lapkin, started to work closely with the Singapore team, brining in his expertise in continuous multiphase processes and system-level process analysis. The project also expanded into the area of *ab initio* calculations to support the work on advanced catalysts.

Over the period IRP1 researchers have made significant advances in several areas. In CO_2 capture and conversion significant progress was made in the synthesis of novel nanostructured CO_2 capture materials, developing mechanistic understanding of the material' requirements for an efficient CO_2 capture process and in CO_2 hydrogenation. Thus, MgO-carbon nanocomposites were shown to possess high CO_2 sorption capacity at conditions mimicking flue gas. New mixed oxide catalysts for CO_2 methanation were demonstrated to have exceptional activity and stability.

Avoiding CO_2 emissions is achieved through improved process efficiency, novel process concepts such as chemical looping combustion, and synthesis of chemical products not from primary fossil feedstocks but from biomass waste. In these three areas IRP1 is making significant progress. Novel materials were proposed for chemical looping combustion and initial experiments show good performance. Novel catalysts and a process concept were developed for a two-step waste biomass conversion to platform molecules.

Finally in multi-scale modeling area research progressed to validated DEM models of gas-solid flow that are now ready to be coupled with kinetics and mass/heat transfer to develop true multi-scale simulation of complex reactors for carbon capture and conversion.



IRP1 Research Fellows and Students with Prof Alexei Lapkin at the IRP 1 Research Seminar held at the CREATE Tower in March 2016.

3.1.2 Update on work packages

Work package 1: Chemical looping with advanced oxide carriers

Two types of chemical looping materials have been synthesised, both of novel morphological features. Dr Wen LIU (SRF, NTU and NUS, IRP1) et al have performed preliminary tests of these materials at the temporary facilities at NTU and have obtained positive results. Further investigations of the performance of these materials and the scaling up of the synthesis are ongoing. This is work in progress and owing to the novelty, details will follow in future reports once publication has occurred.

Jijiang HUANG (PhD student, IRP1, NTU) has been meanwhile focussing on the development of high performance oxygen carriers for chemical looping processes. To date several oxygen carriers have been prepared, including ZrO_2 supported Fe_2O_3, NiO and CuO via impregnation method, and Al_2O_3 supported NiO derived from layered double hydroxides (LDH) materials. The synthesized oxygen carriers were characterized with XRD, SEM and BET to evaluate their phase composition, morphology and specific surface area, which may have vital impact on the reactivity and redox stability of the corresponding materials. During the reporting period, the ratio of active oxide in Al_2O_3 supported NiO materials was determined by temperature programmed reduction with a TGA under 5% hydrogen in N_2, which is confirmed in accordance with the theoretical value. LDH derived oxygen carriers were also tested using a fixed-bed reactor at 800 ^{o}C with 5% H_2 in N_2 as fuel and 5% O_2 in N_2 as oxidant. It was found that about 80% oxygen carrier conversion can be achieved in 5 min with 100 mg oxygen carrier and a gas flow rate of 220 ml/min, and it showed excellent redox stability within 100 cycles.

Work Package 2: CO_2 methanation and biomass conversion

CO_2 methanation

YAN Yong (PhD student, NTU, IRP1) and Prof YANG Yanhui (PI, NTU, IRP1) have prepared a series of W-doped Ni-Mg mixed oxide powder catalysts by a homogeneous precipitation method and investigated the use of these in CO_2 methanation. $NiWMgO_x$ with Ni:W:Mg molar ratio being 1:1:1 exhibited both the excellent methanation activity and CH_4 selectivity. The stability test at 400 ^{o}C for 100 h revealed only a negligible activity loss for $NiWMgO_x$. The promotion effect of adding W to the Ni-Mg mixed oxide catalyst was further investigated by *in situ* DRIFTS, CO_2-TPD and H_2-TPR. This workstream resulted in a technology disclosure in July 2015, which has now been converted to a patent application.

JIA Chunmiao (PhD student, IRP1, NTU) has been studying application of the fluidized bed technology to CO_2 methanation. Recently, the concentration profiles of different components along the fluidized bed height have been obtained under the isothermal condition with the use of mass balances in bubble phase and emulsion phase. The concentration profiles under adiabatic condition using the mass balances and energy balances are currently being calculated. In addition, a comprehensive thermodynamics analysis of CO2 hydrogenation has been obtained and the paper for publication is in preparation.

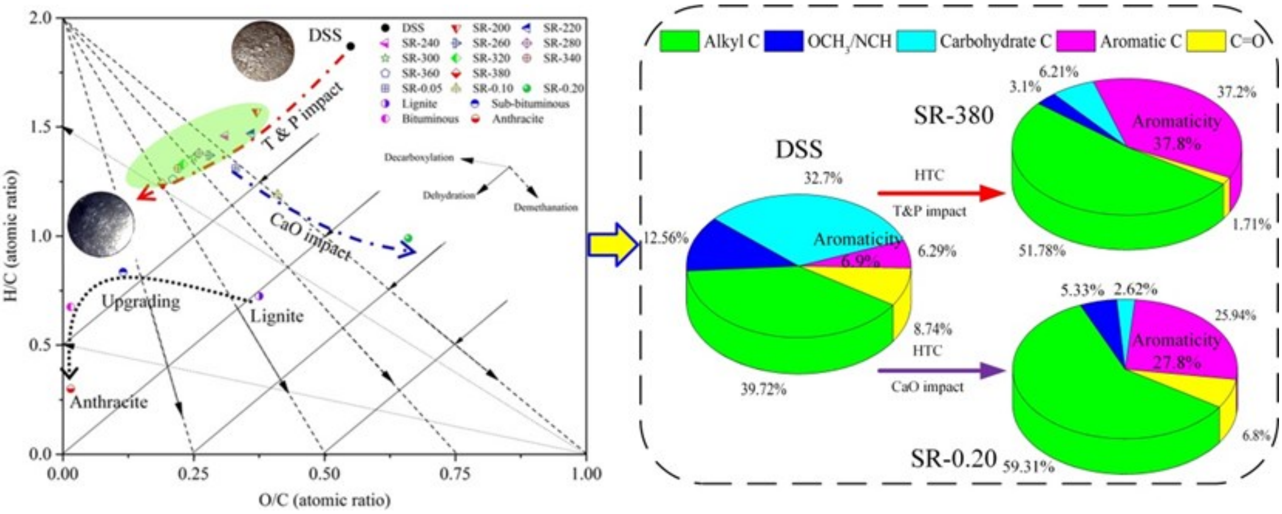
Dr DAI Yihu (SRF, IRP1, NTU) reports that Ru-based heterogeneous catalysts demonstrate excellent low-temperature performance in CO_2 methanation reaction, and considerable work has been aimed at their synthesizing. The activity is very sensitive to the size and the shape of Ru particles dispersed on the support, as well as to the interaction between the Ru species and oxide supports. In our study, a series of Ru/CeO_2 catalysts with Ru content in the 0.25-5.0wt% range were prepared by using coprecipitation method to achieve catalytic CO_2 methanation. Dr DAI found that the Ru loading amount largely determines the catalytic stability for both CO_2 conversion and CH_4 selectivity. At high Ru loading (2.5%), non-calcination Ru/CeO_2 catalyst reveals slight increase in CO_2 conversion, while catalysts after reduction in H_2 or calcination in air show steady CO_2 conversion, towards mathanation reaction at 300 ^{o}C for 10 h. The CH_4 selectivities of those three catalysts keep flat with around 99%. However, calcination parameters significantly affect the catalytic stabilities over 0.25% Ru/CeO_2. Over this catalyst, non-calcination or calcination in air leads a stable performance, whereas H_2-reduction causes rapid deactivation on both conversion and CH_4 selectivity within 4h. To figure out the evolution of the state of Ru species during the deactivation process is of significant to achieve better design of Ru-based methanation catalysts.

Biomass Conversion

Dr. HE Chao (RF, NTU, IRP1) *et al*. have established and tested the catalytic CO_2 gasification setup for simultaneous carbon reduction and sustainable energy generation for IRP 1.

Dr. HE Chao (RF, NTU, IRP1) has continued with experiments pertaining to catalytic wet oxidation of humic substances using highly efficient Ni/ZrO_2 catalyst, which has resulted in one Technology Disclosure (NTU Ref: TD/312/15) on “Nickel Catalyst for Highly Efficient Destruction of Humic Substances Using Catalytic Wet Oxidation”

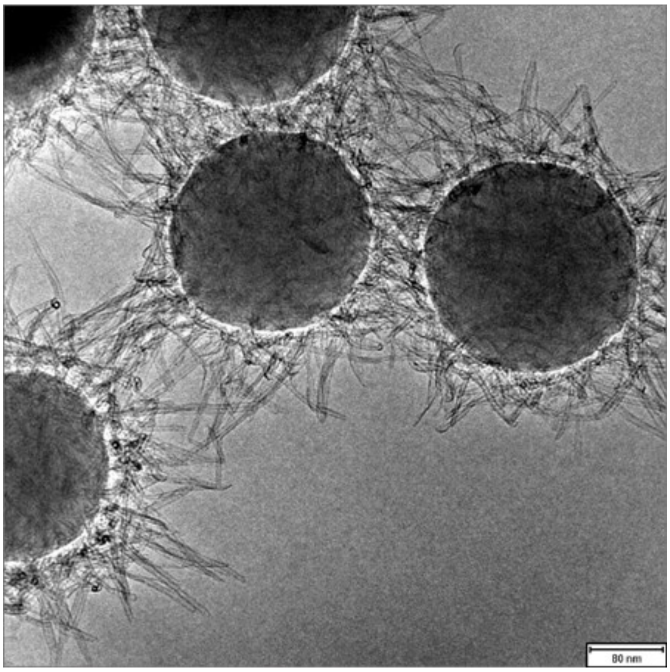
Dr. HE Chao (RF, IRP1, NTU) *et al* performed experiments on conversion of wet biomass waste streams using Low-Carbon Technologies. Based on the outcome of these experiments, one Singapore Patent (Provisional, Application number: 10201504349U) entitled “Efficient Energy Recovery from Wet Biomass Waste Streams Using a Two-Stage Hydrothermal Conversion System” is under further conversion and commercialization. Dewatered sewage sludge was upgraded to hydrochar using hydrothermal conversion in sub- and near-critical water. Three characteristic temperature regimes responsible for the upgrading were identified. Drastic hydrolysis of carbohydrates, amide II or secondary amines occurred at 200 ^{o}C while noticeable decarboxylation initiated above 260 ^{o}C. Elevated temperature improved porosity but did not induce higher surface area. Aliphatic C was mainly transformed to aromatic hydrocarbon rather than aromatic C−O in subcritical water, whereas COO/N−C=O and aromatic C−O were decomposed to carbohydrate C at 380 ^{o}C. Below 300 ^{o}C, carbon functionalities in hydrochars were thermally stable and faster decomposition of N than $\underline{C}$−(C,H) resulted in dramatic decline of N/C. Above 300 ^{o}C, $\underline{C}$−H was gradually polymerized to aromatic $\underline{C}$−(C,H) which was considerably transformed to $\underline{C}$−(O,N) and $\underline{C}$−H at 380 ^{o}C. CaO favored intense destruction of aromatic C−C/C−H, anomeric O−C−O, $\underline{C}$−H and $\underline{C}$−(O,N) functionalities but introduced more aromatic C−O and O=$\underline{C}$−O.



Work Package 3: New materials and MOFs

Project 1. MgO and carbon nanocomposite for CO_2 capture: Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1) are developing a facile strategy to synthesize a family of three-dimensional hierarchical-structured flower-like porous MgO/C nanocomposites based on the combination of solvothermal process with pyrolysis. Owing to its unique hierarchical architecture, ultrathin nanosheets building blocks with abundant nanopores, large surface area, highly dispersed nanoscale MgO crystallites (3 nm in size), together with the coexistence carbon species acting as stabilizer to prevent agglomeration of MgO NPs, the resultant MgO/C nanocomposites exhibit extraordinary CO_2 capture performance with the maximum capacity up to 30.9 wt% at 27 °C, 1 bar CO_2 and 21.0 wt% under conditions mimicking flue gas (27 °C, 0.15 bar CO_2). Besides, the nanocomposite adsorbents are highly durable and can be applied in the wide working temperature range from 27 to 200 °C.

Project 2. Sandwich-like graphene-based nanocomposites for CO_2 adsorption and electrocatalysis: Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1) are preparing a series of two-dimensional (2D) sandwich-like nanocomposites with hierarchical architecture based on reduced graphene oxide (RGO), amorphous carbon and M_xO_y (M = Mg, Fe, Co, Ni, Mn, Co) through solvothermal process followed with pyrolysis treatment. During the synthesis, 2D graphene oxide (GO) sheets are used as the structure-directing agent and support for metal-containing coordination polymer precursors to construct sheet-on-sheet nanohybrids. Among the resulting nanocomposites, RGO@MgO/C system has demonstrated great performance in CO_2 uptake. In addition, RGO@$Ni_xCo_yO_4$/C could also act as a competitive electrocatalyst for oxygen evolution reaction. The work on the electrocatalysis is currently in progress.



In addition, QIN Runze (PhD student, IRP1, NUS) has been working to develop new kinds of nano-catalysts that combine MOF materials and silicate materials. After calcination in nitrogen or air, it is possible to obtain silicate materials loaded with metal or metal oxides evenly dispersed, facilitating the catalyzing efficiency. QIN Runze's first step is to utilize copper salt and alkali to react with silicate sphere to produce copper silicate and control the morphology. By introducing copper as precursor, it is possible to grow HKUST-1 or some other MOFs in copper silicate. The work is currently in the morphology control step.

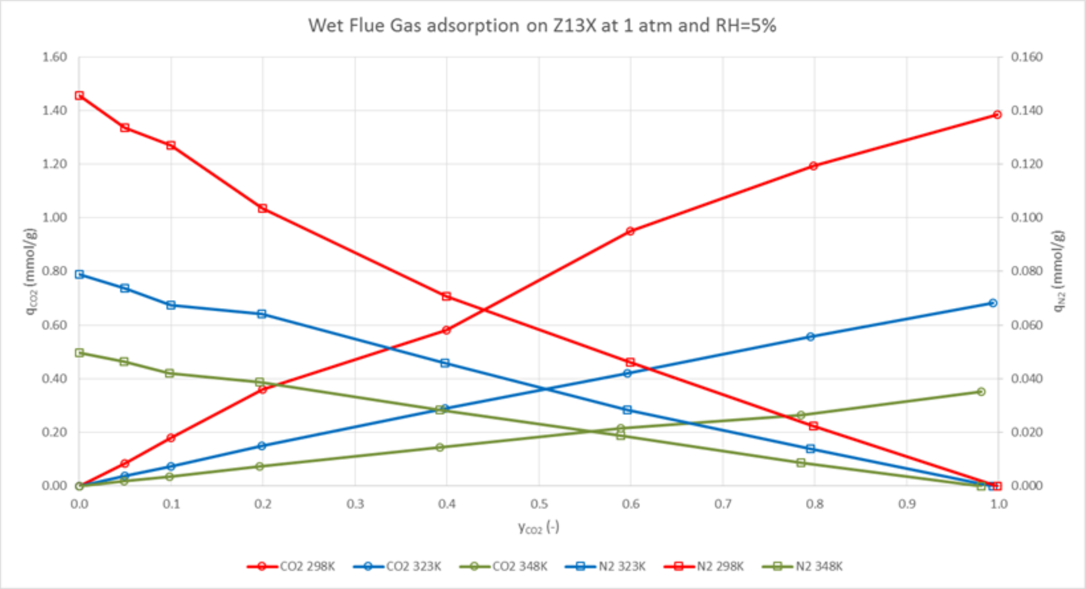
Work Package 4: Multi-scale modelling

Dr. Liangqi ZHANG (RF, IRP1, NTU) has been working on the mathematical description of the fluid dynamics with the coupling of the chemical reactions. Firstly, the alternative computational fluid dynamics method, lattice Boltzmann equation method derived from the kinetic theory, is investigated and extended to the application of axisymmetric flows. Secondly, the impact of the chemical reaction on the conservation of the mass, momentum and energy of the fluid dynamics system is studied currently. A rigorous mathematical representation on the coupling of the various physicochemical processes, and then its numerical solution, is the ultimate goal.

Understanding the scale-up effect of the reactors adopted in the chemical looping technologies is essential for the design and optimization of the process. YANG Shiliang (RF, IRP1, NTU) et al. conducted work targeted at investigating the bed hydrodynamics and quantifying the interaction intensity of two inter-connected chambers in a three-dimensional spout-fluid bed via the CFD-DEM coupling approach. The results show that inter-chamber interactions lead to unique characteristics distinct from that for a single-chamber system and provide meaningful understanding needed for the scale-up of the spout-fluid bed. Corresponding results have been published in the AIChE Journal. Furthermore, the effect of a submerged partition plate on improving the gas-solid flow robustness and stability in a three-dimensional spout-fluid bed with multiple inter-connected chambers is numerically investigated. The results demonstrate that inserting a partition plate with height above a certain threshold can effectively improve the stability of spouting and uniformly re-distribute the flux load in each chamber, giving rise to parallel fountains and lower circulation flux of the solid phase. Results indicate that the plate height should be at least 80% of the packed bed height, with the most optimal being about 92 % based on steady spouting, and the maximum solid and gas exchanging fluxes between the chambers.

Work Package 5: Fundamentals of adsorption and PSA

Adsorption technology is one of the leading options currently being explored for carbon dioxide capture and concentration (CCC) from flue gas. Among the adsorption based processes, Vacuum Swing Adsorption (VSA) on 13X Zeolite has been widely studied for CCC from (synthetic) dry flue gas containing 10-15% CO2 in balance nitrogen. However, real flue gas from any source will always contain moisture. An objective techno-economic evaluation of the VSA process on 13X Zeolite for CCC from wet flue gas is necessary to establish a reference point for assessing new materials and process developments. An essential pre-requisite for that is availability of detailed equilibrium data for CO2/N2/H2O mixtures on 13X Zeolite. Grand Canonical Monte Carlo molecular simulations for the adsorption of CO_2, N_2 and H_2O and associated gas mixtures on 13X Zeolite have been completed or are well underway. The simulations cover the entire mixture composition range, including humidity levels from dry up to saturated conditions with temperatures spanning 25°C up to 75°C. Results demonstrate the severe impact of even low levels of moisture on the CO_2 capture performance of 13X. Preparations are underway for the fabrication of a dynamic column breakthrough (DCB) rig for experimental characterization of the equilibrium and kinetic behaviour of adsorbents with different sample sizes. Local engineering firms have been contacted with regard to mechanical construction, electrical wiring & safety and software development for data acquisition and process control. Furthermore, the current intention is to construct an integrated pilot plant and DCB rig with appropriate precautions taken to ensure data reliability. Key aspects of the design work involved humidification of flue gas with feedback control and accurate humid gas flow measurement with a varying stream composition combined with scale-up potential across a suitable range of flowrates.



Other Activities and Achievements

- A group from CARES C4T IRP1 have developed a joint proposal with fellow CREATE programme E2S2 (Energy and Environmental Sustainability Solutions for Megacities) on “An Integrated Gasification - Carbon Abatement System for Manures and Municipal Solid Waste In Management and Utilisation”.
- IRP1 has now submitted four technology disclosures and has successfully progressed two of these to patent applications. One start-up company has been formed to commercialise one of the patented technologies.
- IRP1 is also carrying out consultancy work with several local Singapore companies with a view to licensing some of its patented IP.

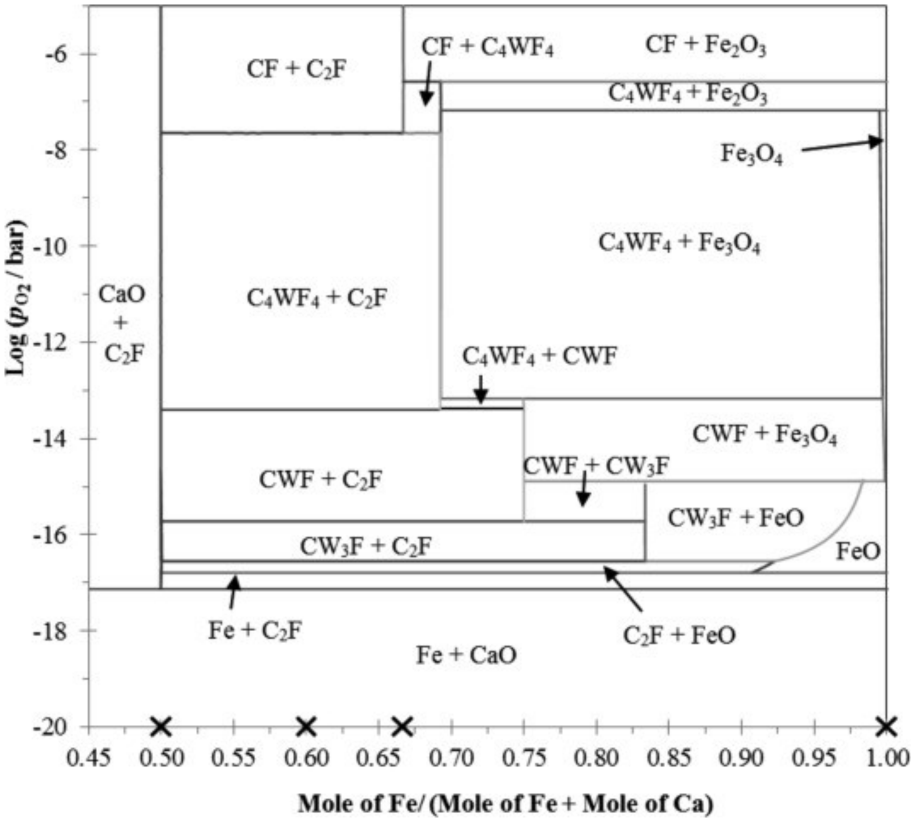
3.1.3 Scientific output of IRP1

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP1 during the reporting period. A full list of publications may be found in Appendix A.

Development and performance of iron based oxygen carriers containing calcium ferrites for chemical looping combustion and production of hydrogen

Ismail, Mohammad; Liu, Wen; Dunstan, Matthew T.; Scott, Stuart A.

DOI: 10.1016/j.ijhydene.2015.11.066



Highlights:

- CaO-modified iron oxide oxygen carriers have been synthesised. The CaO-modified oxygen carriers gave more stable performance over chemical looping cycles than unmodified Fe2O3.
- The Fe in the calcium ferrites fully participated in the redox cycles, which changed the relative proportions of the ferrites.
- The Fe in di-calcium ferrites is unavailable for CLC but makes more Fe available for H2 production.

Chemical looping combustion (CLC) is a cyclic process in which an oxygen carrier (OC), is firstly reduced by a fuel, e.g. syngas, and then oxidised in air to produce heat. If the OC is Fe2O3, the oxidation can take place in steam to produce hydrogen, i.e. chemical looping hydrogen production (CLH). This paper presents an investigation of CaO modified Fe2O3 OCs for CLC and CLH. The performance of the mechanically mixed OCs were examined in a thermogravimetric analyser and a fluidised bed. It was found that the addition of CaO gives cyclic stability and additional capacity to produce hydrogen via CLH, at the expense of reduced oxygen carrying capacity for CLC, owing to the formation of calcium ferrites, such as Ca2Fe2O5.

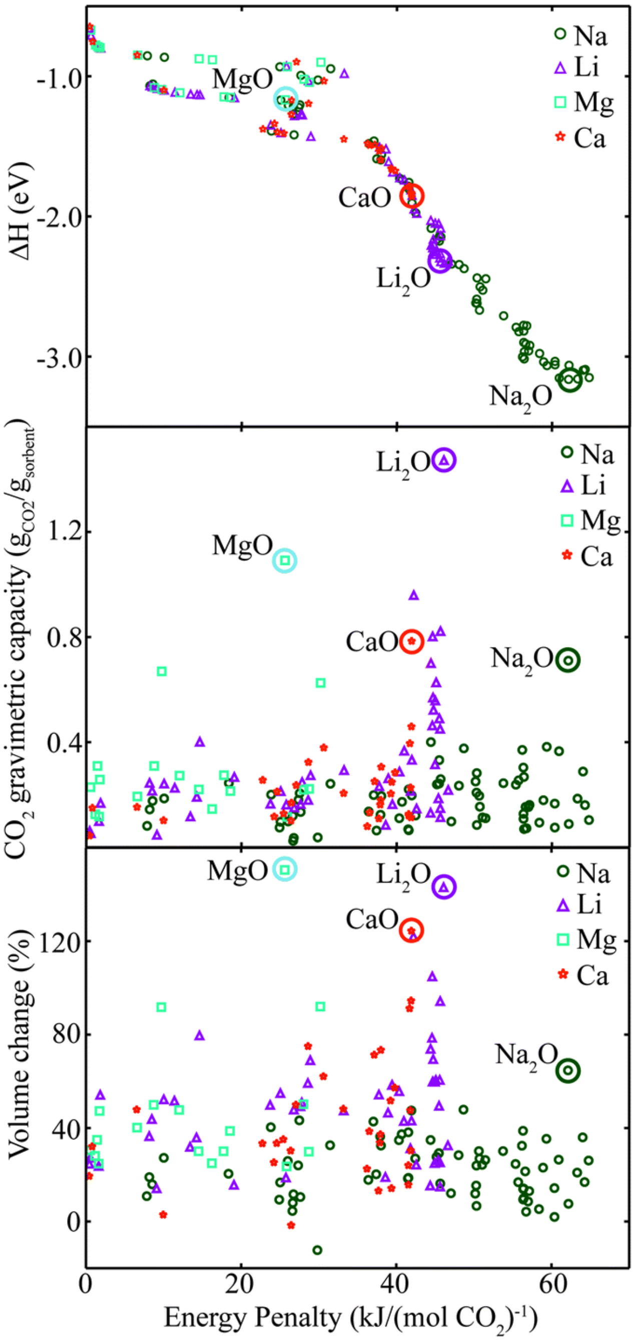
Large scale computational screening and experimental discovery of novel materials for high temperature CO2 capture

Dunstan, Matthew T.; Jain, Anubhav; Liu, Wen; Ong, Shyue Ping; Liu, Tao; Lee, Jeongjae; Persson, Kristin A.; Scott, Stuart A.; Dennis, John S.; Grey, Clare P.

DOI: 10.1039/C5EE03253A

Abstract:

The implementation of large-scale carbon dioxide capture and storage (CCS) is dependent on finding materials that satisfy several different criteria, the most important being minimising the energy load imposed on the power plant to run the process. The most mature CCS technology, amine scrubbing, leads to a loss of 30% of the electrical work output of the power station without capture, which is far too high for widespread deployment. High-temperature CO2 absorption looping has emerged as a technology that has the potential to deliver much lower energy penalties, but further work is needed to find and develop an optimal material. We have developed a combined computational and experimental methodology to predict new materials that should have desirable properties for CCS looping, and then select promising candidates to experimentally validate these predictions. This work not only has discovered novel materials for use in high-temperature CCS looping, but analysis of the entirety of the screening enables greater insights into new design strategies for future development.



The effect of steam on a synthetic Ca-based sorbent for carbon capture

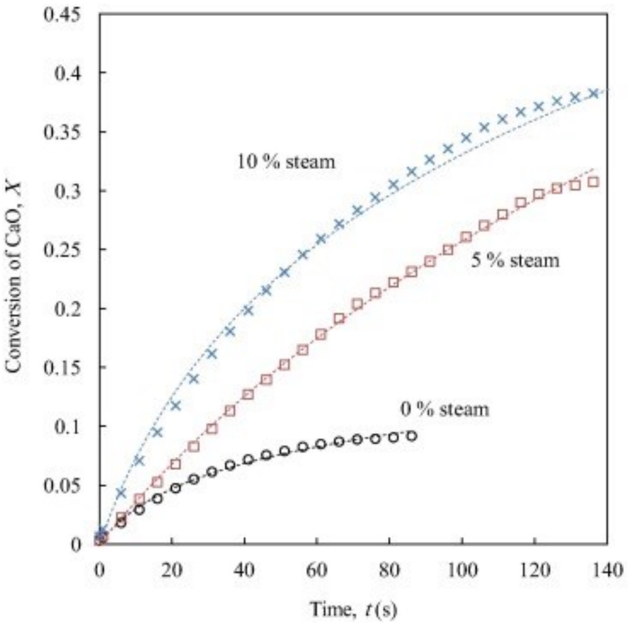
González, B.; Liu, W.; Sultan, D. S.; Dennis, J. S.

DOI: 10.1016/j.cej.2015.09.107

Highlights:

- Steam improves the performance of a synthetic sorbents, HAM83 for carbon capture.
- The presence of steam promotes the generation of meso-porosity with cycling.
- Steam favours the development of thicker product layers during carbonation.

The rate and extent of a synthetic sorbent containing 83 wt% CaO, 14 wt% MgO and 3 wt% $Ca_{12}Al_{14}O_{33}$ to react with CO2 at ⍰750 °C was investigated in the presence of 5 or 10 vol% steam. Similar to the natural sorbents and their derivatives, the rate and extent of carbonation by the synthetic sorbent was found to increase substantially with the partial pressure of steam. This improvement appears to be due to the ability of steam to promote the growth of product islands of CaCO3 in the direction normal to the surface, as well as affecting the porosity of the calcined material.



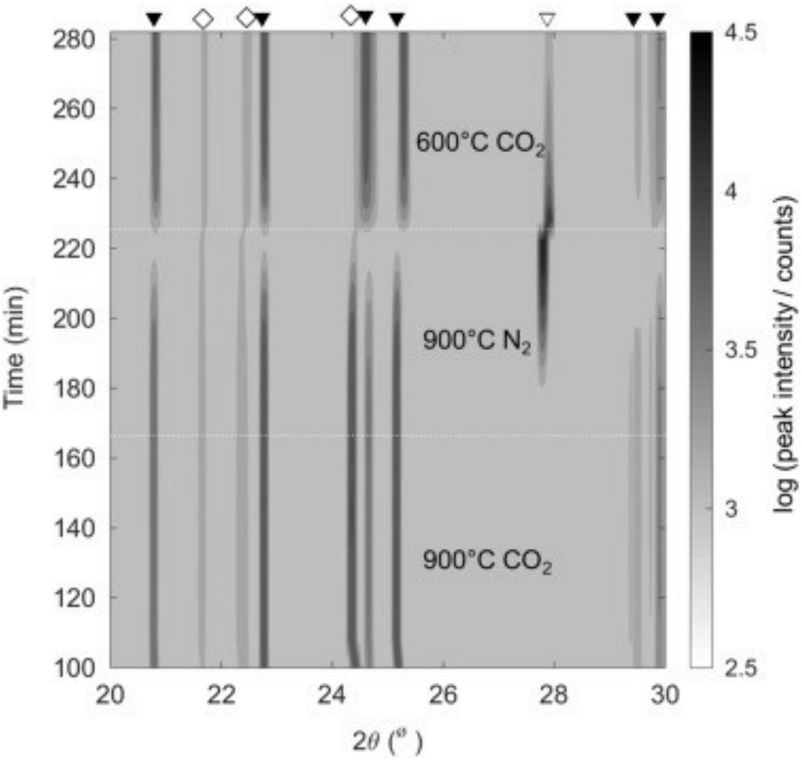
Structural evolution in synthetic, Ca-based sorbents for carbon capture

Liu, Wen; González, Belén; Dunstan, Matthew T.; Saquib Sultan, D.; Pavan, Adriano; Ling, Chris D.; Grey, Clare P.; Dennis, J. S.

DOI: 10.1016/j.ces.2015.09.016

Highlights:

- The Ca-based synthetic sorbents shows improving performance with cycling.
- The performance of the synthetic sorbents depends on their cycling history.
- The effect of cycling history on the sorbent's performance is cumulative.
- A surface cracking model explains the behaviour of the sorbent over cycling.
- The reaction model proposed maybe applicable to natural sorbents.



The carbonation of CaO-based materials at high temperatures (e.g. >600 °C) is a promising method of capturing CO2 emitted from, e.g. the combustion of carbonaceous fuels. The resulting CaCO3 can be regenerated by calcination at a temperature at which the equilibrium partial pressure exceeds that of the local partial pressure of CO2 (e.g. 950 °C). A process involving repeated cycles of carbonation and calcination of a calcareous material is called calcium looping. The capacity of a CaO-based sorbent to accept and reject CO2 over many cycles is governed by a number of factors, such as chemical composition, surface morphology and pore structure, all of which often evolve with cycling. The present paper investigates the underlying mechanisms controlling the evolution of the micro-structures of a series of synthetic sorbents consisting of CaO mixed with the inert supports Ca12Al14O33 and MgO. These sorbents were subjected to cycles of calcination and carbonation and were characterised using a variety of in situ and ex situ techniques. It was found that the balance between the degree of surface cracking during calcination and the extent of sintering during carbonation was responsible for changes in uptake during cycling, giving an increase in uptake for the supported CaO and a decrease for the unsupported CaO.

CFD–DEM investigation into the scaling up of spout-fluid beds via two interconnected chambers

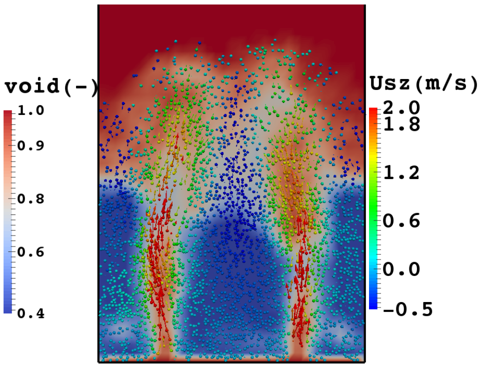
Yang, Shiliang; Cahyadi, Andy; Sun, Yuhao; Wang, Jingwei; Chew, Jia Wei

DOI: DOI:10.1002/aic.15188

Highlights:

- CFD-DEM has been adopted to simulate the gas-solid flow in a three-dimensional spout-fluid bed with two inter-connected chambers to study the gas-solid hydrodynamics and chamber interaction.
- The general solid motion, spouting evolution and spout-annulus interface is studied.
- The spout-annulus interaction and inter-chamber interaction are quantified.

The hydrodynamics and chamber interaction in a three-dimensional spout-fluid bed with two interconnected chambers are investigated via computational fluid dynamics coupled with discrete element method (CFD–DEM), because multiple interconnected chambers are key to scaling up spout-fluid beds. The overall solid motion, spouting evolution, and spout-annulus interface is studied, followed by time-averaged hydrodynamics, particle-scale information, spout-annulus interaction, and inter-chamber interaction. The results show that inter-chamber interactions lead to unique characteristics distinct from that for a single-chamber system, including (1) asymmetry of the hydrodynamics within each chamber, (2) alternative spouting behavior in the two chambers, (3) smaller pressure drop in terms of magnitude and fluctuations, (4) two peaks in the solid residence time (SRT) frequency histogram of the annulus, (5) average SRT in the spout is twice that in a single-chamber, and (6) larger solid dispersion in all three directions. The results provide meaningful understanding for the scale-up of spout-fluid beds.



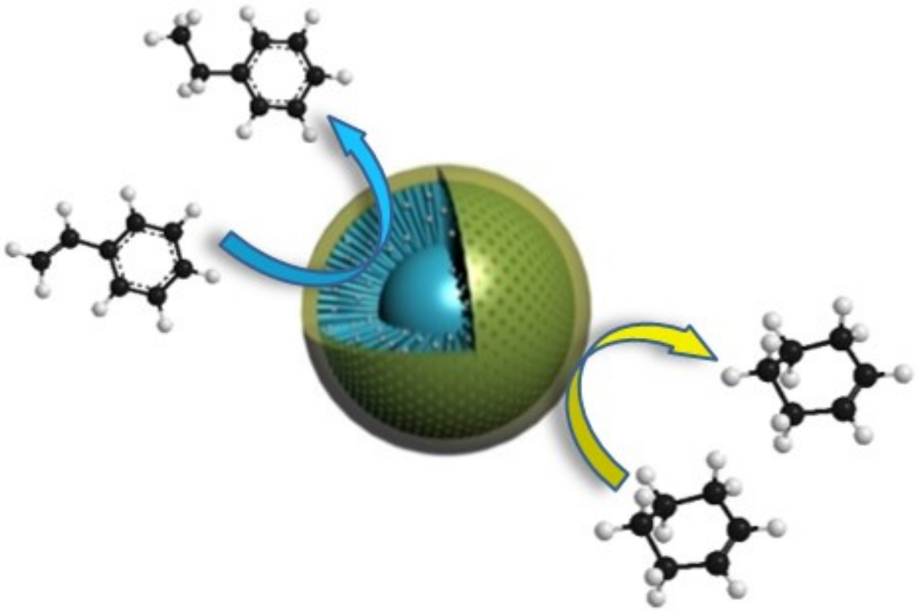
Influence of operating parameters and flow regime on solid dispersion behavior in a gas–solid spout-fluid bed

Yang, Shiliang; Sun, Yuhao; Wang, Jingwei; Cahyadi, Andy; Chew, Jia Wei

DOI: http://dx.doi.org/10.1016/j.ces.2015.11.038

Highlights:

- Solid dispersion behavior in a 3-D spout-fluid bed was investigated via CFD–DEM.
- Detailed trends of both local and overall solid dispersion behavior.
- Impact of various operating parameters on lateral and vertical solid dispersion.
- Solid dispersion is the most effective in the Jet-in-fluidization regime.
- Total gas flow rate plays dominated role on the overall solid dispersion.



The dispersion behavior of the solid phase in a three-dimensional spout-fluid bed was numerically investigated via the approach of coupled computational fluid dynamics and discrete element method (CFD–DEM), in which the fluid and solid phases were solved using the Eulerian and Lagrangian framework, respectively. Detailed trends of both the local and overall dispersion behaviors of the solid phase in the system were quantitatively studied, and the impact of various operating parameters (namely, spouting gas velocity (Usp), background velocity (Ubg), particle diameter (dp), the bed depth (L) and bed height) and flow regime on lateral and vertical solid dispersion was investigated. The results show that varying Usp, Ubg and dp affects the local solid dispersion in the spout and fountain regions more than the annulus. To enhance the overall solid dispersion, either Usp or Ubg or L can be increased, or dp and bed height can be decreased. Meanwhile, the total gas flow rate plays the dominated role for overall dispersion of solid phase. Finally, solid dispersion is the most effective in the Jet-in-fluidization regime, followed by the Spouting-with-aeration then the Intermediate/spout-fluidization regimes.

A General Synthetic Approach for Integrated Nanocatalysts of Metal-Silica@ZIFs

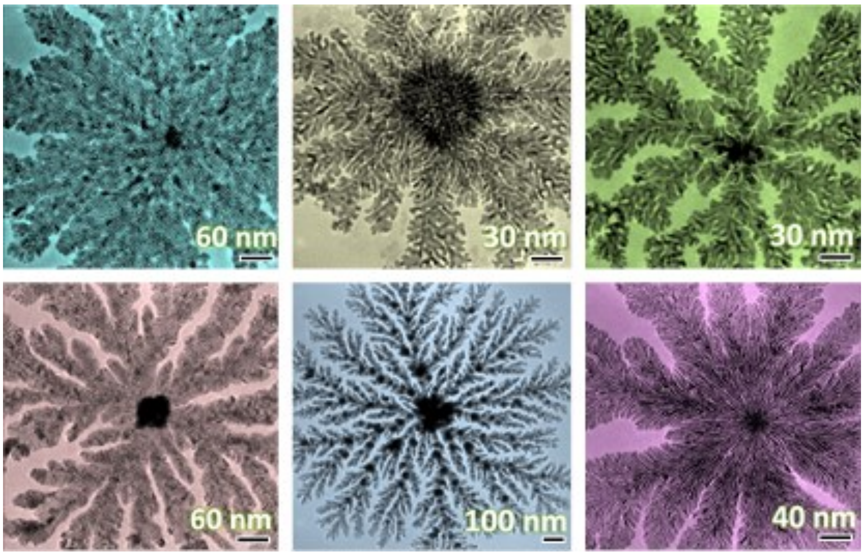
Xi, Baojuan; Tan, Ying Chuan; Zeng, Hua Chun

DOI: 10.1021/acs.chemmater.5b04147

Highlights:

- Integration of different nano-components into a greater assemblage or object for applications poses a significant challenge to nanotechnology.
- A versatile stepwise approach has been developed for preparation of integrated nanocatalysts of metal-mSiO2@ZIFs.
- Fundamental study and optimization have also been carried out, aiming at a greater generality of this synthetic approach.
- The workability of these catalysts has been demonstrated with hydrogenation of different alkenes using as-produced Pd-mSiO2@ZIF-8 catalyst.
- Reactant-selective hydrogenation has been achieved based on different interactions of the alkene molecules with the shell structure of ZIF-8, possibly influencing the flexible gate opening of ZIF-8.

Integration of different nanocomponents into a greater assemblage or object for applications poses a significant challenge to materials chemists. At present, it still remains extremely difficult to achieve high monodispersivity for such assembled products. To gain better synthetic controllability, ideally, an integration of this type should be done in a stepwise manner. Herein, we report a versatile stepwise approach for preparation of integrated nanocatalysts of metal-mSiO2@ZIFs (metal = Pt, Pd, Ru, Ag, and Pt53Ru47; mSiO2 = mesoporous silica; and ZIFs = ZIF-8 and ZIF-67). Starting with uniform solid Stöber silica spheres in submicrometer scale, mesoporous channels with desired length and diameter can be created for silica which serves as a support. With measurements of amino-modification of mesopores and selection of metal precursors applied, subsequently, ultrafine metal nanoparticles (2–5 nm) can be deposited evenly onto the inner walls of silica channels. Resultant metal-mSiO2 spheres are then modified by a layer of anionic polymer which imparts negative charges around and facilitates coating of ZIF-8 shell and thus formation of metal-mSiO2@ZIF-8. Through coordination interaction between polyvinylpyrrolidone (PVP; as surfactant molecules) and unsaturated Zn2+ ions exposed on the ZIF-8 shell, uniform metal-mSiO2@ZIF-8 spheres with desired shape and size can be obtained and simultaneously well-dispersed. Fundamental study and optimization are also carried out, aiming at a greater generality of this synthetic approach. The workability of these catalysts is demonstrated with hydrogenation of different alkenes using as-produced Pd-mSiO2@ZIF-8 catalyst. Indeed, reactant-selective hydrogenation is achieved based on different interactions of the alkene molecules with the shell structure of ZIF-8, possibly influencing the flexible gate opening of ZIF-8.



Kinetically Controlled Growth of Fine Gold Nanofractals from Au(I) via Indirect Galvanic Replacement Reaction

Zhou, Yao; Zeng, Hua Chun

DOI: 10.1021/acsami.5b06818

Highlights:

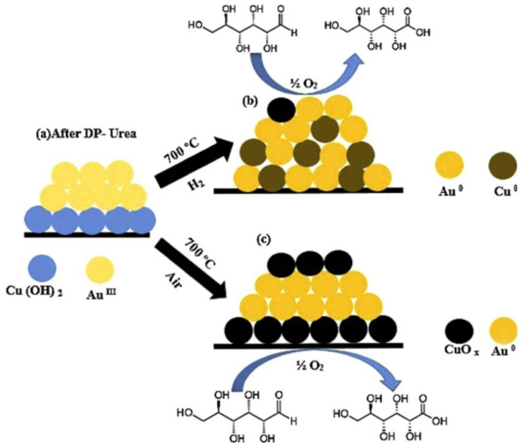
- An indirect galvanic replacement (IGR) strategy has been developed, where the electrons generated in a galvanic replacement reaction from anode oxidation are channeled out into a separate conducting film on which the cathodic metal can be deposited.
- Reduction of Au(I) ionic species with relatively low standard oxidative potential has been conducted with the IGR experimental setting.
- Two-dimensional finely hyperbranched Au fractals (4.0 nm in diameter and a few micrometers in length) with high structural integrity have been produced.
- Controls over the deposition density, location and micro-features of Au nanofractals have

been demonstrated through a mechanistic study.

- The Au nanofractals have been tested for electrochemical sensing; this type of nanostructured electrodes will also be investigated in producing H2 for hydrogenation of CO2.

Two of the most important features of Au nanostructures, size and shape, are significantly affected by the reduction kinetics of the relevant metal precursors. Because of the high standard oxidative potential of gold ionic species, AuCl4– in particular, Au fractals formed via various chemical or electrochemical approaches often have very coarse branches with diameters varying from tens of nanometers to submicrometers, even though extensive chemicals and/or complicated processes have been deployed to control the reduction kinetics. Herein we report an indirect galvanic replacement (IGR) strategy where the electrons generated in a galvanic replacement reaction from anode oxidation are channeled out to a separate conducting film on which the cathodic metal can be deposited. Reduction of Au(I) ionic species with relatively low standard oxidative potential has been conducted with the IGR experimental setting. 2D finely hyperbranched Au fractals (4.0 nm in diameter and a few micrometers in length) with high structural integrity were produced. Controls over the deposition density, location, and microfeatures of Au nanofractals were demonstrated through a mechanistic study. In addition, the thus-prepared Au nanofractals were also thoroughly tested in electrochemical sensing of H2O2.

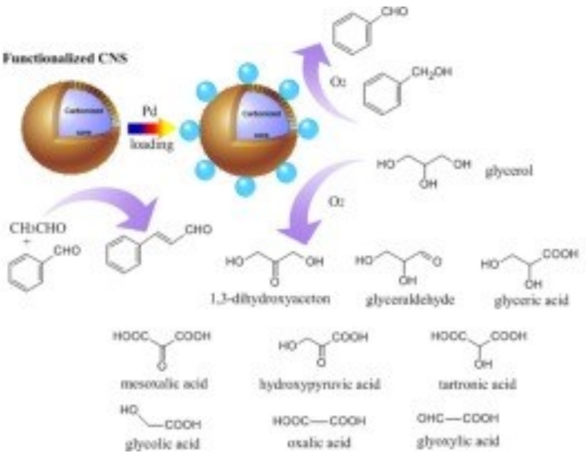
High-temperature reduction improves the activity of rutile TiO2 nanowires-supported gold-copper bimetallic nanoparticles for cellobiose to gluconic acid conversion



Amaniampong, Prince Nana; Booshehri, Amin Yoosefi; Jia, Xinli; Dai, Yihu; Wang, Bo; Mushrif, Samir H.; Borgna, Armando

DOI: 10.1016/j.apcata.2015.07.027

Titania nanowires (NW) supported gold–copper (Au–Cu) bimetallic nanoparticles were synthesized and pretreated in hydrogen and air at 300, 500 and 700 °C, for the one-pot conversion of cellobiose to gluconic acid. Catalyst samples were characterized by temperature-programmed desorption of NH3, Fourier transform infrared spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy, Field emission scanning electron microscopy (FE-SEM), X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The structure and activity of Au–Cu/TiO2 NW were highly affected by the pretreatment conditions. Catalyst samples reduced in H2 and at higher temperatures resulted better catalytic performance as compared with those calcinated in air at the same temperature. The influence of support, calcination temperature and atmosphere as well as gold content on the catalytic performance of Au–Cu/TiO2 NWs are investigated. The characterization results suggested high hydrogen reduction temperature created oxygen vacant sites on the titania NW support. This is consequently associated with the stabilization of highly reactive oxygen species at the periphery of the metal–support interface. Interactions between the metals and the titania NWs support and between the promoter and the active metal enhanced the formation of gluconic acid.

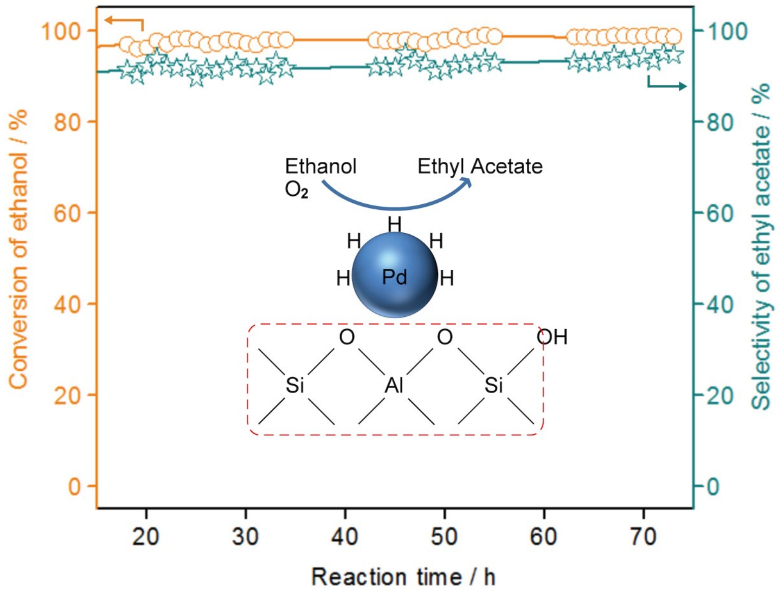


Catalytic applications of alkali-functionalized carbon nanospheres and their supported Pd nanoparticles

Yan, Yibo; Dai, Yihu; Wang, Shuchao; Jia, Xinli; Yu, Hao; Yang, Yanhui

DOI: 10.1016/j.apcatb.2015.11.024

Carbon nanospheres (CNSs) prepared by hydrothermal approach and post-functionalization with alkali solutions were employed as solid base catalysts in aldol condensation. The negative charge and alkalinity of CNS surfaces were controlled by the concentration of alkali solutions, leading to the high selectivity superior to aqueous NaOH as the traditional catalyst. Furthermore, CNSs with varying surface alkalinity can be adopted as proper supports for highly dispersed Pd nanoparticles with well-controlled size distribution. The optimized alkaline CNS-supported Pd catalysts demonstrated enhanced reactivities in the solvent-free selective oxidation of benzyl alcohol and the aerobic oxidation of glycerol. In-depth characterizations of their structural and electronic properties by transmission electron microscope (TEM), field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscope (FTIR) and X-ray photoelectron spectroscopy (XPS) were performed to elucidate the nature of the active sites and the mechanism. The effect of electron density, size of Pd nanoparticles as well as the surface alkalinity of supports on the catalytic performance has been unveiled.



Promoting role of bismuth on carbon nanotube supported platinum catalysts in aqueous phase aerobic oxidation of benzyl alcohol

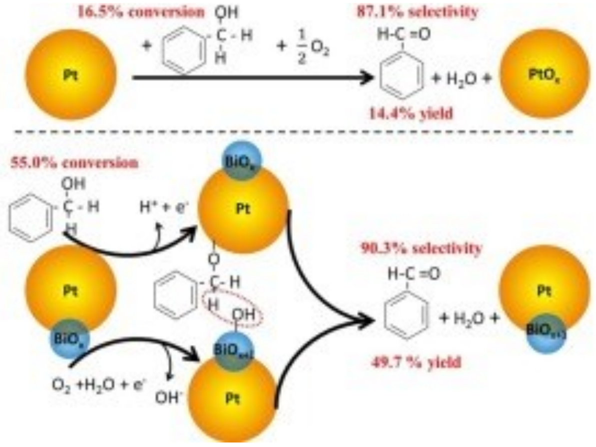
Zhou, Chunmei; Guo, Zhen; Dai, Yihu; Jia, Xinli; Yu, Hao; Yang, Yanhui

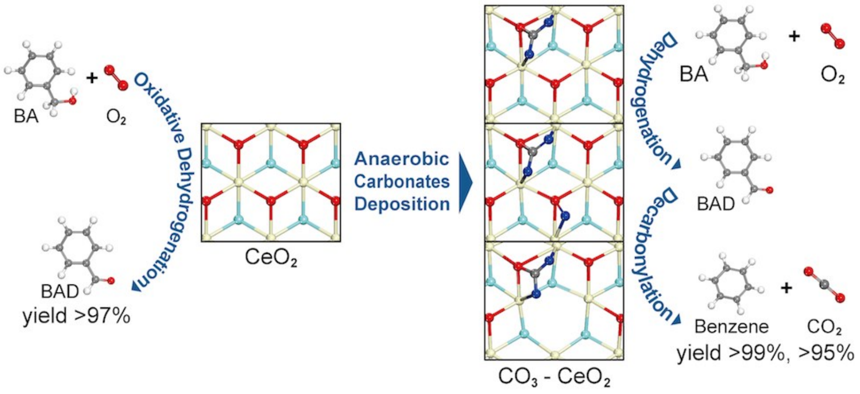
DOI: 10.1016/j.apcatb.2015.07.048

Highlights:

- Close contact between Bi and Pt affords enhanced catalytic activity in aerobic oxidation. Activation of both oxygen and alcohol is remarkably improved by Bi promoters.

PtBi/CNT catalyst was synthesized by a one-step polyol reduction method assisted by microwave radiation, and its catalytic performance was investigated in aerobic oxidation of benzyl alcohol in the aqueous phase. Pt and BiOx species uniformly dispersed on the CNT surfaces and strong synergic interaction between them occurred, which confirmed by the comprehensive analysis of TEM, XRD, XPS and electrochemical characterizations. Further investigations revealed that the synergic effect effectively promoted the activation of both molecular oxygen and benzyl alcohol substrate; also protected Pt active sites from over-oxidization. The advantage of such synergic effect was reflected in the increased yield for the desired product benzaldehyde: PtBi/CNT catalyst exhibited about 3.5 times higher yield toward benzaldehyde compared to Pt/CNT catalyst. Furthermore, owing to the positive effect of Bi avoiding Pt from oxidizing, the deactivation of PtBi/CNT (with 2% selectivity and 9% conversion decrease) is much slower than that of Pt/CNT (with 8% selectivity and 39% conversion decrease) after six reaction cycles. PtBi/CNT catalyst was proved as a remarkably effective catalyst with high stability for the aerobic oxidation of benzyl alcohol.





Highly selective gas-phase oxidation of ethanol to ethyl acetate over bi-functional Pd/zeolite catalysts

Chen, Hong; Dai, Yihu; Jia, Xinli; Yu, Hao; Yang, Yanhui

DOI: 10.1039/C5GC02593A

Biomass-based ethanol is a potentially promising feedstock and its transformation into value-added chemicals has attracted growing attention. Herein we reported that bi-functional zeolite supported Pd nanoparticle catalysts achieved superior performance in gas-phase selective aerobic oxidation of ethanol to acetaldehyde and ethyl acetate under mild conditions. The selectivity to ethyl acetate and the ethanol conversion remained at 94.7% and 98.6%, respectively, after a long-term reaction for 73 h over the 2Pd/HY catalyst, while acetaldehyde selectivity of 89.0% was obtained on 2PdO/HY at a low temperature of 150 °C. The reaction selectivity can be readily tuned by controlling the oxidation state of the Pd species, the type of zeolite support and the reaction conditions. The coexistence of the Pd0 and Pd2+ species and a moderate oxygen supply played critical roles in following the partial oxidation route to form ethyl acetate rather than formation of acetaldehyde or acetic

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

EMSET is divided into three work packages:

WP 2.1: Multi-Scale Electrochemical Modelling and Analysis

WP 2.2: Electrode Design and Development

WP 2.3: Electrochemical Reactor Engineering

The EMSET group is led by PIs:

Prof Adrian FISHER (Cam)

Prof Xin WANG (NTU)

Prof Jim Yang LEE (NUS)

Dr. Adrian Fisher,

University of Cambridge

PI, IRP2

March 2016

3.2.1 IRP2 Research Overview

The renaissance of electrochemistry internationally across a broad and diverse research community continues at great pace. The renewed interest in electrochemical approaches for chemical production and the continued focus on energy storage has been driven by the current international demand for energy efficient and low carbon technologies.

Electrochemical methods offer great promise for the prevention of pollution in the process industry and the inherent advantage arises from the potential to supply a key reagent, the electron, from renewable, clean electricity supplies. Of course for decades, electrochemical processes have been employed successfully in a selected range of industries e.g. production of metals such as aluminium and copper, the synthesis of fine chemicals and electroplating. It has been shown that electrochemical technology can provide cost-effective, environmentally friendly and highly controllable industrial process development offering potential advantages over tradition conventional chemical processes. These electrochemical processes have the advantages of versatility, energy efficiency, cost-effectiveness and amenability to automation. The potential options offered by electrochemistry are: (1) alternative industrial processes; (2) environmental protection; (3) pollution monitoring; and (4) non-polluting energy sources.

In IRP2 we are focused on exploring these aspects from a modelling and experimental perspective, with the aim of designing improved conversion technologies, novel synthetic routes and energy efficient electrocatalytic materials. In each of the three IRP2 work packages significant progress has been made in the investigation of low carbon technologies and analysis.

In the modelling WP we continue to explore the use of computational strategies to design and control energy efficient electrochemical pathways. In this reporting phase we have been working on the use of identifiability as a tool to explore optimal reactor and chemical pathways, as well as developing quantitative analysis tools to better understand the optimal route for a chemical process from an energy efficiency perspective. In WP2 we have focused on a variety of chemical conversions of CO_2 and water splitting. In WP3 we have continued our industrial engagement with joint publications in the sensor and analysis areas.

The industrial links within IRP2 have continued to strengthen in the past 6 months with further contributions and support in place for developing new research collaborations.

In addition to the growing research and industrial base the IRP2 training programmes continue to develop. The aim of these courses is to provide targeted education and “hands on” training in the area of electrochemical technology. In December we held an international Master Class in Beijing which was attended by a range of academic and industrialists, the programme was presented by Dr Fisher and Dr Song and was focused on advanced analysis techniques. We are currently in discussion with industrial partners in Singapore and plan to hold several further programmes in 2016 both in Singapore and China.

3.2.2 Update on work packages

Work Package 2.1 Numerical Multi-Scale Electrochemical Modelling and Analysis

One of the challenges in finding efficient and low carbon electrochemical technologies is identifiability, i.e., determining the suitable pathway that transforms electrochemical reactions and the optimal electrochemical reactors design. The process to optimise the overall efficiency begins with identifying and characterizing the electrochemical reactions using electroanalytical techniques followed by the design of electrochemical reactors that can be controlled electrically in a direct manner. In this research project, we have taken up this challenge of identifiability as our goal and are working on developing electroanalytical tools to identify the reaction mechanism and characterize them and also to identify appropriate reactor designs to replace conventional industrial processes. Mathematical modelling, numerical simulations, scaling and dimensional analysis will be employed as tools to carry out the research that will be properly supported by relevant experiments.

Rocking disk electrode (RoDE)

Hydrodynamic electrochemical method based on a rocking disc electrode (RoDE) is analysed and studied numerically at various frequencies and rocking amplitudes. The four-bar mechanism shown in Fig. 1 designed to generate the rocking motion is subjected to a kinematic analysis to derive its angular speed. Various rocking amplitudes could be obtained by changing the length of the links in the four-bar linkage satisfying Grashof conditions. The rocking motion from kinematic analysis is coupled to the model governing the fluid flow and species transport for the given redox reaction to determine the limiting current at various frequencies. A modified Levich equation for the limiting current is obtained by replacing the rotational speed for a rotating disk electrode (RDE) with the rocking speed for a RoDE. The limiting current under rocking motion is found to be proportional to the square root of the angular speed similar to the RDE from our initial modelling work and analysis [Sunyhik et al., 2016]. The results are validated with experiments for a rocking amplitude of 90 degree at various frequencies and is shown in Fig. 2. In this part of the work, this is now being verified by simulating the system at different rocking amplitudes and frequencies and comparing them with the modified Levich equation for the rocking motion.

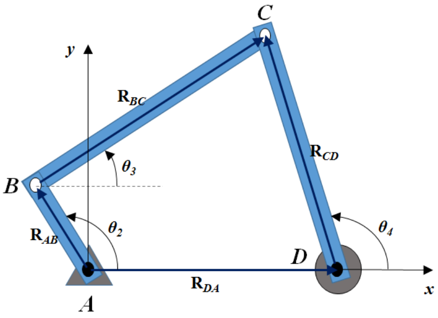


Figure 1. Schematic of the four-bar mechanism generating the rocking mechanism

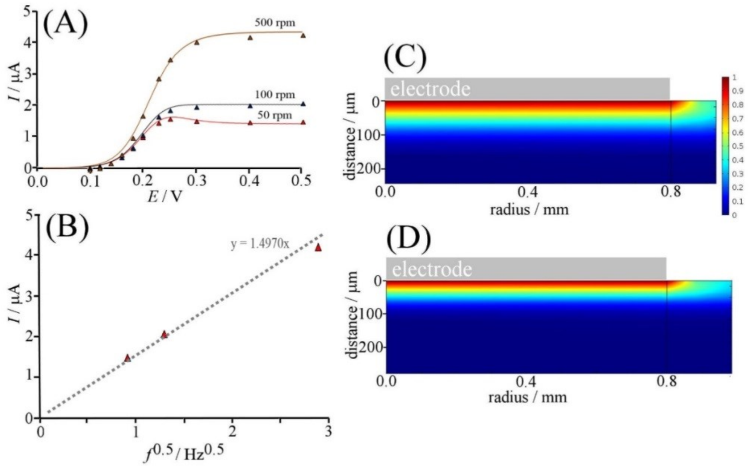


Figure 2. (A) Voltammograms (scan rate 10 mVs^{-1}, 1 mM redox active species, D = 0.65 × 10^{-9} m^{2}s^{-1}, 1.6 mm diameter disc electrode) at various rocking rates: model predictions (lines) versus experimental data (symbols, vide infra). (B) Plot of limiting current versus rocking frequency: model predictions (lines) versus experiments (symbols, vide infra). (C,D) Contour maps of the diffusion layer show-

ing the concentration of product at the end of the potential sweep at 0.5 V for (C) 50 rpm and (D) 100 rpm

The four-bar linkage shown in Fig. 1 consists of an input link (AB), an output link (CD), a ground link (DA) and a floating link (BC). The lengths of the links are $R_{DA} = L_1, R_{AB} = L_2, R_{BC} = L_3$, $R_{CD} = L_4$. The dimensions of these different links define the movement of the four-bar linkage. Grashof condition for a 4-bar linkage states that the sum of the shortest (S) and longest (L) links of a planar four-bar linkage cannot be greater than the sum of the remaining two links (P, Q) if there is to be continuous relative motion between two links. The different possibilities based on the length of the links are stated below:

$L + S < P + Q$: four different kind of input-output motions - crank-rocker, double-crank, rocker-crank, and double-rocker.

$L + S = P + Q$: same four possible mechanisms as in case 1 but has a special condition called change point where the follower link might change direction. Also, there is a special case called the parallelogram linkage where the opposite links are of equal length.

$L + S > P + Q$: double-rocker mechanisms only possible

Since the angular velocity of the crank ω_2 is known, the velocity equations can be rearranged to give

$$\omega_3 = \frac{L_2}{L_3}\omega_2 \frac{\sin(\theta_2 - \theta_4)}{\sin(\theta_4 - \theta_3)}$$

$$\omega_4 = \frac{L_2}{L_4}\omega_2 \frac{\sin(\theta_2 - \theta_3)}{\sin(\theta_4 - \theta_3)}$$

The equations above are subject to appropriate initial conditions for θ_3 and θ_4 from geometry of the mechanism. The expression for the Levich equation for a RDE is $i_{Levich,RDE} = 0.62\, nFAc^* D^{\frac{2}{3}} \nu^{-\frac{1}{6}} \sqrt{\omega_2}$

where $c^* = \lim_{z \to \infty} c$ represents the bulk concentration of the oxidized or reduced species for cathodic or anodic limiting currents. For a RoDE, we employ the rocking rate instead of the rotational rate to obtain $i_{Levich,RoDE} = 0.62\, nFAc^* D^{\frac{2}{3}} \nu^{-\frac{1}{6}} \sqrt{\omega_4}$

$$i_{Levich,RoDE} = 0.62\, nFAc^* D^{\frac{2}{3}} \nu^{-\frac{1}{6}} \sqrt{\frac{L_2}{L_4}\omega_2 \frac{\sin(\theta_2(t) - \theta_3(t))}{\sin(\theta_4(t) - \theta_3(t))}}$$

In order to verify that the limiting current follows the modified Levich equation, we have chosen a range of lengths for the links satisfying Grashof conditions (case 1 and 2, with crank-rocker and crank-crank motions for the input-output links) in the four-bar linkage that will yield different rocking amplitudes and simulate them at selected frequencies as given in Table 1. The combination of lengths that satisfy Grashof condition and yields crank-rocker and crank-crank motion for the input-output links are simulated at the selected frequencies.

Parameter	Values
L1 (mm)	20, 30, 40
L2 (mm)	3,5,7
L3 (mm)	7, 10, 15
L4 (mm)	20, 30, 40
N (rpm)	50, 100, 500

Table 1: Various lengths of the link in the four bar and selected speeds of the input link

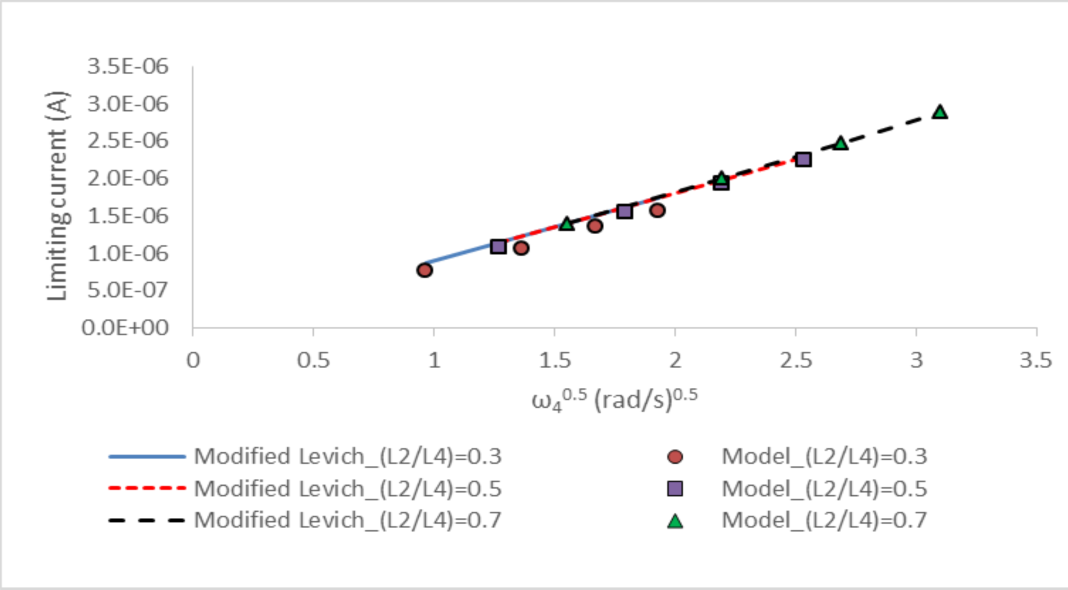
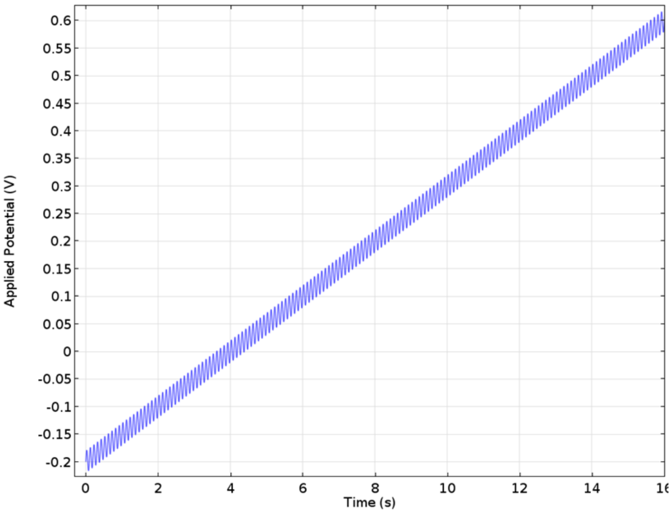


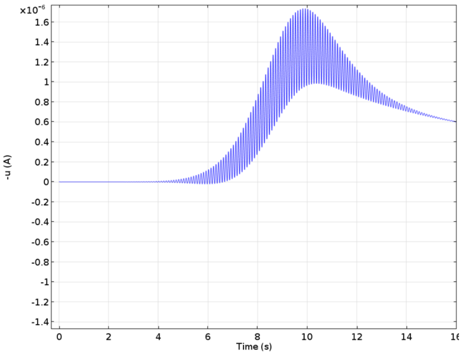
Fig. 3. Preliminary simulation results: Limiting current predicted by the model (symbols) and modified Levich equation (line)

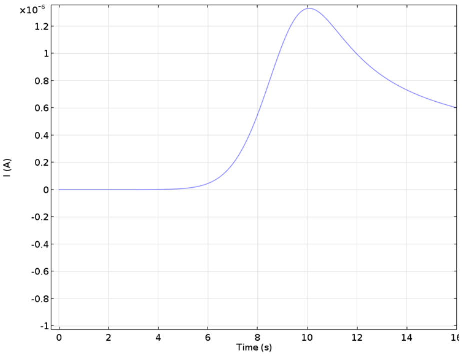


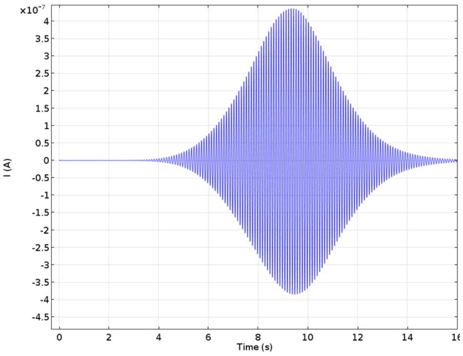
The initial results obtained from model simulations match well with modified Levich equation predictions for the limiting current as shown in Fig. 3. The model predictions are validated for the given length ratio of L2/L4=0.7 at different angular speed for the input crank.

Large Amplitude AC Voltammetry

Large amplitude AC Voltammetry typically involves the application of a sinusoidally oscillating voltage to an electrochemical cell. The experiment when used in conjunction with a lock in amplifier or frequency analyser offers considerably increased sensitivity and can also reveal important mechanistic and kinetic information not easily available using more tradition voltammetric techniques. A large amplitude AC voltammetric measurement is usually performed in an electrochemical cell where diffusion is the dominate mode of transport. The sinusoidal varying voltage is often combined with







either a steady DC signal or voltage sweep. Traditionally an amplitude of 5 mV or less is employed in AC measurement, this small perturbation ensures only slight changes in concentrations occur close to the electrode surface and allows mathematical analysis to assume that the effect on the electrode kinetics can be calculated in a linear manner, even though the electrode kinetics strictly have an exponential dependence on the applied voltage. Theoretical solutions to the ac techniques are very limited compared to the dc case and we aim to study this using a numerical approach similar to others. The numerical simulation will be carried out in a time domain and the resulting mixed response obtained will be subjected to a Fast Fourier Transform (FFT) to split the AC and DC components as well as identify the harmonics. Alternatively, we would like to carry out the transformation of time domain equations to frequency domain under certain conditions that will yield a steady state equation similar leading to a quicker simulation.

Diffusion of an electroactive species with its generation/consumption at an active electrode surface assuming Butler-Volmer kinetics is solved numerically for a one-dimensional geometry for an AC Voltammetry signal as shown in Fig. 3a. The response of the system predicted by the model is shown in Fig. 3b. Using a FFT, the voltammetric response is split into its AC and DC components and are represented in Fig. 4a and 4b. Identifying the harmonics from the voltammetric response of the system using FFT is under progress.

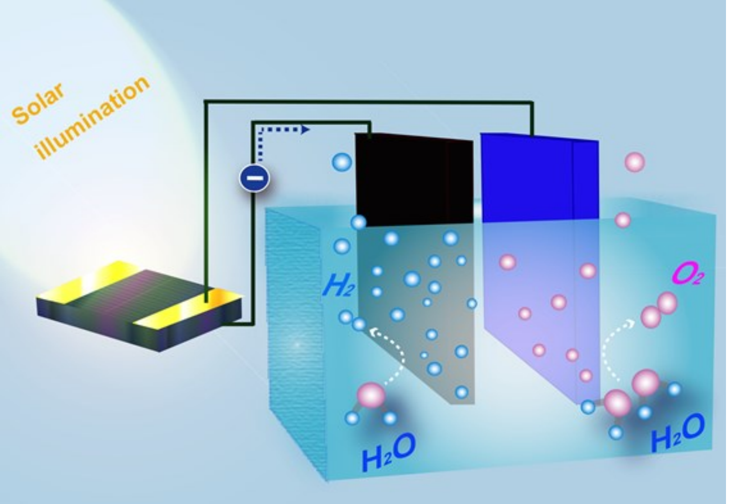
Work Package 2.2 Electrode Development and Testing

The electrode development and testing projects have continued to explore materials and processes which can lead to efficient electrolytic conversions.

Prof Xin WANG (PI, IRP2, NTU) *et al* have been preparing and designing nanostructured electro-catalysts for water splitting so as to harvest sustainable energy source and simultaneously working on the design of efficient gas evolution electrode. This IRP2 group has reported a flexible electrode based on carbon cloth substrate and iron phosphide nanotube coated with an iron oxide/phosphate layer, for overall water splitting. The as-prepared flexible electrode demonstrates remarkable electrocatalytic activity for both H_2 evolution reaction (HER) and O_2 evolution reaction (OER) at modest overpotentials. The surface iron oxide/phosphate formed *in-situ* is proposed to improve the HER activity by facilitating the water dissociation step and serves directly as the catalytically-active component for the OER process.

For the first time, IRP2 (Prof Xin WANG's group) report an efficient method for the synthesis of highly monodispersed surfactant-free, composition segregated octhedral PtNi alloy nanoparticles with an average edge length of 4 nm. The pristine octahedral PtNi nanoparticles showed Pt-rich corners/edges and slighly concave Ni-rich (111) facets. After thermal annealing at high temperature under H_2 atomosphere, the Pt-rich surface atoms at the corners/edges diffused onto and subsequently covered the concave Ni-rich (111) surfaces, leading to perfectly flat Pt-rich (111) surfaces with Ni-rich subsurface layers. More importantly, by using the same method, well-defined Pd@PtNi core-shell composites were also obtained. It was demonstrated that the Pd@PtNi composites exhibited an improvement factor of more than 1 order of magnitude in activity versus octahedral PtNi nanoparticles and 2 order of magnitude more active than the current state-of-the-art conventional Pt/C catalysts for PEMFC.

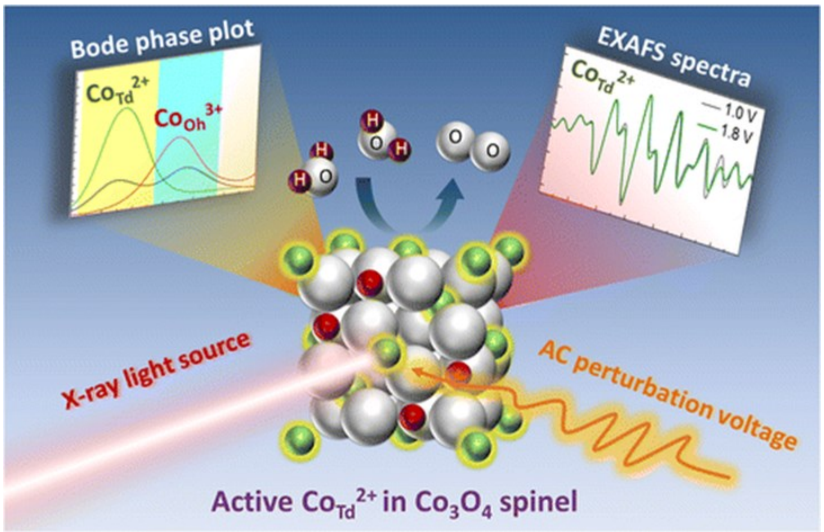
A further exploration of in water splitting utilised Pd in alkaline media which explored inefficiencies in the water dissociation mechanisms, where, the Volmer process of producing hydrogen is the rate-determining step. In order to accelerate the Volmer process, surface modification with metal (hydr) oxide is a simple and efficient strategy due to the synergistic effect of Fe−OH group and Pd atoms on the surface. Prof XU Zhichuan (Co-I, IRP2, NTU) has reported a novel to-down design of electrochemical strategy to deliberately modify the catalytic surfaces of Pd NPs with $Fe^{2+\delta}O^{\delta}(OH)_{2-\delta}$. This strategy not only solves the shortage of electrochemical deposition for NPs, but also has the remarkable ability of finely control the surface coverage. The results of electrochemical characterizations exhibited the superior intrinsic HER and OER catalytic behaviors of $Pd/Fe^{2+\delta}O^{\delta}(OH)_{2-\delta}$ in alkaline media. Specifically this novel catalyst had about 18.6 and 3.6 times of current density for the HER (−0.25 V) and OER (1.70 V), respectively, as high as that with pure Pd NPs. This work suggests that the top-down design of selective electrochemical dissolution of excess 3d-metal components from noble metal surface can serve as a general strategy toward tuning surface electrocatalytic properties.



Dr HSU Shao-Hui (RF, IRP2, NTU) and Prof Bin LIU (Co-I, IRP2, NTU) have been working on several projects to contribute to the overall effort in electrode development and testing.

Water oxidation, as a crucial reaction for water splitting and rechargeable metal-air battery, has currently held interests in reaction mechanisms and intermediates on each elementary step. Although they have been explored for understanding of oxygen evolution reaction, the electronic spin states that play a more important role in water splitting are still less concerned. In this work, the intermediate electronic spin configuration of Co^{3+} ($t_{2g}^{5}e_{g}^{1}$) and the hybridization between cobalt 3d and oxygen 2p orbitals were evidently observed by X-ray absorption spectrum. This configuration obviously affects the catalytic kinetics and onset overpotential for oxygen evolution reaction, resulting from the similar spin states between catalyst (Co_3O_4) and the intermediate (γ-CoOOH) as well as the stronger overlap of e_g orbital (Co^{3+}) with oxygen related adsorbates. Our finding may provide a general protocol for rational catalyst design by considering electronic spin states and the hybridization of molecular orbital in catalytic reactions.

Spinel Co_3O_4, comprising two types of cobalt ions: one Co^{2+} in the tetrahedral site (Co^{2+}Td) and the other two Co^{3+} in the octahedral site (Co^{3+}Oh), has been widely explored as a promising oxygen evolution reaction (OER) catalyst for water electrolysis. However, the roles of two geometrical cobalt ions toward the OER have remained elusive. Here, we investigated the geo- metrical-site-dependent OER activity of Co_3O_4 catalyst by substituting Co^{2+}Td and Co^{3+}Oh with inactive Zn^{2+} and Al^{3+}, respectively. Following a thorough in operando analysis by electrochemical impedance spectroscopy and X-ray absorption spectroscopy, it was revealed that Co^{2+}Td site is responsible for the formation of cobalt oxyhydroxide (CoOOH), which acted as the active site for water oxidation.



For water electrolysis, the energy loss at the anode is significant because water oxidation requires four-electron transfer. Therefore, it is highly desirable to design efficient oxygen evolution reaction (OER) catalysts and ensure their assembly into practical OER electrodes. In this study, we have developed a facile and scalable co-precipitation method to prepare stable colloidal NiFe-LDH nanoparticles at room temperature. The as- prepared NiFe-LDH nanoparticles showed outstanding water oxidation activity in basic electrolyte with a low Tafel slope of 21.2 mV dec^{-1} and a high mass activity of 200 mA mg^{-1} at an overpotential of 260 mV. Furthermore, to overcome poor conductivity of LDH and weak connection between LDH and the conductive support in practical applications, we scrolled NiFe-LDH nanoparticles into well-aligned MWCNT sheets to form binder-free hybrid microfiber electrodes. The microfiber electrode showed excellent OER activity, reaching 180 mA cm^{-2} at a small overpotential of 255 mV with outstanding durability. Moreover, the microfiber electrodes are highly flexible and could be woven into fabrics with arbitrary patterns. Our study could provide a general strategy to couple active electrocatalysts with porous, flexible and conductive carbon nanotubes for a wide range of electrochemical and catalytic applications.

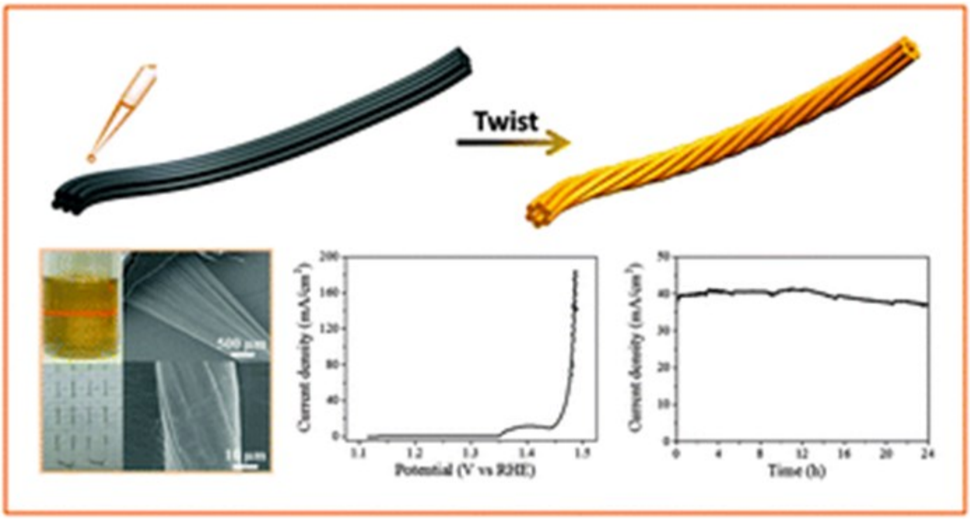
Naziah LATIFF (PhD student, IRP2, NTU) has been focused on three projects. The effect of impurities in transition metal dichalcogenides (TMDs) as electrocatalysts for the hydrogen evolution reaction (HER) has been previously explored and is currently being prepared for publication. LATIFF is currently investigating the capacitive properties and boron- and nitrogen-doped graphene oxides exfoliated through microwave plasma treatment to see whether these materials can have potential application in electrochemical capacitors. The cytotoxicity of three new exfoliated TMDs (VS_2, VTe_2, VSe_2) that have potential applications in energy-related devices. Is also being studied.

Work Package 2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

Work has been ongoing in the area of online analysis for sensing of chemical products. Dr Peng SONG has been working with Dr. Nathan LAWRENCE from Schlumberger Gould Research (SGR) for pH sensing electrodes. This work applies a range of substituted phenols, including salicylaldehyde and salicylic acid, for use as a voltammetric pH sensor for the determination of pH in both buffered and unbuffered media via electrochemical response. This work studied the chemicals using for pH sensing. This research not only shows a potential ability to monitor pH value of the aqueous solution, but also demonstrates which composition is crucial to show an accurate pH value in both buffered and unbuffered solutions.

Chemical conversions aspects have continued to explore the rapidly emerging area of C1 chemistry. Prof Richard WEBSTER *et* al (PI, IRP2, NTU) have investigated a novel electrochemical method for converting CO_2 into methanol using vitamin B6 as the electrocatalyst for the conversion. The work was published in a leading electrochemical journal was focused on electrochemically ameliorating carbon dioxide (CO_2) into methanol using pyridoxine, a member of the vitamin B_6 family, to enhance the reduction process. At a platinum electrode, an aqueous solution (pH ≈ 5) of pyridoxine showed a quasi-reversible redox couple with the cathodic peak detected at ca. -0.55 V vs. Ag/AgCl (3 M KCl) in the presence of CO_2 and argon. An increase in the corresponding cathodic peak current was observed following saturation of the solution with CO_2 using a Pt electrode, but with no detectable reduction current recorded at a glassy carbon electrode for the same system. Confirmation of methanol formation during the pyridoxine-assisted CO_2 reduction was conducted by using gas chromatography analysis of the electrolyzed solutions and faradic yields of ca. 5% were afforded. A combination of the results from the cyclic voltammetry and constant current chronopotentiometry experiments revealed an overpotential of ≤ 200 mV was required. The results indicate a potential utility of pyridoxine as an alternative reagent to the more toxic pyridine during the electrochemical reduction of CO_2.

Further work in the reactors area has focused on small scale generation of fuels/disinfectants electrolytically and their potential usage for cleaning or propelling objects at the microscopic scale. These concepts for example may be exploited to produce a cleaning agent electrochemically with a membrane or as in the case of Dr Bahareh KHEZRI (RF, IRP2, NTU) who has been working on micro/nanomotors, where the propelled objects the use chemical energy from their surroundings for motion. In collaboration with Prof Martin PUMERA (Co-I, IRP2, NTU) and Dr Peng SONG (RF, IRP2, Cambridge) Bahareh has been working on a project to engineer electrochemical microreactors. The purpose of the project is to study the mechanism of micro/nanomotors and develop multiscale electrochemical platforms for the production fuels or cleaning agents. Under the propulsion principle generated by H_2O_2, the motors are motivated to move within the microchannels.



A further new interest with Prof Pumera is the miniaturization of energy storage microcapacitors to develop portable electronic devices. Using membrane template-assisted electrodeposition of WS_2 nanoparticles (WS_2NPs) / polyaniline and platinum (Pt) layers, an on-chip micro-supercapacitors is demonstrated. The microrobots attaches itself on a gold microelectrode as part of the whole electrode. Within a microfluidic channel, IRP2 is studying the development of smart and miniaturized supercapacitor based on micromotors and the result demonstrates a large capacitive behaviour and the possibility of transport of electric charge to specific destinations.

Hydrogen is a promising candidate as chemical fuel for sustainable energy application. Currently, large-scale H_2 production is mainly achieved through industrial steam reforming using fossil fuels, particularly natural gas, which in turn would result in the equal immense emission of greenhouse gases. In collaboration with Prof Bin Liu we developed a photoelectrochemical device, which links III-V triple-junction solar cell and well-developed electrocatalysts. The integrated device provides ability for hydrogen production in neutral water and seawater splitting under solar light illumination for sustainable applications. A high solar-to-hydrogen efficiency with astonishing durability is achieved in our demonstration. The design meets the demand of carbon reduction for chemical fuel production by electro-synthesis and further achieves the goal of sustainable energy usage.

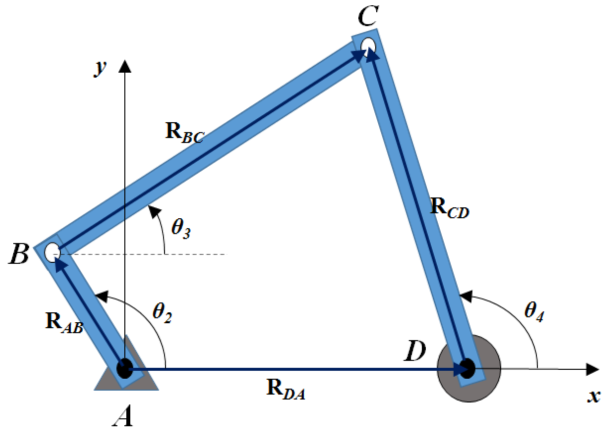
Other Activities and Achievements

- Dr Bahareh KHEZRI (RF, IRP2, NTU) has been working to develop a collaboration with A*STAR SIM Tech.

3.2.3 Scientific output of IRP2

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP2 during the reporting period. A full list of publications during the period may be found in Appendix A.

Hydrodynamic Voltammetry at a Rocking Disc Electrode: Theory versus Experiment

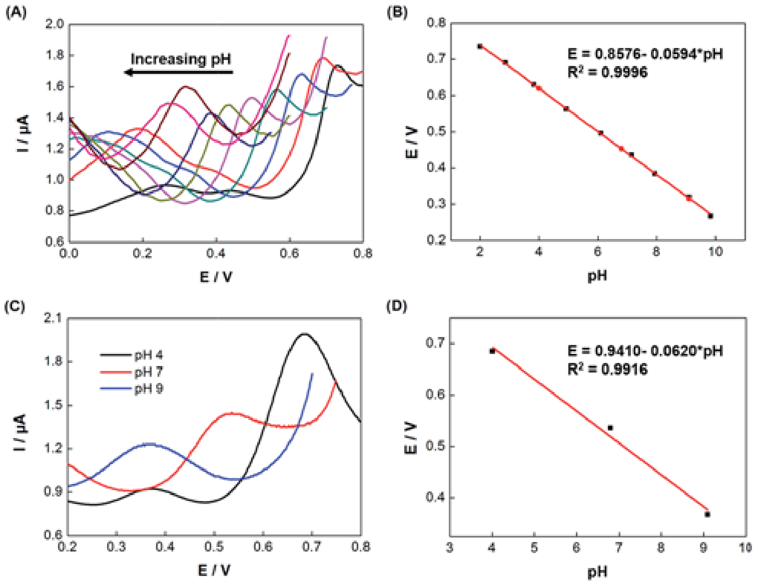


Sunyhik D. Ahn, Karthik Somasundaram; H.Viet Nguyen, Erik Birgersson; Jim Yang Lee, Xiangming Gao; Adrian C. Fisher, Paul E. Frith; Frank Marken

DOI: 10.1016/j.electacta.2015.11.143

Rocking disc electrode voltammetry (RoDE) is introduced as an experimentally convenient and versatile alternative to rotating disc voltammetry. A 1.6 mm diameter disc electrode is employed with an overall rocking angle of θ = 90 degree applied over a frequency range of 0.83 Hz to 25 Hz. For a set of known aqueous redox systems (the oxidation of Fe(CN)6 4- in 1 M KCl, the reduction of Ru(NH3)6 3+ in 0.1 M KCl, the oxidation of hydroquinone in 0.1 M pH 7 phosphate buffer, the oxidation of I- in 0.125 M H2SO4, and the reduction of H+ in 1 M KCl) the mass transport controlled limiting current Ilim is demonstrated to follow in good approximation the Levich-type expression Ilim = 0.111 nFAD^(2/3)v^(-1/6)(θf)^(1/2) with n, the number of electrons transferred per molecule diffusing to the electrode surface, F, the Faraday constant, A, the geometric area, c, the concentration of the active redox species, D, the diffusion coefficient, v, the kinematic viscosity, θ is the overall rocking angle in degree, and f, the rocking rate in Hz. Quantitative theory is developed based on a two-dimensional (2D) axisymmetric laminar flow model accounting for the conservation of mass, momentum and species along with the kinematic analysis of a “four-bar mechanism” to obtain the rocking motion.

A novel sensor based on electropolymerized substituted-phenols for pH detection in unbuffered systems

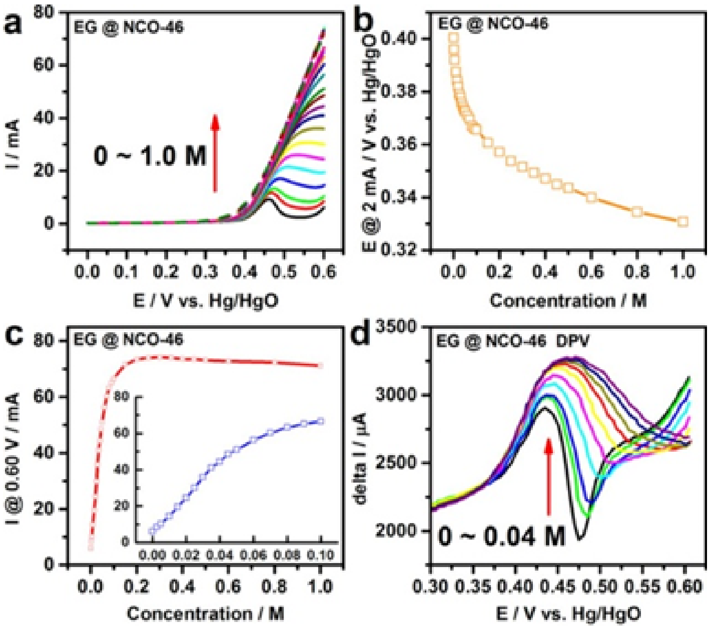


Dai, Chencheng; Crawford, Lynne P.; Song, Peng; Fisher, Adrian C.; Lawrence, Nathan S.

DOI: 10.1039/c5ra22595g

This work summarizes the electrochemical response of a range of substituted phenols, including salicylaldehyde and salicylic acid, for use as a voltammetric pH sensor for the determination of pH in both buffered and unbuffered media. Suitable candidates are identified and mechanistic insights into oxidation mechanism of the electro-polymerization by comparing with other substituted phenols are given. Square wave voltammetry measurements suggest the peak achieved through the electrochemical polymerization directly after the 1-electron 1-proton oxidation for both salicylaldehyde and salicylic acid shows a Nernstian response with good definition through a pH range from 2 to 10. In addition, hydrogen bonding enables the compound to sense the pH of unbuffered solutions with an error of less than 1%.

Ethylene Glycol and Ethanol Oxidation on Spinel Ni-Co Oxides in Alkaline



Sun, Shengnan; Zhou, Ye; Hu, Benlin; Zhang, Qichun; Xu, Zhichuan J.

DOI: 10.1149/2.0761602jes

Highlights:

- Ni-Co oxide with 46% Ni (NCO-46) showed the best oxidation performance for both EG and EtOH.
- EIS study reveals that the more Ni component in the oxide may facilitate the oxidation reaction. The NCOs with low Ni contents exhibited low reaction rates and it is probably due to the strong adsorption of oxidation intermediate products, which blocked the reaction sites.
- The high concentration of KOH can facilitate the oxidation reaction because OH− is a reactant in EG and EtOH oxidation reactions.

This article presents a systematic study on the composition dependence of Ni-Co oxides (NCOs) on their electrocatalytic activities toward ethylene glycol (EG) and ethanol (EtOH) oxidation. NCO electrodes were prepared by co-electrodeposition method followed by annealing in air. The atomic ratios of Ni / (Ni + Co) (Ni content) in NCOs were controlled by adjusting the concentration ratio of Ni and Co precursors. As the Ni content increased, the phase of materials changed from the spinel to the mixture of spinel and rock salt. The electrocatalytic activities of these NCOs toward EG and EtOH oxidation were investigated by cyclic voltammetry, differential pulse voltammetry, multi-step chronoamperometry, and electrochemical impedance spectroscopy techniques. It was found that the performance of NCOs for EG and EtOH oxidation exhibited a firstly-increase-then-decrease trend with the increase of Ni content and the best performance was found at 46% Ni. The presence of Ni probably can facilitate EG and EtOH oxidation. Increasing the concentration of reactants or pH can improve the reaction rates. The products from EG and EtOH oxidation were analyzed by nuclear magnetic resonance, which indicated that the oxidation reaction was a process from hydroxyl group to carboxyl group.

Fe2O3 Nanoparticle/SWCNT Composite Electrode for Sensitive Electrocatalytic Oxidation of Hydroquinone

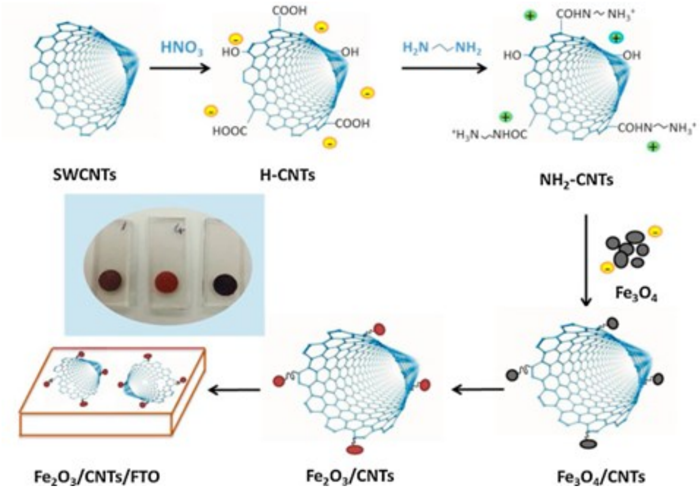
Liu, Ying; Liao, Hanbin; Zhou, Ye; Du, Yonghua; Wei, Chao; Zhao, Jian; Sun, Shengnan; Loo, Joachim S. C.; Xu, Zhichuan J.

DOI: 10.1016/j.electacta.2015.09.046

Highlights:

- This paper present a simple strategy to fabricate CNTs supported Fe2O3 nanoparticles, which are subsequently deposited onto FTO glass to make the Fe2O3/CNTs/FTO electrode for sensing HQ electrochemically.

- A sensitive and selective sensor was further developed based on the catalytic property of Fe2O3/CNTs/FTO electrode towards the oxidization of HQ.
- The Fe2O3/CNTs/FTO electrode has a good respond and anti-interference ability for determination of HQ in neutral medium.



This article reports a composite electrode of Fe2O3 nanoparticles/SWCNTs for hydroquinone electrochemical sensing. The synthesis includes the wet-chemical synthesis of Fe3O4 nanoparticles and the assembly of Fe3O4 nanoparticles onto single walled carbon nanotubes. Fe3O4/NH2-CNTs composite is formed via the electrostatic attraction between positively-charged ammonia-terminated CNTs and negatively-charged Fe3O4 nanoparticles. Subsequent heat treatment oxidizes Fe3O4 to Fe2O3. The composite can be applied onto FTO glass to form Fe2O3/CNTs/FTO electrode and the electrode shows good performance in electrochemical sensing of hydroquinone as compared to Fe2O3/FTO and CNTs/FTO electrodes. SEM and TEM results show the iron oxide NPs were uniformly dispersed onto the surface of SWCNTs. The iron oxide NPs which uniformly anchored on the SWCNTs could accelerate the electron transfer rate which was evidenced by electrochemical impedance spectroscopy. The enhancement of electrochemical response further confirms the synergy between Fe2O3 NPs and SWCNTs. Differential pulse voltammetry was successfully used to quantify hydroquinone within the concentration range of 1.0�80.0 µM under optimal conditions. The detection limit of Fe2O3/CNTs/FTO electrode for hydroquinone was 0.50 µM (S/N = 3). The electrode was further applied to test for hydroquinone in tap water and the Fe2O3/CNTs/FTO electrode also presents good stability and high reproducibility, proofing the potential of Fe2O3/CNTs electrode as a promising electrochemical sensor. This work presents an electrode using FTO substrate for the first time. It shows that FTO can be a potential alternative to glassy carbon electrode with lower cost, but without compromising too much on the sensitivity.

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

Hu, Nantao; Zhang, Liling; Yang, Chao; Zhao, Jian; Yang, Zhi; Wei, Hao; Liao, Hanbin; Feng, Zhenxing; Fisher, Adrian; Zhang, Yafei; Xu, Zhichuan J.

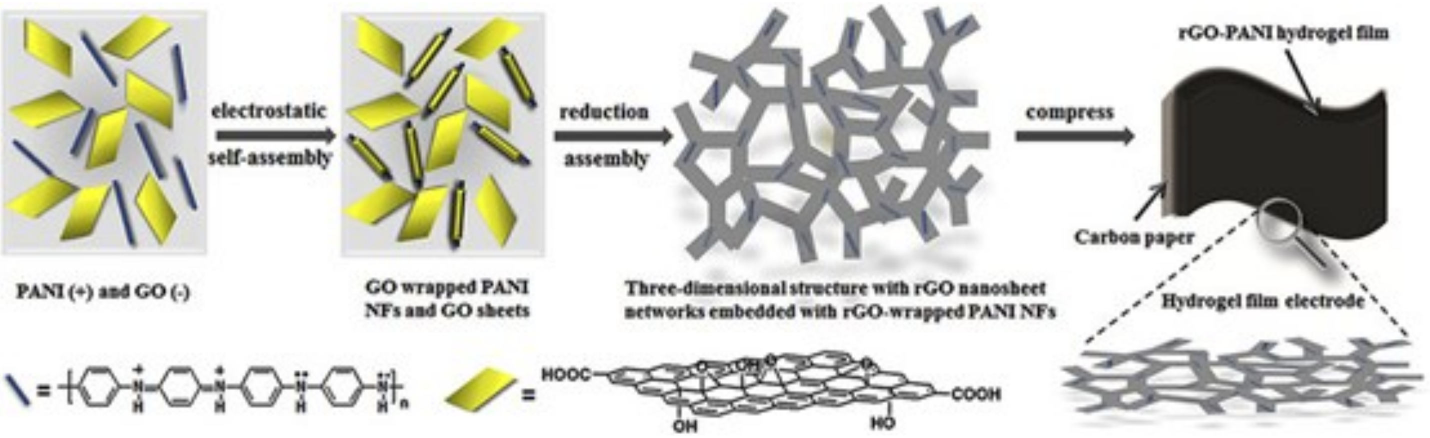
DOI: 10.1038/srep19777

Highlights:

- A design of high-performance flexible electrodes based on a hierarchical three-dimensional structure has been demonstrated.
- The intimate incorporation of PANI NFs in rGO sheet skeletons and the direct interconnection of all rGO nanosheets in the hybrid electrodes enable rapid electron and ion transport as well as excellent electrochemical behavior.
- Superior areal and volumetric energy storage capability, high-rate capability as well as excellent cycling stability under bending state without structural failure and loss of performance

have been achieved.

Thin, robust, lightweight, and flexible supercapacitors (SCs) have aroused growing attentions nowadays due to the rapid development of flexible electronics. Graphene-polyaniline (PANI) hybrids are attractive candidates for high performance SCs. In order to utilize them in real devices, it is necessary to improve the capacitance and the structure stability of PANI. Here we report a hierarchical three-dimensional structure, in which all of PANI nanofibers (NFs) are tightly wrapped inside reduced graphene oxide (rGO) nanosheet skeletons, for high-performance flexible SCs. The as-fabricated film electrodes with this unique structure showed a highest gravimetric specific capacitance of 921 F/g and volumetric capacitance of 391 F/cm3. The assembled solid-state SCs gave a high specific capacitance of 211 F/g (1 A/g), a high area capacitance of 0.9 F/cm2, and a competitive volumetric capacitance of 25.6 F/cm3. The SCs also exhibited outstanding rate capability (~75% retention at 20 A/g) as well as excellent cycling stability (100% retention at 10 A/g for 2000 cycles). Additionally, no structural failure and loss of performance were observed under the bending state. This structure design paves a new avenue for engineering rGO/PANI or other similar hybrids for high performance flexible energy storage devices.



The electrochemical reduction of carbon dioxide (CO2) to methanol in the presence of pyridoxine (vitamin B6)

Lee, Jazreen H.Q.; Lauw, Sherman J.L.; Webster, Richard D.

DOI: 10.1016/j.elecom.2016.01.016

Highlights:

- CO2 was electrochemically reduced in the presence of pyridoxine at a Pt electrode.
- CO2-saturated solutions gave larger currents than Ar-purged solutions.
- No observable cathodic processes were recorded on a glassy carbon electrode.
- Preparative scale reductions of CO2 gave 5% faradic yields for methanol formation.

Experiments aimed at ameliorating carbon dioxide (CO2) into methanol were explored using pyridoxine, a member of the vitamin B6 family, to enhance the reduction process. At a platinum electrode, an aqueous solution (pH ≈ 5) of pyridoxine showed a quasi-reversible redox couple with the cathodic peak detected at ca. − 0.55 V vs. Ag/AgCl (3 M KCl) in the presence of CO2 and argon. An increase in the corresponding cathodic peak current was observed following saturation of the solution with CO2 using a Pt electrode, but with no detectable reduction current recorded at a glassy carbon electrode for the same system. Confirmation of methanol formation during the pyridoxine-assisted CO2 reduction was conducted by using gas chromatography analysis of the electrolyzed solutions and faradic yields of ca. 5% were afforded. A combination of the results from the cyclic voltammetry and constant current chronopotentiometry experiments revealed an overpotential of ≤ 200 mV was required. The results indicate a potential utility of pyridoxine as an alternative reagent to the more toxic pyridine during the electrochemical reduction of CO2.

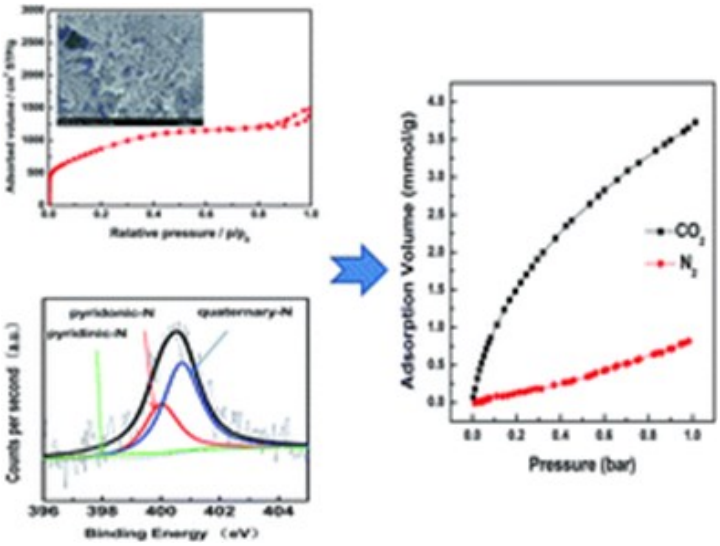
From fish scales to highly porous N-doped carbon: a low cost material solution for CO_2 capture

Huang, Bicheng; Shao, Hongyuan; Liu, Naiqiang; Xu, Zhichuan J.; Huang, Yaqin

DOI: 10.1039/C5RA16745K

Highlights:

- A strategy that uses fish scales to produce highly porous N-doped carbon for CO2 capture have been demonstrated.
- Upon optimization of the pore structure and N content (up to 2.90%), the CO2 capture capacity of the carbon sorbent can be 171 mg g−1 at 25 °C.
- NFPC-750 showed high affinity for CO2 (isosteric heat of adsorption is 17 kJ mol−1), high selectivity for CO2 over N2 (at the ratio of 5.21 at 0 °C), and good regeneration performance (up to 91.8% of the initial capacity after 10 cycles).

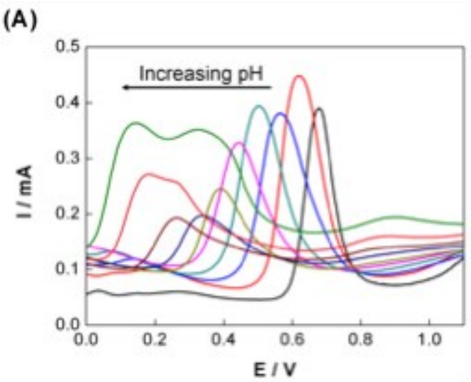


This article reports a strategy to use fish scales as raw materials for synthesizing CO2 capture materials. The synthesis employs thermal and chemical treatment to convert fish scales into N-rich porous carbons. The proteins in the fish scales are the major source of carbon and nitrogen. By varying the reaction conditions, the porosity and N content can be controlled in the produced porous carbons. It was found that the porosity first increases and then decreases with an increase in thermal treatment temperature; the N content decreases with an increase in the temperature. The capture capacity of the as-synthesized carbon (NFPC-750) for CO2 can be up to 171 mg g−1 at 25 °C, 1 bar. This high capacity is attributable to its porous structure with a high specific surface area (up to 3206 m2 g−1) and large pore volume (micropore volume up to 0.76 cm3 g−1 and total pore volume up to 2.29 cm3 g−1). More attractively, quaternary nitrogen is effectively preserved (2.90% N), which should be another contributor to enhance the CO2 capture capacity through the chemical adsorption between nitrogen groups and CO2. In addition, the sorbent preliminarily exhibits high cycle stability with retention of 91.8% of its initial CO2 capacity after 10 cycles. This highly porous N-doped porous carbon obtained from fish scales is thus considered a promising material for CO2 capture. performance were observed under the bending state. This structure design paves a new avenue for engineering rGO/PANI or other similar hybrids for high performance flexible energy storage devices.

A Route to Unbuffered pH Monitoring: A Novel Electrochemical Approach

Dai, Chencheng; Chan, Chun-Wai I.; Barrow, William; Smith, Anna; Song, Peng; Potier, Francois; Wadhawan, Jay D.; Fisher, Adrian C.; Lawrence, Nathan S.

DOI: 10.1016/j.electacta.2016.01.004



Carbon paste electrodes modified by alizarin, 1,4-dihydroxyanthraquinone, 1,2,3,4-tetrafluoro-5,8-dihydroxyanthraquinone and 2,3-dichloro-5,8-dihydroxy-1,4-napthoquinone are investigated by cyclic voltammetry and square wave voltammetry in order to ascertain suitability as voltammetric pH sensors. These electrodes show a Nernstian response to the change of pH, with a potential shift close to the theoretical value, 59.2 mV per pH unit at 298 K. Moreover, their capability of measuring the pH of the unbuffered solution with less than 5% error can be attributed to the occurrence of both inter- and intra- molecular hydrogen bonding present within the system. The efficacy of the compounds to be used as materials for solid state pH sensors is discussed.

A Flexible Electrode Based on Iron Phosphide Nanotubes for Overall Water Splitting

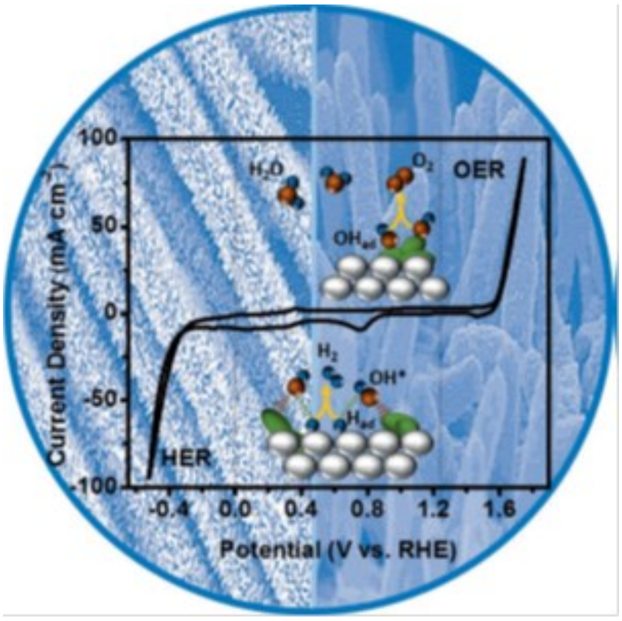
Yan, Ya; Xia, Bao Yu; Ge, Xiaoming; Liu, Zhaolin; Fisher, Adrian; Wang, Xin

DOI: 10.1002/chem.201503777

Highlights:

- A flexible electrode based on iron phosphide nanotubes was successfully prepared
- The flexible IPNT electrode demonstrates remarkable activity and stability for overall alkaline electrolysis
- These findings open up new possibilities with respect to the fabrication of efficient low-cost Janus catalysts for overall water splitting.

The design of cheap and efficient water splitting systems for sustainable hydrogen production has attracted increasing attention. A flexible electrode, based on carbon cloth substrate and iron phosphide nanotubes coated with an iron oxide/phosphate layer, is shown to catalyze overall water splitting. The as-prepared flexible electrode demonstrates remarkable electrocatalytic activity for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) at modest overpotentials. The surface iron oxide/phosphate, which is formed in situ, is proposed to improve the HER activity by facilitating the water-dissociation step and serves directly as the catalytically-active component for the OER process.

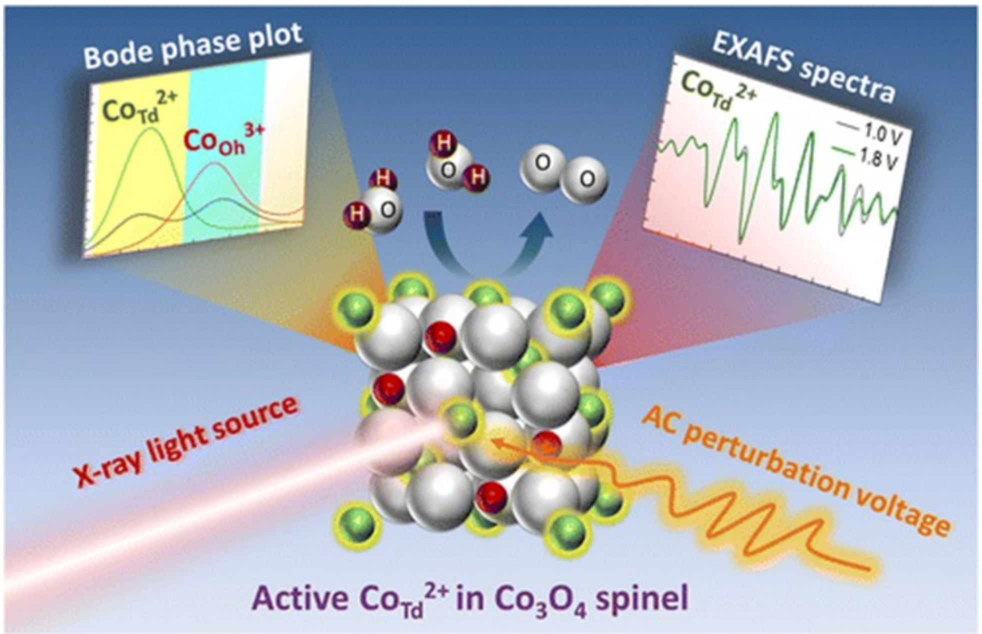


In Operando Identification of Geometrical-Site-Dependent Water Oxidation Activity of Spinel Co_3O_4

Wang, Hsin-Yi; Hung, Sung-Fu; Chen, Han-Yi; Chan, Ting-Shan; Chen, Hao Ming; Liu, Bin

DOI: 10.1021/jacs.5b10525

Spinel Co_3O_4, comprising two types of cobalt ions: one Co^{2+} in the tetrahedral site ($Co^{2+}Td$) and the other two Co^{3+} in the octahedral site ($Co^{3+}Oh$), has been widely explored as a promising oxygen evolution reaction (OER) catalyst for water electrolysis. However, the roles of two geometrical cobalt ions toward the OER have remained elusive. Here, we investigated the geometrical-site-dependent OER activity of Co_3O_4 catalyst by substituting $Co^{2+}Td$ and $Co^{3+}Oh$ with inactive Zn^{2+} and Al^{3+}, respectively. Following a thorough in operando analysis by electrochemical impedance spectroscopy and X-ray absorption spectroscopy, it was revealed that $Co^{2+}Td$ site is responsible for the formation of cobalt oxyhydroxide (CoOOH), which acted as the active site for water oxidation.



Achieving stable and efficient water oxidation by incorporating NiFe layered double hydroxide nanoparticles into aligned carbon nanotubes

Chen, Rong; Sun, Gengzhi; Yang, Cangjie; Zhang, Liping; Miao, Jianwei; Tao, Huabing; Yang, Hongbin; Chen, Jiazang; Chen, Peng; Liu, Bin

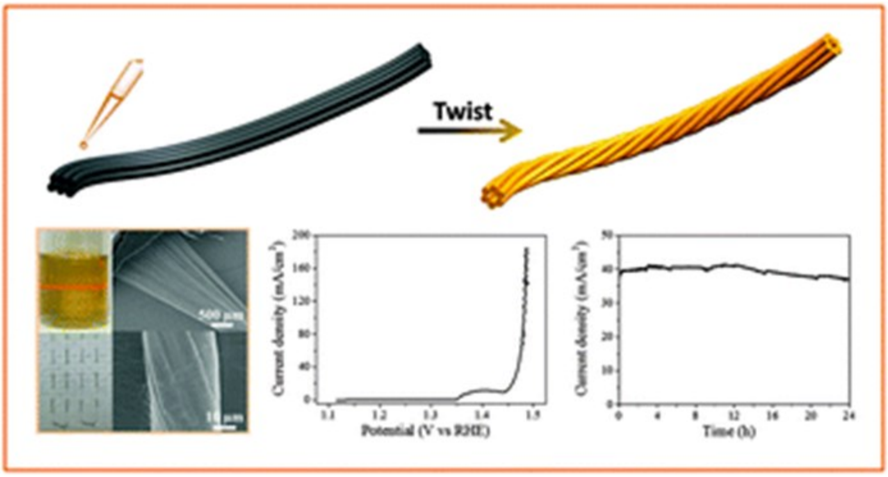
DOI: 10.1039/C5NH00082C

A facile and scalable co-precipitation method is developed to prepare stable colloidal NiFe-LDH nanoparticles at room temperature. We further scrolled NiFe-LDH nanoparticles into well-aligned multi-walled carbon nanotube (MWCNT) sheets to form binder-free hybrid microfiber electrodes, which showed excellent OER activity, reaching 180 mA cm−2 at a small overpotential of 255 mV with outstanding durability.

Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons

Xie, Ming Shi; Xia, Bao Yu; Li, Yawei; Yan, Ya; Yang, Yanhui; Sun, Qiang; Chan, Siew Hwa; Fisher, Adrian; Wang, Xin

DOI: 10.1039/C5EE03694A



For the first time, we report an efficient method for the synthesis of highly monodispersed surfactant-free, composition segregated octahedral PtNi alloy nanoparticles with an average edge length of 4 nm. The pristine octahedral PtNi nanoparticles showd Pt-rich corners/edges and slighly concave Ni-rich (111) facets. After thermal annealing at high temperature under H2 atomosphere, the Pt-rich surface atoms at the corners/edges diffused onto and subsequently covered the concave Ni-rich (111) surfaces, leading to perfectly flat Pt-rich (111) surfaces with Ni-rich subsurface layers. More importantly, by using the same method, well-defined Pd@PtNi core-shell composites were also obtained. We demonstrated that the Pd@PtNi composites exhibited an improvement factor of more than 1 order of magnitude in activity versus octahedral PtNi nanoparticles and 2 order of magnitude more active than the current state-of-the-art conventional Pt/C catalysts for PEMFC.

3.3 IRP3 — CAPRICORN

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

CAPRICORN is split into five interacting work packages:

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

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

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

WP 3.4: Modelling and optimisation of unit operations

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

The CAPRICORN group is led by PIs:

Prof Markus KRAFT (Cam)

Prof Raymond Wai Man LAU (NTU)

Prof Iftekhar KARIMI (NUS)

Prof. Markus Kraft,

University of Cambridge

PI, IRP3

March 2016

3.3.1 IRP3 Research Overview

The research activities of IRP3 are grouped into five work packages which address three overarching themes. In all three areas we were able to make significant progress.

Theme 1 focuses on creating a comprehensive model environment to study and optimise the activities on Jurong Island. This model environment is called the J-Park Simulator (JPS) and covers the work packages WP1, WP4, and WP5. In this reporting period we managed to couple an electrical grid model with a chemical plant model in close collaboration with the electrical engineers from IRP4. This can be considered a breakthrough as, for the first time, a process flow sheet model describing the material transport and chemical reactions has been shown to have a direct influence on a detailed model of the electrical grid. This was achieved both with the original software applications and with a parameterised version of the models. The parameterisation was obtained using the new software package MoDS. We were also able to include several other process flow sheet models for processes that can be found on Jurong Island. Our aim was to look into ways that allow us to make use of waste heat at plant and inter-plant level. We also systematically investigated the parameterisation of process flow sheet models which resulted in the submission of two papers. Parameterisation of complex models will be one key technology used in the JPS. Another key technology we apply in the JPS is the Semantic Web. We are in the process of developing an ontology to combine data sets with domain knowledge, which will allow for example natural language queries, similar to the IBM Watson expert system.

Themes 2 and 3 both have a heavy experimental component and we are therefore very excited to have access to the newly opened C4T laboratory for the next reporting period. The experimental work for the current reporting period was carried out in the labs at Cambridge, NTU and NUS. We were also able to collaborate with Prof Houston Miller from George Washington University and Prof Hai Wang from Stanford University. In Theme 2 we were able to conduct both fundamental studies on the properties of soot with respect to relevant fuel components as well as practical studies concerning questions such as how fuels influence engine operations. We managed to publish a number of papers in this area. In Theme 3 we investigated the question how we can use flame synthesis in the scale-up of catalyst production relevant to CO_2 reduction. We successfully identified metal-free water splitting catalysts with enhanced activity and improved stability. We also continued to work on improving the flame assisted coating with titania particles which was also submitted as an invention disclosure. Finally, it is our pleasure to report that three new Cambridge CARES PhD students have commenced their studies and are working towards their first papers.

Our focus during the next reporting period shall be on our first experiments in the new C4T lab, the JPS stakeholder meeting in May and the C4T mid-term review in July.

3.3.2 Update on work packages

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

The integrated project “J-Park Simulator” combines all aspects of WP 1, 4 and 5 in one. The set objective is to build a model of a cluster of smart factories within a fully virtualised eco-industrial park. A wealth of data has been added to the database of the software platform covering multiple model hierarchies across a wide range of industry domains from chemical engineering, electrical engineering, to finance, and building information management.

During the reporting period several features and functions were added to the Java frontend of the software platform under development. They include interactive online editing and updating capabilities of feature attributes and remote execution of chemical process models using Web services. Five chemical plants were modelled representing a diverse portfolio of chemical processes, operating conditions, and finished products including biodiesel, butyl-rubber, butadiene rubber, industry gases, and hydro carbon middle distillates from hydro cracking. Waste heat recovery modules were modelled for each of these plants, and waste heat recovery solutions implemented that allow a direct comparison of CO_2 emissions with and without intra-plant waste heat recovery.

A chemical process plant was modelled in the chemical process simulation software package AspenPlus, and in two electrical engineering process simulation software packages, first the steady-state simulation application PowerWorld, followed by the transient states simulation application eMEGAsim running on an OPAL-RT OP5600. Modelling the electrical engineering processes involved close collaboration with IRP 4. The modular system architecture combined with multiple cross-disciplinary modelling and feedback loops across domains allows running simulations and producing steady-state solutions that have not been realised before.

The modular character enables the software platform to integrate multiple models from a wide variety of industry domains ranging from chemical engineering, to electrical engineering, finance, and building information management.

In January, a comprehensive project team review was held in Singapore, with Cambridge team members attending. It delivered the roadmap for the J-Park Simulator project to the Mid-term Review in July 2016.

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

During the past six months there has been intensive work towards the understanding of pollutant formation from the combustion of hydrocarbons as well as the formulation of cleaner fuels. Our research comprises the fundamental study of the mechanisms of soot formation up to the characterisation of emissions on internal combustion engines using alternative fuels. The commissioning the C4T laboratory at the Research Building has also been achieved during the reporting period with a tremendous effort from all CARES Team.

Soot particle diameters range in size from as small as 3 nm to over 2 µm complex aggregate structures. The nanostructure of the particles will influence their toxicity for the environment and human health, as well as its possible application in industry.

One of our principal motivations is to gain fundamental understanding on the influence of fuel molecular structure on the characteristics of soot particles formed during combustion. The knowledge of the effect of fuel on soot particles sizes and morphology can guide the formulation of surrogate fuels with a lower environmental impact. Experimental data of particle sizes, morphology, nanostructure and optical properties will expand the understanding of soot particle formation and aid its prediction through modelling.

Four papers have been published by Dr. Maria BOTERO (Research Fellow, NUS, IRP3) and Edward YAPP (PhD Student, University of Cambridge, IRP3) concerning the experimental and numerical study of soot formation from the combustion of fossil fuels, their pure components, and surrogate fuels. The nano-structure of soot particles, formed in flames of relevant transportation fuels was analysed by means of high-resolution transmission electron microscopy. Further information on the structure soot particles is obtained through optical band gap diagnostics of their main constituents: polycyclic aromatic hydrocarbons (PAHs). Numerical simulations on such PAHs in similar flame set-ups were also performed.

Furthermore, two papers have been submitted for publication. One consists of a fundamental study on the role of PAH curvature in soot formation developed by Edward YAPP. In the other study soot particle sizes were produced in a novel stretch-stabilized flame configuration. The method was developed by Dr. Weijing WANG (Research Fellow, NTU, IRP3) in collaboration with Prof. Hai WANG (Stanford University). It can broaden the experimental conditions for studying soot formation.

Recent experiments planned and under commissioning in the new C4T laboratory involve the study of pollutant formation from the combustion of alternative fuels. The use of different additives (such as biofuels or oxygenates) to fossil fuels is also being considered in order to reduce the emission of soot particles.

Three flame systems are being assembled in the new C4T laboratory for the characterisation of soot particles in the combustion of fuels: 1- The smoke point burner, that enables the study of a wide range of liquid hydrocarbon and their mixtures, 2- The Yale burner, that allows better control of the flame conditions and a more detail characterisation of the soot particles and 3- The Burner Stabilised Stagnation Flame, which is a premixed burner that can be used to study soot formation and oxidation.

All the modelling and experimental knowledge obtained from the study of pollutant formation in flames is applied to more complex combustion systems. Five papers were published investigating the performance and emissions formation of various fuels in internal combustion engines and transportation. Dr. Sebastian MOSBACH (Research Associate, University of Cambridge, IRP3) has investigating soot produced from a wall film of fuel in internal combustion engines – a source of emissions that is relatively poorly understood.

Similarly, Prof. Wenming YANG (CO-I, NUS, IRP3) has been working on a comprehensive investigation on the spray properties of various fuels such as fossil diesel, biodiesel and kerosene and their blends under different fuel injection pressure and back pressure. Numerical simulation has been conducted to investigate the cavitation in the small injection hole and the major factors affecting the cavitation, all of these ensure a more accurate prediction on the performance and emissions of the engine. A three dimensional numerical simulation platform by combining KIVA 4 and CHEMKIN is being developed, detailed chemical reaction mechanisms have been developed for fossil diesel, biodiesel and their blends. An experimental setup is being built-up to investigate the formation mechanism of soot in the flame of various fuels.

A mathematical model called “Moment projection method” (MPM) has been developed that solves particle population balance equations with loss terms efficiently and accurately. It uses several weighted particles to represent the PSD and transforms the soot particle balance equations into a set of moment equations to update the weights and positions of these weighted particle This model builds on detailed analyses of several classic models, namely the Monte-Carlo method, the sectional method, the Method of Moments with Interpolation Closure (MOMIC), the Quadrature Method of Moments (QMOM), and the Extended Quadrature Method of Moments (EQMOM).

Compared with traditional Monte-Carlo method, MPM is much simpler and faster. Compared with MOMIC, MPM is able to solve the closure problem caused by the oxidation process, which has been a long standing problem for moment methods.

These studies have led to a paper named “A moment projection method for population balance dynamics with loss term” describing the mathematic model. The paper is currently under review.

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

Flame burners are used to synthetize nanoparticles in a controlled manner with scalability to large production otherwise infeasible by conventional wet chemistry methods. The different flame conditions and configurations allow the fabrication of nanoparticles with tailored properties. This is of main interest for the production of new materials and the improvement of the properties of existing ones.

The research in this area is currently focused on the production of catalysts with improved properties for the capture of CO2 in processes such as chemical looping performed within IRP1. Another aim is to produce coatings for electrodes and fuel cells in which can be tested and useful to by IRP2 research.

The development of thermodynamics and kinetics of some precursors in the formation of titania and silica nanoparticles (titanium tetraisopropoxide and tetraethoxysilane) in flames have been actively studied. A paper presenting an improved and reduced kinetic mechanism of the oxidation of a silicon nanoparticle precursor, and a second paper on outlier analysis for a silicon nanoparticle population balance model have been submitted for publication.

In the research conducted by Dr. Weijing WANG (Research Fellow, NTU, IRP3) a flame synthesis burner (FSRS) bought from Stanford University was used to produce titanium oxide nanoparticles and studying their characteristics. Utilizing the FSRS system with fuel lean and rich flames, both anatase and rutile titania nanoparticles were synthesized and collected as films on glass slides. SEM and TEM images were taken to compare the size and morphology of these particles to previous work done on similar setups from Professor Hai WANG’s group (Stanford University), thus the functionalities of this burner system were verified. The catalytic effect of synthesized titania nanoparticles was studied by oxygen evolution reactions on an electrochemical station.

Designing of future synthesis experiments in the C4T laboratory involves alternations of the FSRS burner and also incorporation with the BSSF burner system (also from Stanford University and under commissioning stage at C4T laboratory) to make composite nanofilms as well as other morphologies of nano materials such as nanowires or nanotubes. Combination of multiple burner systems will facilitate in synthesizing and processing of such nano materials with desirable catalytic capabilities.

Prof. XU Rong (Co-I, NTU, IRP3) has also been investigating the synthesis of nanoparticles for CO2 reduction and water splitting using traditional wet-chemistry approach. Photocatalytic water splitting and carbon dioxide reduction provide us clean and sustainable energy resources. The carbon dioxide reduction is also the redemption of the greenhouse effect. She has published three papers on these investigations during the reporting period. One of the papers reports the synthesis of titania nanoplates with well dispersed MoS3 on surface via hydrothermal routes as photocatalysts. The as-synthesized material is active for simultaneous photocatalytic water and carbon dioxide reduction in aqueous solutions. In the other papers she reviews important advances in metal-free water splitting technology and present results of the synthesis of polyoxometalates catalysts for water oxidation with enhanced activity and improved stability.

Another application of nanoparticles synthesized though combustion has been explored in the coating of PET bottles with photocatalytic titania to reduce microbial growth. Synthesis of titania coatings on glass and PET substrates using pyrotechnic mixtures was studied experimentally by Manoel MANUPUTTY (PhD student, NTU, IRP3) and SHENG Yuan (Student intern, NUS, IRP3). Flammability and stability of various fuel/oxidizer/titanium source combinations were compared and an optimal formulation identified. The coatings obtained were characterized by SEM, XRD, EDX, and photocatalytic dye degradation experiments. Photocatalytic performance of titania coatings prepared by wet-chemical and premixed flame methods was also studied as benchmark. Practical potential of the pyrotechnic method was then evaluated.

WP 3.4: Modelling and optimisation of unit operations

A variety of extreme event scenarios have been investigated and quantified, such as the dispersion speed of toxic gas emanating from a leak in ammonia and chlorine tanks in both liquid and vapour phase. A report covering these scenarios has been completed.

As part of the J-Park Simulator project, several chemical process plants have been modelled with and without waste heat recovery modules using AspenPlus. The process conditions and the inter-plant CO_2 reduction potential from waste heat recovery are being investigated using an inter-plant waste heat optimisation algorithm. A paper describing an inter-plant optimisation algorithm is in progress.

Continuing and complementing the work being carried out in WP1, the Geographic Information System (GIS) database has been remodelled in RDF/XML format, the widely accepted Semantic Web enabling standard.

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

Backend development included parameterisation of high-dimensional models using the model development suite MoDS. A standard parameterisation methodology for modelling and studying physical models of equipment, industrial processes, plants and parks has been established. It involves sampling data within the operating range of the physical model and producing a fast response surrogate model. Those surrogates then connect into a network and simulate the modelled processes, but require substantially less computing power.

Up-to-date activities include parameterising and solving a system of simultaneous surrogate models based on an AspenPlus model and connecting the electrical engineering solver eMEGAsim running on an OPAL-RT OP5600 to the J-Park Simulator.

A paper on the “effects of dimensionality and surrogate type on the parameterisation accuracy of AspenPlus simulations of chemical processes” is in progress.

A paper on “Parameterization and Surrogate Approximations of Complex Chemical Processes” is in progress. In it, a novel sampling technique has been described that reduces the computational cost of the surrogate construction by smart space sampling. Preliminary results of this work appear promising. More generalised cases are therefore being investigated. A C++ implementation of the technique in the model development suite MoDS is currently under way.

A preprint studying the possibility of describing AspenPlus simulations of a biodiesel plant with surrogate models and assessing their quality has been written. The model under investigation includes reaction and separation steps with auxiliary equipment. It was solved for steady-state operation.

Experimental work is ongoing to develop an enhanced parameter estimation model for the J-Park Simulator. The primary objective is to estimate the kinetic parameters of the biodiesel plant model within the J-Park Simulator. Once completed, parameter estimation will be adopted generally to update the parameters of the various other models existing in the J-Park Simulator upon receiving measured data.

Significant progress has been made with applying semantic Web technologies to fully automate modelling and providing a decision support system for an eco-industrial park such as Jurong Island. A key first step has been taken by introducing the chemical engineering ontology OntoCAPE ("Ontology in Computer Aided Process Engineering"). Ontology is a theory that describes how to define things and the relationships between things. OntoCAPE specifies them in the form of XML and OWL files, to represent data on industrial plants and their relationships within the eco-industrial park. A paper on multi-level hierarchical modelling and optimisation of networks in eco-industrial parks has been submitted for publication.

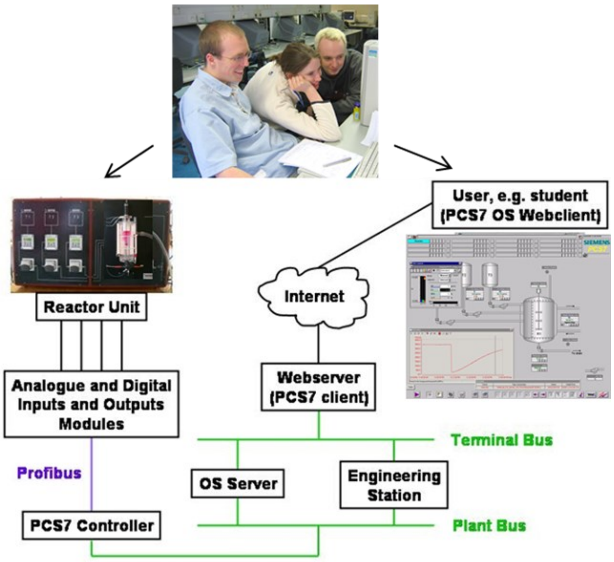
A new ontology is being developed based on OntoCAPE as the starting point and extending it to include other domains, for example the electrical engineering domain with the software application and equilibrium solver PowerWorld, and building information management ontologies. With OntoCAPE, a chemical process can be described with very detailed information, including the geometry of the plant equipment, the phenomenological description of the process material, or the economic evaluation of the process. OntoCAPE is subdivided into layers, in which general knowledge is separated from knowledge about particular domains and applications.

Industry contact to Siemens was further developed in meetings that took place in December 2015 and March 2016. The discussion was focussed on ways to integrate the multi-domain, object-oriented data platform COMOS into the system architecture of the J-Park Simulator. Collaboration with respect to the PCS 7 system was discussed under The Siemens Automation Cooperates with Education (SCE) package.

Other Activities and Achievements

- **Member of editorial board**

Professor Kraft has been made a member of the editorial board of the "Proceedings of The Combustion Institute" beginning with Volume 36. This appointment is for a 6 year term and will conclude in December 2020.



- **IRP 3 to host Global Engineering Programme (GEP) intern**

In May – July 2016 IPR 3 will host an intern from the NUS Global Engineering Programme. SNG Yi Ren will work with the IRP 3 research team on Work Packages 1, 4 and 5 (the industrial network model of Jurong Island, modelling and optimisation of unit operations, and automated model development and experimental design/decision support). It continues a successful collaboration with the NUS GEP that started last year. CARES is looking forward to welcoming Yi Ren to the team.

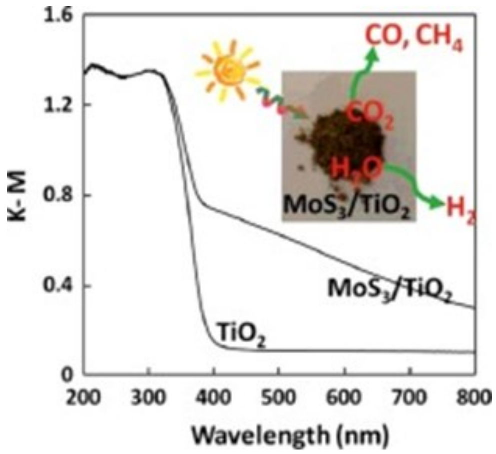
Poster presentation by Manoel MANUPUTTY (PhD student, IRP3, Cambridge) entitled "Numerical simulation of TiO_2 nanoparticles in flame reactor" at Cambridge Fluids Network Day, 14 March 2016.

- **Cambridge Weblabs: a Process Control System using industrial standard SIMATIC PCS 7**

Professor Markus KRAFT (PI, IRP3, Cambridge) has been invited to contribute to the special issue of the Journal of Education for Chemical Engineers: “Current trends in virtual labs, remote or simulated experiments”. He has submitted a paper in collaboration with Dr. Mukta BANSAL (Co-I, IRP3, NTU) and Dr. Maria BOTERO (RF, IRP3, NUS) on his experience with the implementation of an experiment remotely controlled using a SIEMENS system for reactor engineering teaching at the University of Cambridge.

3.3.3 Scientific output of IRP3

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP3 during the reporting period. A full list of publications during the period may be found in Appendix A.



MoS3 loaded TiO2 nanoplates for photocatalytic water and carbon dioxide reduction

Zhang, Wei; Zhou, Tianhua; Hong, Jindui; Xu, Rong

DOI: 10.1016/j.jechem.2016.01.016

Highlights:

- TiO2 nanoplates with well dispersed MoS3 on surface were synthesized via hydrothermal routes as photocatalysts
- The as-synthesized material is active for simultaneous photocatalytic water and carbon dioxide reduction in aqueous solutions.

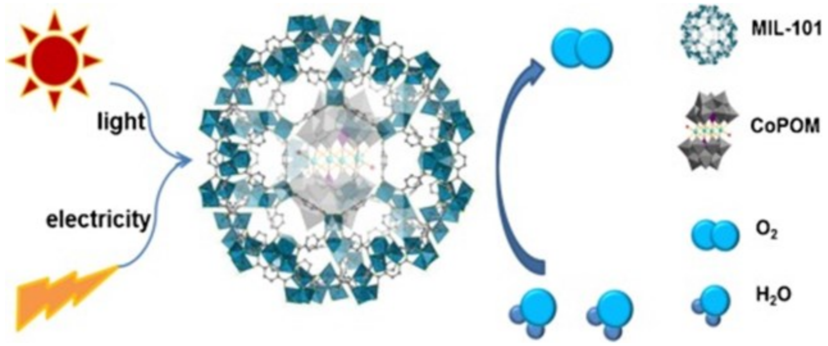
Photocatalytic water splitting and carbon dioxide reduction provide us clean and sustainable energy resources. The carbon dioxide reduction is also the redemption of the greenhouse effect. MoS3/TiO2 photocatalysts based on TiO2 nanoplates have been synthesized via a hydrothermal acidification route for water and carbon dioxide reduction reactions. This facile approach generates well dispersed MoS3 with low crystallinity on the surface of TiO2 nanoplates. The as-synthesized MoS3/TiO2 photocatalyst showed considerable activity for both water reduction and carbon dioxide reduction. The thermal treatment effects of TiO2, the loading percentage of MoS3 and the crystalline phase of TiO2 have been investigated towards the photocatalytic performance. TiO2 nanoplate synthesized through hydrothermal reaction with the presence of HF acid is an ideal semiconductor material for the loading of MoS3 for photocatalytic water and carbon dioxide reduction simultaneously in EDTA sacrificial solution.

Polyoxometalate immobilized in MIL-101(Cr) as an efficient catalyst for water oxidation

Han, Jianyu; Wang, Danping; Du, YongHua; Xi, Shibo; Chen, Zhong; Yin, Shengming; Zhou, Tianhua; Xu, Rong

DOI: 10.1016/j.apcata.2015.10.015

Highlights:



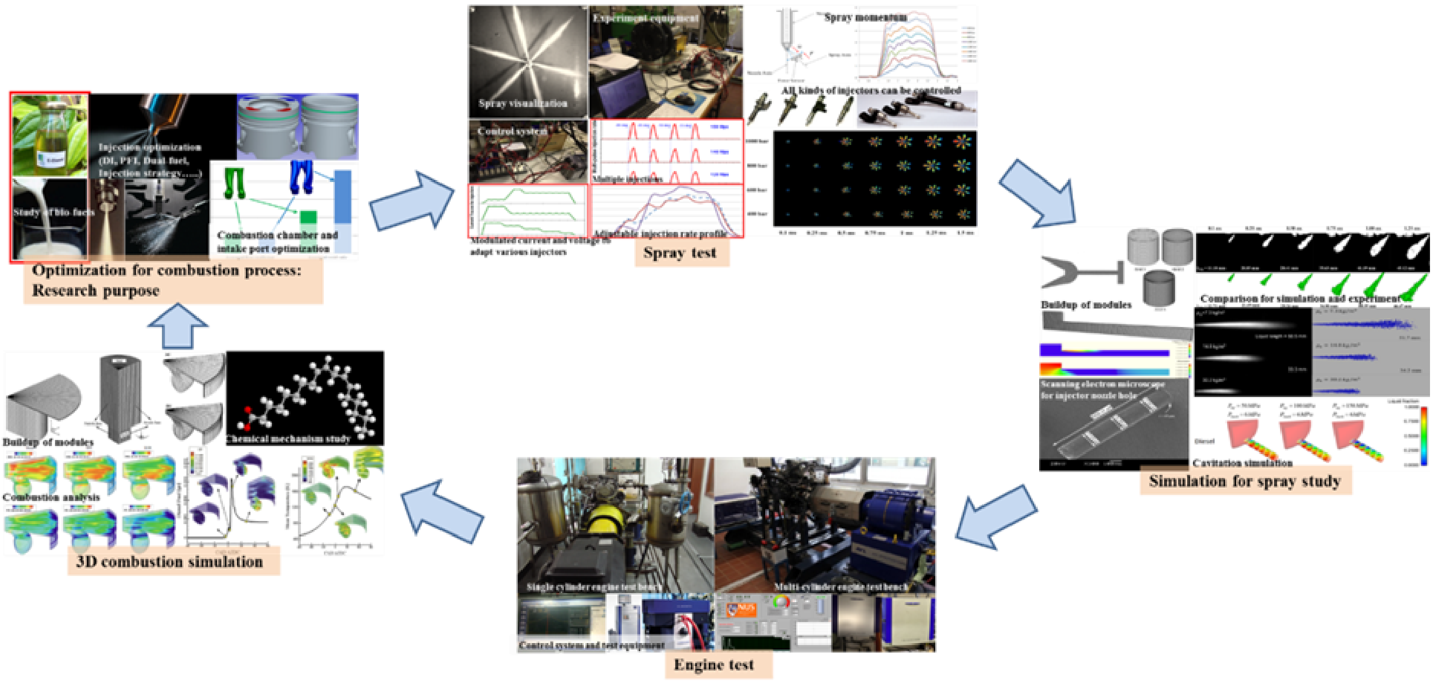
- Polyoxometalate (CoPOM) is immobilized in cavities of MIL-101 (Cr) with a good dispersion by a facile ion exchange method.
- Immobilized CoPOM exhibits enhanced photocatalytic and electrocatalytic water oxidation activities and improved stability due to its interaction wit MIL-101.

- Heterogenization of homogeneous CoPOM makes it easier to be recycled.

Water oxidation is an essential reaction in artificial photosynthesis. Finding efficient and stable catalysts for this reaction is still a challenging task. Recently, a series of polyoxometalates (POMs) comprised of earth abundant materials are reported to be efficient water oxidation catalysts (WOCs). In this study, we investigated the effect of a support material to the catalytic performance of $[Co(H2O)2(PW9O34)2]10-$ (CoPOM) by immobilizing this molecular POM-based catalyst on MIL-101(Cr), a highly porous and robust metal-organic framework (MOF). The successful encapsulation of CoPOM in MIL-101 achieved by a facile ion exchange method was evidenced by combined XRD, FTIR, XPS, XANES, TEM and elemental mapping analyses. Both the photocatalytic and electrochemical studies have indicated that the CoPOM loaded on MIL-101 displays enhanced activity and improved stability due to the its electrostatic interaction with MIL-101. In addition, the heterogenization of the homogeneous CoPOM also makes it easier to be recycled.

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

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



DOI: 10.4271/2016-01-0839

Highlights:

An advanced combustion investigation system (ACIS) was proposed.

The internal nozzle flow and macroscopic spray characteristics of kerosene was investigated with both numerical and experimental approaches.

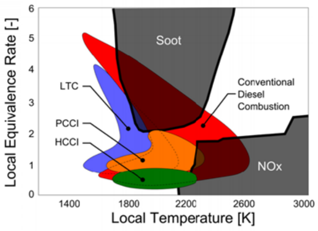
A piezoelectric injector was used for both numerical and experimental spray study.

In this study, the internal nozzle flow and macroscopic spray characteristics of a kind of wide distillation fuel (WDF) - kerosene were investigated both with numerical and experimental approaches.

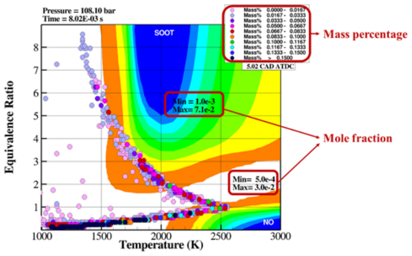
Simulation results indicate that compared with diesel fuel, kerosene cavitates more due to higher turbulent kinetic energy as a result of lower viscosity. The results from experiment indicate that under lower charge density, the spray penetration for kerosene is obviously shorter than that for diesel, especially for the lower injection pressure. This is because lower fuel viscosity results in a reduction in the size of the spray droplets, leading to lower momentum. However the spray angle of kerosene is larger compared with diesel due to stronger turbulence in the nozzle flow caused by increased cavitation for kerosene, which also accords well with the simulation results.

Application of Dynamic φ–T Map: Analysis on a Natural Gas/Diesel Fueled RCCI Engine

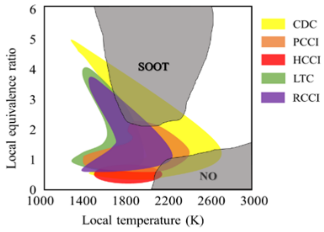
Li, Jing; Yang, Wenming; An, Hui; Zhou, Dezhi; Kraft, Markus



Commonly known ϕ-T map



Generated ϕ-T map



Completed ϕ-T map

DOI: 10.1115/1.4032712

Highlights:

- Dynamic φ-T map is applied to study emissions from an RCCI engine
- Natural gas and diesel were selected as the low and high reactivity fuels
- Premixed natural gas (clean fuel) can reduce soot emissions

Soot and NO emissions are considered as major pollutants to the atmosphere from the compression ignition engines. Researchers have been dedicated to the reduction of soot and NO emissions. Thus, an advance combustion regime, i.e., RCCI, was proposed to mitigate the formation of these emissions. In this study, dynamic φ-T map analysis was applied to an RCCI (reactivity controlled compression ignition) engine fueled with NG (natural gas) and diesel. The combustion process of the engine was simulated by coupled KIVA4-CHEMKIN with a DOS (diesel oil surrogate) chemical mechanism. The φ-T maps were constructed by the mole fractions of soot and NO obtained from SENKIN and φ-T conditions from engine simulations. Five parameters, namely NG fraction, 1st SOI (start of injection) timing, 2nd SOI timing, 2nd injection duration and EGR (exhaust gas recirculation) rate were varied in certain ranges individually, and the φ-T maps were compared and analyzed under various conditions. The results revealed how the five parameters would shift the φ-T conditions and influence the soot-NO contour. Among the factors, EGR rate could limit the highest temperature due to its dilute effect, hence maintaining RCCI combustion within LTC (low temperature combustion) region. The second significant parameter is the premixed NG fraction. It could set the lowest temperature; moreover, the tendency of soot formation can be mitigated due to the lessened fuel impingement and the absence of C-C bond. Finally, the region of RCCI combustion was added to the commonly known φ-T map diagram. Take the effect of EGR as an example, as shown in Figure 1, with increase in EGR rate, the combustion state would shift from the high temperature to the low temperature, consequently, staying away from the high generation islands of soot and NO emissions. Thus, the dynamic φ-T map analysis would assist the investigation on the effect of various engine parameters on the emissions formation.

An Enhanced Primary Reference Fuel Mechanism Considering Conventional Fuel

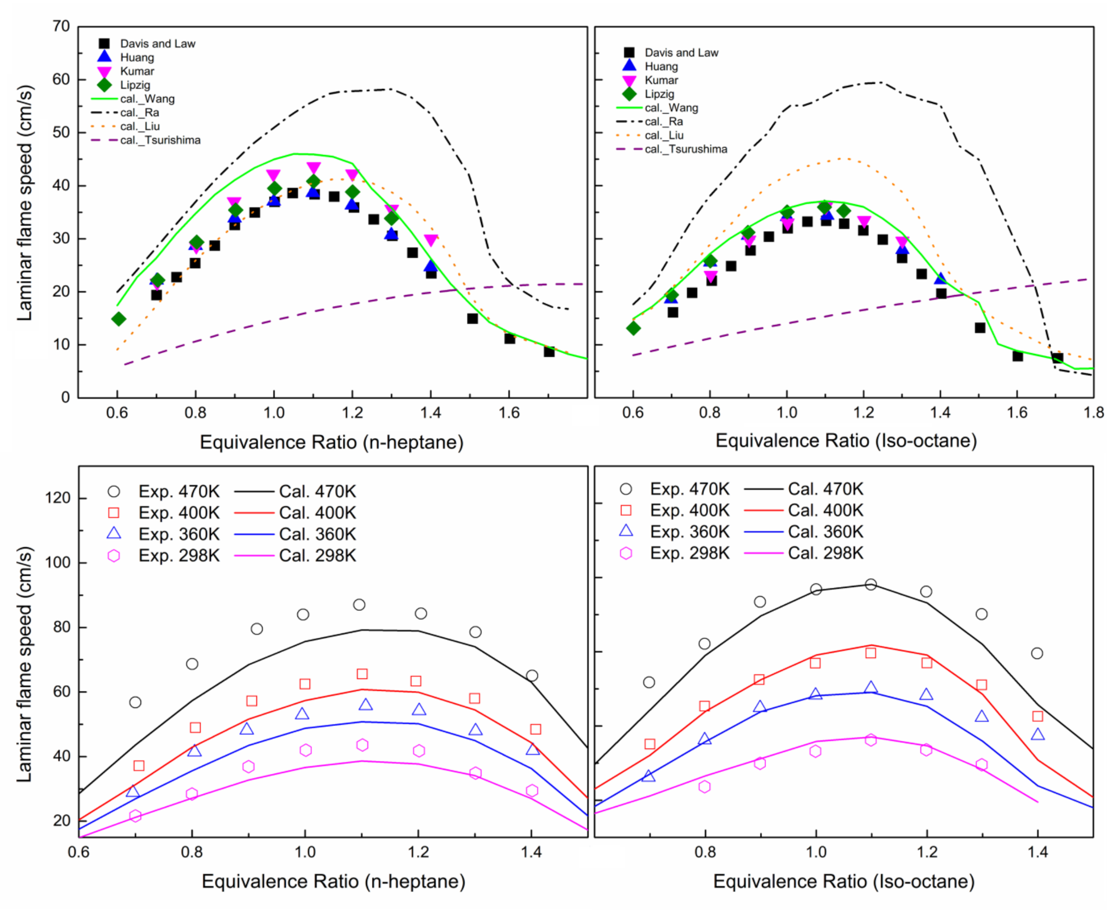
Chemistry in Engine Simulation

Zhou, Dezhi; Yang, Wenming; An, Hui; Li, Jing; Kraft, Markus

DOI: 10.1115/1.4032713

Highlights:

- The role of fuel cracking process in reduced mechanism development was investigated and discussed.



- A new PRF kinetic mechanism was developed.
- The proposed mechanism was extensively validated in different combustion devices.
- The proposed mechanisms were also proved to be trustworthy for combustion prediction in HCCI, PCCI and RCCI engines.

A compact and accurate primary reference fuel (PRF) mechanism was developed and validated to consider the fuel chemistry in combustion simulation. This enhanced PRF mechanism consists of 46 species and 144 reactions, which was developed based on a simple PRF mechanism for homogenous charged compression ignition (HCCI) engine simulation. Crucial reactions including H atom abstraction of n-heptane and iso-octane at high temperature and ketohydroperoxide decomposition at low temperature were retained to ensure its capabilities for predicting combustion characteristics of PRF fuels. To maintain high computational efficiency as well as a compact size, a reduced and well-validated methanol mechanism was integrated into this PRF mechanism. In addition, to better predict laminar flame speed in combustion, the relevant C2-C3 carbon reactions was coupled into it. The significant reaction pathway was identified and discussed in this work. This enhanced PRF mechanism was validated by available experimental data from references including ignition delay times, laminar flame speed, premixed flame species concentrations in jet stirred reactor, rapid compression machine and shock tube. Firstly, ignition delay data from shock tube, rapid compression machine was compared with the calculated data from this mechanism by CHEMKIN-II codes, including neat n-heptane, iso-octane and fuel mixtures under different equivalence ratios, pressures and temperatures. In addition, laminar flame speed from reference data was compared with calculated data from PREMIX codes. In jet stirred reactor, the premixed flame species profiles were also used to validate the proposed mechanism. All the comparisons between experimental and calculated data indicated high accuracy of this mechanism to capture intermediate species, laminar flame speed, and ignition delay. Also, this mechanism was integrated into KIVA-CHEMKIN codes. The engine simulation data (including in-cylinder pressure and heat release rate) was compared with experimental data both in PRF fuel mixture HCCI, PCCI and diesel/gasoline RCCI engines. The in-cylinder pressure and heat release rate comparison results implied that this mechanism could well predict PRF and gasoline/diesel combustion in CFD engine simulations. The overall results show that this small PRF mechanism could provide credible predictions including ignition delay, laminar flame speed, intermediate species and engine combustion characteristics. Fig. 1 shows the better performance on predicting laminar flame speed by this mechanism than the previous mechanisms.

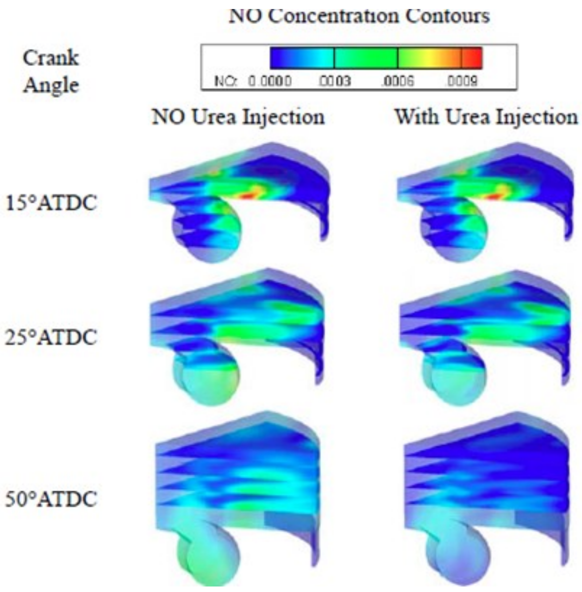
Impact of Urea Direct Injection on NOx Emission Formation of Diesel Engines Fueled by Biodiesel

Yang, Wenming; An, Hui; Li, Jing; Zhou, Dezhi; Kraft, Markus

DOI: 10.1115/ICEF2015-1059

Highlights:

- Detailed chemical reaction mechanism was developed for the combined combustion of biodiesel and urea.
- Direct aqueous urea solution injection could significantly reduce NOx emission of the engine.
- The reduction of NOx is significantly affected by urea injection timing and angle, the mass fraction *etc*.



In this work, a numerical simulation investigation was conducted to explore the possibility of an alternative approach: direct aqueous urea solution injection on the reduction of NOx emissions of a biodiesel fueled diesel engine. Simulation was performed using the 3D CFD simulation software KIVA4 coupled with CHEMKIN II code for pure biodiesel combustion under realistic engine operating conditions of 2400 rpm and 100% load. To improve the overall prediction accuracy, the Kelvin-Helmholtz and Rayleigh-Taylor (KH-RT) spray break up model was implemented in the KIVA code to replace the original Taylor Analogy Breakup (TAB) model for the primary and secondary fuel breakup processes modeling. The KIVA4 code was further modified to accommodate multiple injections, different fuel types and different injection orientations. A skeletal reaction mechanism for biodiesel + urea was developed which consists of 95 species and 498 elementary reactions. The chemical behaviors of the NOx formation and Urea/NOx interaction processes were modeled by a modified extended Zeldovich mechanism and Urea/NOx interaction sub-mechanism. Developed mechanism was first validated against the experimental results conducted on a light duty 2KD FTV Toyota car engine fueled by pure biodiesel in terms of in-cylinder pressure, heat release rate. To ensure an efficient NOx reduction process, various aqueous urea injection strategies in terms of post injection timing and injection rate were carefully examined. The simulation results revealed that among all the four post injection timings (10 °ATDC, 15 °ATDC, 20 °ATDC and 25 ° ATDC) that were evaluated, 15 °ATDC post injection timing consistently demonstrated a lower NO emission level, as shown in figure 1. In addition, both the urea/water ratio and aqueous urea injection rate demonstrated important roles which affected the thermal decomposition of urea into ammonia and the subsequent NOx removal process, and it was suggested that 50% urea mass fraction and 40% injection rate presented the lowest NOx emission levels.

Stochastic weighted particle methods for population balance equations with coagulation, fragmentation and spatial inhomogeneity

Lee, Kok Foong; Patterson, Robert; Wagner, Wolfgang; Kraft, Markus

DOI: 10.1016/j.jcp.2015.09.031

Highlights:

- Problems concerning multi-compartment population balance equations are studied.
- A class of fragmentation weight transfer functions is presented.
- Three stochastic weighted algorithms are compared to direct simulation algorithm (DSA) - The new algorithms show better numerical performance than DSA
- The algorithms are applied to a multi-dimensional granulation model.

This paper introduces stochastic weighted particle algorithms for the solution of multi-compartment population balance equations. In particular, it presents a class of fragmentation weight transfer functions which are constructed such that the number of computational particles stays constant during fragmentation events. The weight transfer functions are constructed based on systems of weighted computational particles and each of it leads to a stochastic particle algorithm for the numerical treatment of population balance equations. Besides fragmentation, the algorithms also consider physical processes such as coagulation and the exchange of mass with the surroundings. The numerical properties of the algorithms are compared to the direct simulation algorithm and an existing method for the fragmentation of weighted particles. It is found that the new algorithms show better numerical performance over the two existing methods especially for systems with significant amount of large particles and high fragmentation rates.

Numerical simulation and parametric sensitivity study of optical band gap in a laminar co-flow ethylene diffusion flame

Yapp, Edward; Patterson, Robert; Akroyd, Jethro; Mosbach, Sebastian; Adkins, Erin; Miller, Houston; Kraft, Markus

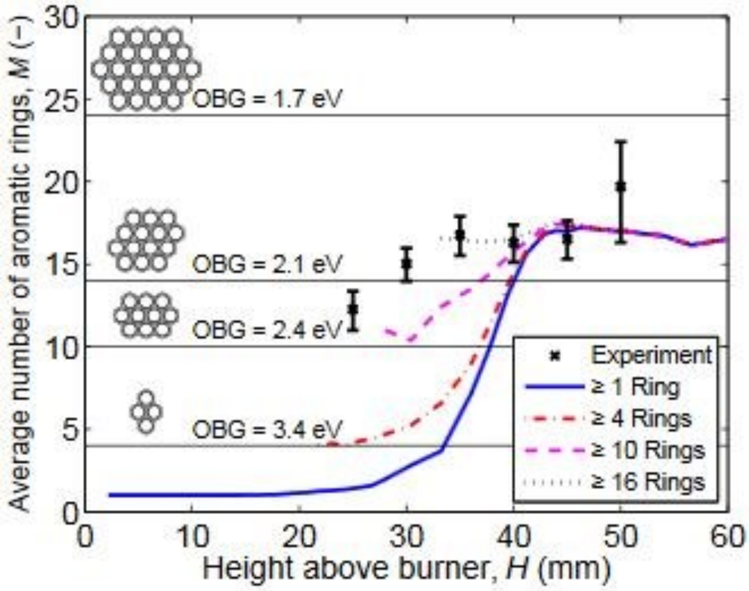
DOI: 10.1016/j.combustflame.2016.01.033

Highlights:

- Modelling of optical band gap (OBG) of polycyclic aromatic hydrocarbons (PAH) .
- PAHs in the gas phase absorbing light at the visible wavelength used for extinction measure-

ments.

- Results consistent with critical PAH size for inception of about 16 aromatic rings



A detailed population balance model is used to perform a parametric sensitivity study on the computed optical band gap (OBG) of polycyclic aromatic hydrocarbons (PAHs) in a laminar co-flow ethylene diffusion flame. Assuming that the OBG of PAHs in soot can be estimated by the energy difference between the highest occupied and lowest unoccupied molecular orbitals in single PAHs, OBG may be correlated with the number of aromatic rings in PAHs. This allows insights into which are the key species involved in the formation of soot. PAH size distributions are computed along the centreline and in the wings of the flame. We compare our simulations with experimentally determined soot volume fraction and OBG (derived from extinction measurements) from the literature. It is shown that the model predicts reasonably well the soot volume fraction and OBG throughout the flame. We find that the computed OBG is most sensitive to the size of the smallest PAH which is assumed to contribute to the OBG. The best results are obtained accounting for PAH contribution in both gas and particle phases assuming a minimum size of ovalene (10 rings). This suggests that the extinction measurements show a significant absorption by PAHs in the gas phase at the visible wavelength that is used, which has been demonstrated by experiments in the literature. It is further shown that PAH size distributions along the centreline and in the wings are unimodal at larger heights above burner. Despite the different soot particle histories and residence times in the flame, the PAH size associated with both modes are similar which is consistent with the near-constant OBG that is observed experimentally. The simulations indicate that the transition from the gas phase to soot particles begins with PAHs with as few as 16 aromatic rings, which is consistent with experimental observations reported in the literature.

Modelling soot formation from wall films in a gasoline direct injection engine using a detailed population balance model

Wang, Buyu; Mosbach, Sebastian; Schmutzhard, Sebastian; Shijin Shuai; Huang, Yaqing; Kraft, Markus

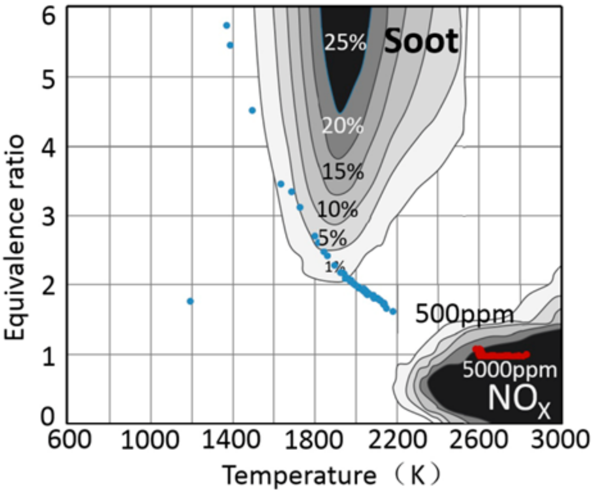
DOI: 10.1016/j.apenergy.2015.11.011

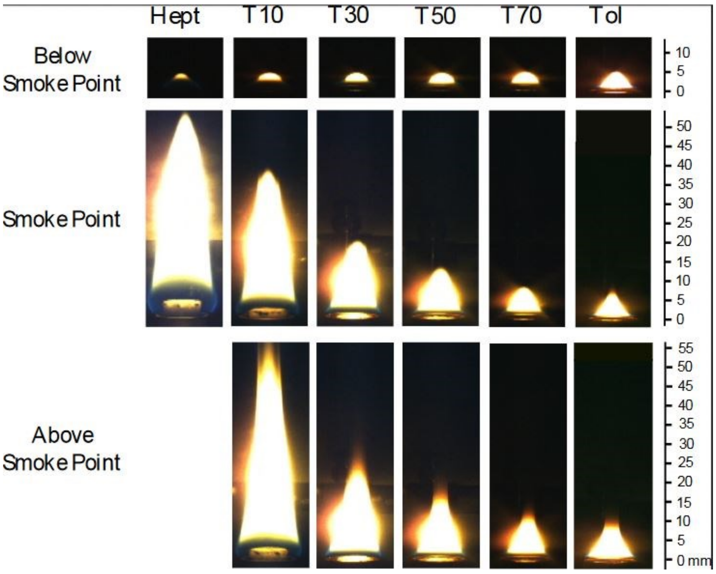
Highlights:

- Soot formation from a wall film in a GDI engine is simulated.
- Spray impingement and wall film evaporation models are added to SRM Engine Suite.
- Soot is modelled using a highly detailed population balance model.
- Particle size distributions are measured experimentally.

- Evolution of wall region is shown in equivalence ratio-temperature diagrams.

In this study, soot formation in a Gasoline Direct Injection (GDI) engine is simulated using a Stochastic Reactor Model (SRM Engine Suite) which contains a detailed population balance soot model capable of describing particle morphology and chemical composition. In order to describe the soot formation originating from the wall film, the SRM Engine Suite is extended to include spray impingement and wall film evaporation models. The cylinder is divided into a wall and a bulk zone to resolve the equivalence ratio and temperature distributions of the mixture near the wall. The combustion chamber wall is assumed to exchange heat directly only with the wall zone. The turbulent mixing within each zone and between the two zones are simulated with different mixing models. The effects of key parameters on the temperature and equivalence ratio in the two zones are investigated. The mixing rate between the wall and bulk zone has a significant effect on the wall zone, whilst the mixing rate in the wall zone only has a negligible impact on the temperature and equivalence ratio below a certain threshold. Experimental data are obtained from a four-cylinder, gasoline-fuelled direct injection spark ignition engine operated stoichiometrically. An injection timing sweep, ranging from 120 CAD BTDC to 330 CAD BTDC, is conducted in order to investigate the effect of spray impingement on soot formation. The earliest injection case (330 CAD BTDC), which produces significantly higher levels of particle emissions than any other case, is simulated by the current model. It is found that the in-cylinder pressure and the heat release rate match well with the experimental data. The particle size distribution in the simulation has the same order of magnitude as the experimental one. By tracing the particles in an equivalence ratio-temperature diagram, it is demonstrated that the rich mixture near the wall becomes the source of the soot formation as a result of the wall film evaporation.





Sooting tendency and particle size distributions of n-heptane/toluene mixtures burned in a wick-fed diffusion flame

Botero, Maria L.; Mosbach, Sebastian; Kraft, Markus

DOI: 10.1016/j.fuel.2015.12.014

Highlights:

- Particle size distributions of heptane/toluene mixtures and gasoline in a diffusion flame were measured.
- The addition of toluene shifts the primary and aggregate size distribution to larger diameters.

The sooting characteristics of binary mixtures of n-heptane and toluene and a commercial gasoline were studied. The experiment involves the non-premixed combustion of the fuel in wick-fed burner. The particle size distributions (PSDs) of soot were measured at the tip of flames of different heights, using a differential mobility spectrometer (DMS). Transmission electron microscopy (TEM) was used to investigate the morphology of the particles formed. Pure n-heptane and toluene were studied along with blends of 10%, 30%, and 50% by volume of toluene in n-heptane. The addition of toluene to heptane shifts the PSD to larger diameters. As toluene is added to n-heptane the dependence of soot particle size on flame height changes from resembling a paraffinic to resembling an aromatic fuel in a non-linear fashion. A tolerance to toluene addition at the lowest flow rates was found, where particles were not detected. A commercial gasoline with approximately 44% by mass of aromatics was also analysed. The smoke point and PSDs are similar to the mixture 50% toluene 50% n-heptane, but the mean aggregate mobility size, number of particles and primary particle size formed by the gasoline are smaller.

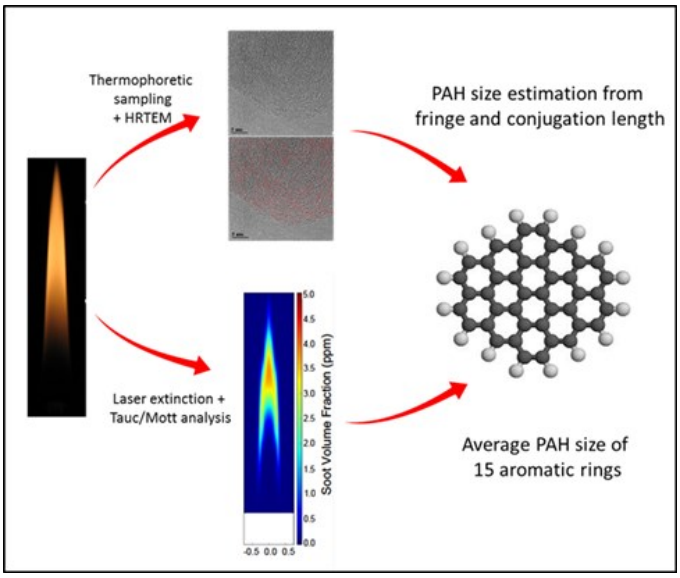
PAH structure analysis of soot in a non-premixed flame using high-resolution transmission electron microscopy and optical band gap analysis

Botero, Maria L.; Adkins, Erin M.; González-Calera, Silvia; Miller, Houston; Kraft, Markus

DOI: 10.1016/j.combustflame.2015.11.022

Highlights:

- Soot particles were characterised by laser extinction and HRTEM. Extinction measurements were used to calculate the soot volume fraction and optical band gap (OBG). - OBG was used to estimate PAHS sizes were estimated from OBG and image analysis applied



Soot particles formed in a system of non-premixed liquid fuel flames supported on a wick-fed, smoke point test burner (ASTM D1322-08) were characterized by in-situ visible light extinction and thermophoretically-sampled high-resolution transmission electron microscopy measurements, HRTEM. The fuels studied were heptane, toluene and their iso-volumetric mixture (H50T50), given their relevance as surrogate fuels. Extinction measurements were used to calculate the soot volume fraction, Fv, and determine the optical band gap (OBG) as a function of flame position. The OBG was derived from the near-edge absorption feature using Tauc/Davis-Mott analysis. A direct band gap (r = 0.5) was selected for this analysis assuming that the electronic properties of soot are dominated by the molecular structure of the PAHs. For the HRTEM analysis, soot samples were collected at different locations in the flame using thermophoretic sampling and a fast-insertion technique. The images were then analyzed using a 'lattice-fringe' algorithm, to determine important parameters such as the fringe length. Polycyclic aromatic hydrocarbon (PAH) sizes were estimated from conjugation lengths obtained from OBG measurements and fringe lengths from HRTEM measurements. Across all studied flames, the peak Fv ranged from 3.4 ppm in the heptane flame to 17.6 ppm in the toluene flame. Despite this wide range, the average OBG across the different flames only varied from 2.05 eV in the H50T50 to 2.10 eV in the toluene flames, which is consistent with molecule lengths of between 0.96 nm and 0.99 nm. Lattice fringe analysis yielded slightly lower average fringe lengths between 0.91 and 0.99 nm throughout the different flames. Results of in-situ and ex-situ characterization of soot suggests that flames of different fuel nature and sooting stage undergo the transition from chemical to physical growth at a similar size, about the size of circumpyrene.

3.4 IRP4 — ICESO

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

The research programme is divided into six work packages:

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

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

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

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

WP 4.5: Model building, integration and maintenance

WP 4.6: Demonstration of proposed algorithms on pilot scale

The ICESO group is led by PIs:

Prof Gehan AMARATUNGA (Cam);

Prof Jan MACIEJOWSKI (Cam);

Prof Keck Voon LING (NTU);

Prof Sanjib Kumar PANDA (NUS)

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

University of Cambridge

PIs, IRP4

March 2016

3.4.1 IRP4 Research Overview

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

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

3.4.2 Update on work packages

WP1: Fast numerical algorithms for solving large MPC problems for networked systems

Work on stochastic event-triggered control over networks has been pursued. The motivation is to reduce the communications load over a network, and to reduce the amount of computation needed for control algorithm implementation.

WP2: Extension of Multiplexed MPC to non-Gaussian noise, nonlinear and hybrid models

Development of global optimization algorithms based on Bernstein polynomials has been continued. The efficacy of this approach to power systems applications have been investigated; specifically to the unit commitment and optimal power flow problems. A self-scheduling problem for a combined cycle gas turbine was solved with one such algorithm (preliminary results for which have been accepted for the 2016 American Control Conference). Currently, the work is focusing on the development of efficient algorithms for solving the optimal power flow problem for small to medium size power networks. A paper has been accepted for the 2016 European Control Conference, and one has been submitted to the 2016 IEEE Conference on Decision and Control.

WP3: Modelling and Control of heterogeneous power generation networks with chemical process loads

An industry-standard real-time power system simulator, OPAL-RT, has been acquired (shared with two projects based at NTU) and is located in the NTU Microgrid Lab. Real-time simulation studies of two benchmark power system models (IEEE 14-bus and 59-bus systems) are currently being pursued. These assume local governor and excitation controls for each power generator, but higher-level coordinated ‘automatic generation control’ is implemented using Model Predictive Control. These studies are being pursued in OPAL-RT’s RT-LAB programming environment, in preparation for full real-time demonstration and evaluation of the MPC control algorithm. Software compatibility issues between various simulation modes are being gradually overcome.

An experimentally enhanced distribution system state estimation with micro phasor measurement units (µPMU) is also being pursued. It is possible to develop linear state estimator with a sufficient number of PMUs. Considering the fact that a PMU can measure not only the bus voltage but also the currents along all the lines incident to the bus, furnishing a selected subset of buses with PMUs can make the entire system observable. Optimal PMU placement is to minimize the amount of PMUs installed while achieving the entire degree of observability. The Optimal PMU Placement (OPP) problem has been studied for decades and several algorithms have been well documented. However, these algorithms were tested on transmission networks only. Exhaustive search approach was used to determine the minimum number of PMUs needed. This method is able to give a globally optimal solution without much calculation burden because of the radial topology of distribution networks. This method has been tested on IEEE distribution test feeder.

Research on Load Demand Forecasting and Fault Prediction in Power Systems has continued. The primary objective is to reduce the probability of faults occurring with the help of accurate fault prediction methods augmented by load demand prediction. Development of the electricity power market has made short-term load demand prediction an essential requirement for electricity pricing. Similar methods are also applicable to the general power system with different load configurations e.g. chemical plant loads on Jurong Island. Additionally, accurate forecasting can also be effective in predicting potential faults in the power systems, and thus provide a reliable and safe basis for grid operation. In this work, the load demand time series is first decomposed into several Intrinsic Mode Functions. Then a Deep Belief Network (DBN) with two Restricted Boltzmann Machines (RBMs) was used to model each of the extracted IMFs, so that the tendencies of these IMFs can be accurately predicted. The predicted results from all IMFs were combined by either unbiased or weighted summation to formulate an aggregated output for load demand. The new method has been evaluated with three electricity load demand datasets from Australian Energy Market Operator (AEMO). Six benchmark methods have been compared to verify the effectiveness of the proposed method: Persistence, SVR, ANN, DBN, EMD-SVR and EMD-ANN. Two error measures (Root Mean Square Error (RMSE) and Mean Absolute Percentage Error (MAPE)) were used to evaluate the performance of these prediction models. The new method has outperformed all the benchmark methods for both half an hour and one day ahead load demand forecasting. Future work will include additional nonlinear features like climate and human activities need to construct a more complex model.

WP4: Modelling of chemical process load and local generator-based electrical network akin to Jurong Island

Work has progressed on the hybrid system approach for power system scheduling problems. The focus is to initially model a network of generators akin to Jurong Island and perform optimal scheduling for their operation. Also methods of minimising losses in the network by optimizing the flow of electric power are being investigated. This will lead to reduced generation and hence lower carbon footprint.

An example power network of the biodiesel plant has been implemented in PowerWorld. The load data for the biodiesel plant was extracted from the chemical process model in AspenPlus. A Python-based script has been written to automate the transfer of the load data from AspenPlus to PowerWorld. Currently work is proceeding on developing particular operating conditions to access the transient response of the power network which will be stored and called up seamlessly by the J-Park Simulator. This work is being done in collaboration with IRP3.

The example biodiesel plant power network is also being modelled using eMEGASim and Hypersim, for simulation on OPAL-RT. The simulation will be performed in real-time with a time step of 50µs. Transient stability studies will be performed to assess the transient response of the power network on OPAL-RT.

Collaboration is proceeding with IRP3 to integrate OPAL-RT with the J-Park Simulator. This involves developing a Python-based script to automate the OPAL-RT simulation and sending the simulation results back to JPS. The current challenge of integrating OPAL-RT with JPS is the communication channel; it is proposed to use cloud services to facilitate the data transfer between NTU, NUS and CREATE tower. This cloud service will act as the communication channel to forward JPS requests to OPAL-RT for simulation and transferring the simulation results from OPAL-RT back to JPS.

To achieve integration into the J-Park Simulator of not only the OPAL-RT simulator but also the physical experimental microgrid at NTU (which can be configured for example to operate as a chemical plant network), a microgrid monitoring and control system has been designed. The system comprises a command & control and display central controller; private cloud for data storage, backup and retransmission; power-line communication modules for local area communications; mBed microcontroller for multiple-standard interface to control hardware for grid connected electrical machines; and blue-tooth for short distance wireless communication to achieve a local physical web.

Modern microgrids raise concerns regarding quality of power and its impact on the electrical network due to the presence of switching elements such as variable speed electronic drives (e.g. as used in pumps in chemical plant). A lumped model of harmonic electrical loads based on condensed harmonic currents signals, which is suitable for a simulation environment has been developed. This approach can accurately represent the lumped nonlinear loads as seen by the network through the measurements performed. This method makes the load easier to simulate and quantitatively analyse for realistic impacts of nonlinear processes such as chemical plant loads on rest of the system.

In a typical petroleum terminal which provides temporary storage and distribution of petrochemical products, variable speed drives (VSDs) are used in vapour recovery systems and pumping operations. Approximately 80% of the electrical load at the petroleum terminal are induction motors which are electronically driven to operate as VSDs. The electronic switching of power at high frequency inherent in VSDs cause distortions to the voltage/ current waveforms in the system, which in turn leads to malfunction of the sensitive devices such as metering instruments, on-line process analysers, and measuring. False readings arising from such malfunction can affect the operation of the plant and in the extreme causes shut down of the plant.

To study this problem in detail an electrical power system simulation model consisting of 'Diesel-engine generators with nonlinear loads (VSDs)' has been developed using MATLAB/Simulink software with both 6-pulse and 12-pulse rectifiers. The model exactly replicates the scenario of an electrical network of a petro-chemical plant in which the dynamics of VSDs has also been included. Through these simulations a methodology to mitigate harmonics in the network has been verified through MATLAB/Simulink simulations.

WP5: Model building, integration and maintenance and WP6: Demonstration of proposed algorithms on pilot scale

Work was pursued on modelling noise in power system measurements by a 't' distribution, leading to improved system state estimation. The use of 'influence functions' for state estimation was also pursued, with a view to improving real-time performance.

WP5: Demonstration of proposed algorithms on pilot scale

There has been no work on this WP to date. It is planned for later in the programme.

Other Activities and Achievements

- Training on the OPAL-RT simulator was provided to Dr Eddy FOO (RF, IRP4, NTU), Dr Anthony TRAN (SRF, IRP4, NTU), and other members of C4T.
- Research papers were presented by Dr Anthony TRAN (SRF, IRP4, NTU) at the AUCC'15 and IEEE APPEEC'15 conferences (Gold Coast and Brisbane, Australia, respectively) in November 2015.
- Dr Anthony TRAN (SRF, IRP4, NTU) spent 5 weeks working with Prof. Jan MACIEJOWSKI (PI, IRP4, Cambridge) in Cambridge, January - February 2016. A first version of a journal paper on a 'general dissipativity constraint', which permits non-monotonic Lyapunov functions to be used, was prepared during this trip. Also a detailed plan of future research was developed.
- A research paper, entitled "The Bernstein branch-and-prune algorithm for constrained global optimization of multivariate polynomial MINLPs", was presented by Dr Bhagyesh PATIL (RF, IRP4, NTU) at the international conference on Mathematical Aspects of Computer and Information Sciences, Zuse Institute Berlin, Germany, 11-13 November 2015.
- Tengpeng CHEN (PhD student, IRP4, NTU) presented a research paper at the ICCAIS'15 conference in Changshu, China in October 2015.

- Thuy Van Dang (PhD student, IRP4, NTU) presented a research paper at the IEEE Conference on Decision and Control in Osaka, Japan, in December 2015.
- Prof. Jan MACIEJOWSKI (PI, IRP4, Cambridge) has been invited to give the Mong Distinguished Lecture (2015-16) at the University of Hong Kong.
- Prof. Jan MACIEJOWSKI (PI, IRP4, Cambridge) gave a 20-hour course on Model Predictive Control at TU Berlin, organised by the European Embedded Control Institute, in March 2016, which was attended by 40 graduate students from various European universities.
- Prof. Keck Voon LING (PI, IRP4, NTU) has been awarded a Bye-Fellowship at Churchill College, Cambridge, for the autumn of 2016.
- Eddy FOO and Ashok KRISHNAN (IRP4) have been awarded the OPAL-RT certificates upon completion of eMEGASim and Hypersim training
- Eddy FOO (RF, IRP4, NTU) has been conferred the NTU PhD degree on 15 Feb 2016
- Prof H B GOOI (Co-I, IRP4, NTU) was appointed Editor, IEEE Transactions on Power Systems December 2015.
- Ashok KRISHNAN (PhD student, IRP4, NTU) had a paper titled: “Predictive Control based Framework for Optimal Scheduling of Combined Cycle Gas Turbines” accepted for presentation at The 2016 American Control Conference to be held at Boston, USA from 6-8 July 2016.
- Ashok KRISHNAN (PhD student, IRP4, NTU) co-authored an abstract which was accepted for presentation at The 2nd International Conference and Summer School on Numerical Computations: Theory and Algorithms to be held at Calabria, Italy from 19-25 June, 2016. The authors of the abstract have also been invited to submit a full paper for peer review to be included in the American Institute of Physics (AIP) proceedings.

3.4.3 Scientific output of IRP4

The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP4 during the reporting period. A full list of publications during the period may be found in Appendix A.

Embedded ADMM-based Quadratic Programming Solver for Model Predictive Control with Polytopic Constraints

Dang, T-V, K-V. Ling; J. Maciejowski

DOI: 10.1109/ECC.2015.7331067

We propose an algorithm for solving quadratic programming (QP) problems with inequality and equality constraints arising from linear MPC. The proposed algorithm is based on the 'alternating direction method of multipliers' (ADMM), with the introduction of slack variables. In comparison with algorithms available in the literature, our proposed algorithm can handle the so-called sparse MPC formulation with general inequality constraints. Moreover, our proposed algorithm is suitable for implementation on embedded platforms where computational resources are limited. In some cases, our algorithm is division-free when certain fixed matrices are computed offline. This enables our algorithm to be implemented in fixed-point arithmetic on a FPGA. In this paper, we also propose heuristic rules to select the step size of ADMM for a good convergence rate.

Ensemble Classification and Regression-Recent Developments, Applications and Future Directions

Ren, Ye, Zhang, Le; P. N. Suganthan

DOI: 10.1109/MCI.2015.2471235

Ensemble methods use multiple models to get better performance. Ensemble methods have been used in multiple research fields such as computational intelligence, statistics and machine learning. This paper reviews traditional as well as state-of-the-art ensemble methods and thus can serve as an extensive summary for practitioners and beginners. The ensemble methods are categorized into conventional ensemble methods such as bagging, boosting and random forest, decomposition methods, negative correlation learning methods, multi-objective optimization based ensemble methods, fuzzy ensemble methods, multiple kernel learning ensemble methods and deep learning based ensemble methods. Variations, improvements and typical applications are discussed. Finally this paper gives some recommendations for future research directions.

Detecting Wind Power Ramp with Random Vector Functional Link (RVFL) Network

Ren Y., X. Qiu; P. N. Suganthan, Gehan Amaratunga

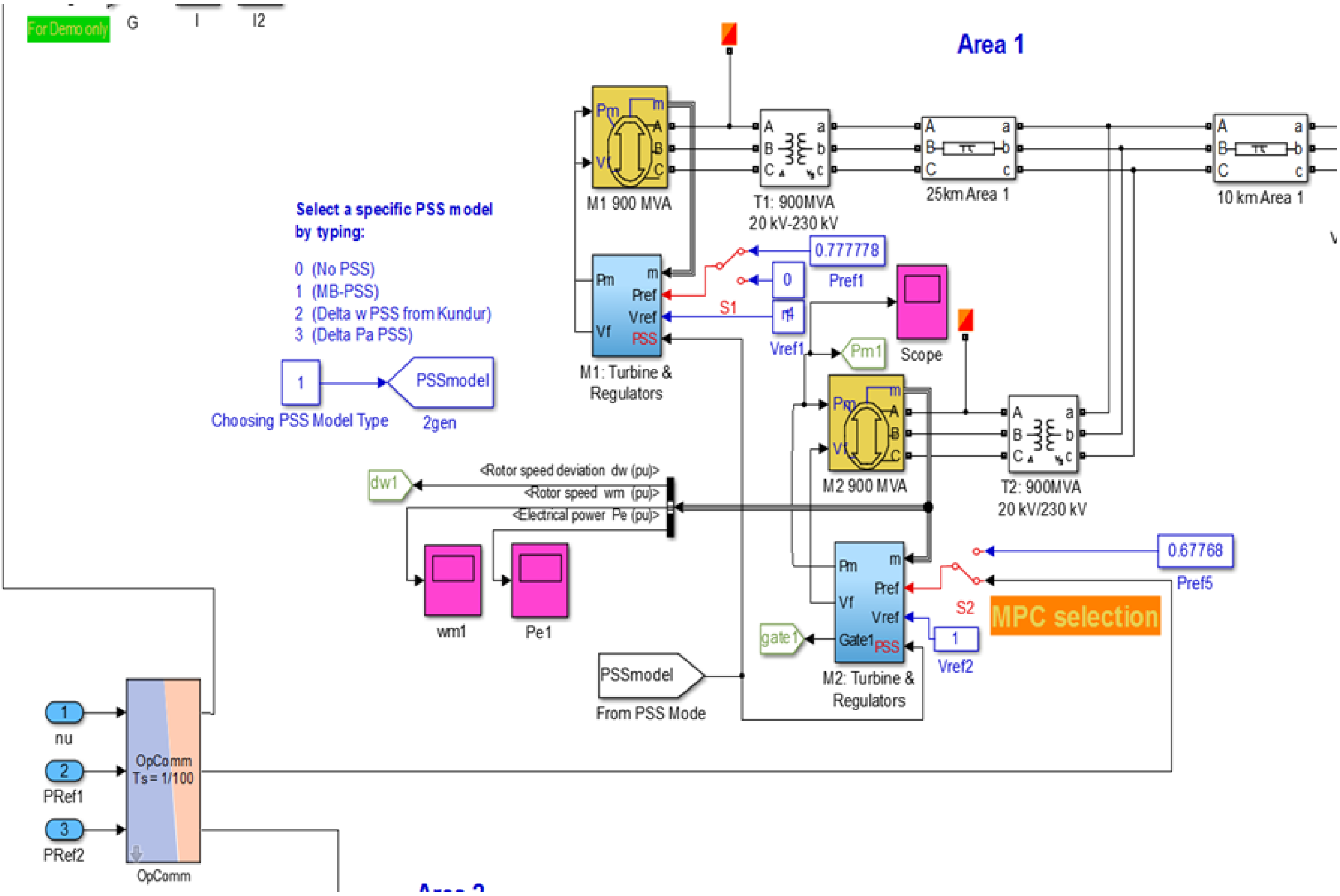
DOI: 10.1109/SSCI.2015.105

Due to the intermittent nature of the wind, the wind speed is fluctuating. Fluctuating wind speed cause even more fluctuation in wind power generation. The sudden changes of the wind power injected into the power grid within a short time frame is known as power ramp, which can be harmful to the grid. This paper presents algorithms to detect the wind power ramps in a certain forecasting horizon. The importance and challenges of wind power ramp detection are addressed. Several different Wind power ramps are defined in this paper. A random vector functional link (RVFL) network is employed to predict the future occurrence of wind power ramp. The forecasting methods are evaluated with a real world wind power data set. The RVFL network has comparable performance as the benchmark methods: random forests (RF) and support vector machine (SVM) but it has better performance than the artificial neural network (ANN). The computation time of training and testing is also in favor of the RVFL network.

State Estimation for Distribution Systems using Micro-Synchrophasors

X-B Chen, K-J Tseng; G. Amaratunga

DOI: 10.1109/APPEEC.2015.7381051



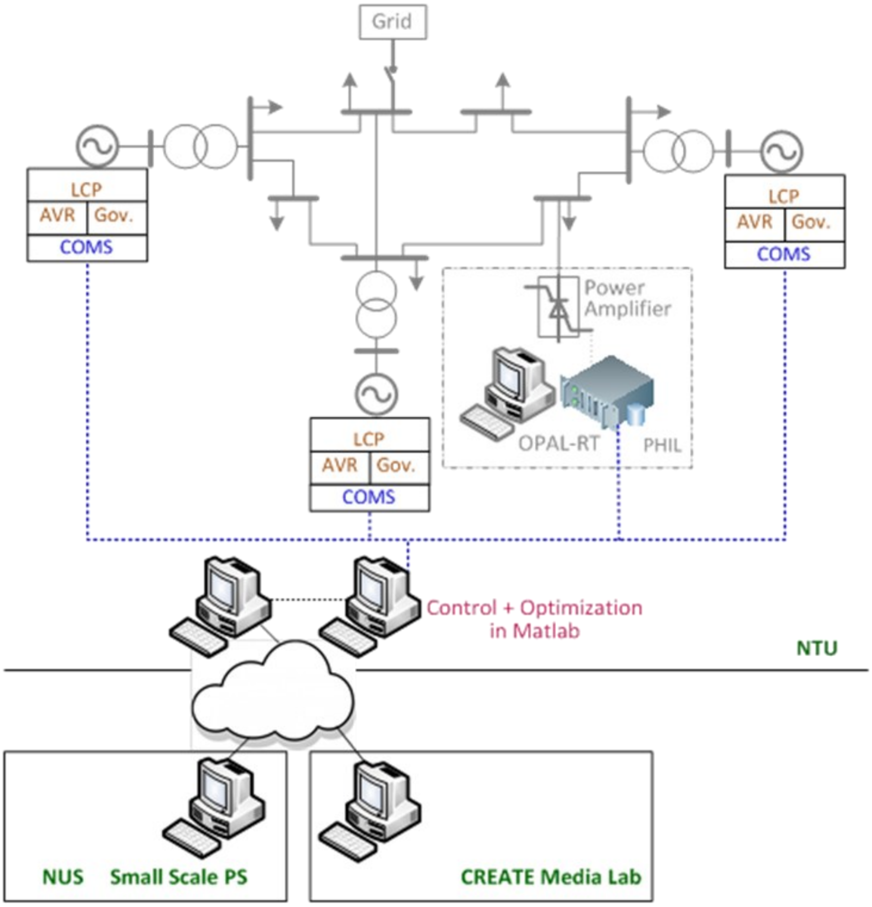
Phasor Measurement Unit (PMU) has contributed greatly to power system state estimation because of its ability to directly measure voltage and current phase angle. PMUs have been used almost exclusively in transmission systems monitoring. Recent years, increasing penetration of renewable energy sources brings new characteristics into distribution system such as bi-directional power flows and voltage profile issues, which has necessitated continuous monitoring of distribution systems. Therefore, fast and accurate measurement device is needed for application in distribution networks. µPMU is such a device that can provide phasor measurements with high precision and low cost. This paper uses a linear three phase state estimator for applications in distribution systems. The proposed estimator can make use of synchrophasor measurements which can be realized by µPMU. This is tested on IEEE 13 bus feeder which has unbalanced three phase transmission lines and loads

Periodic Economic Model Predictive Control with Bounded-State Stability

Tri Tran

Proceedings of the 5th Australian Control Conference (AUCC'15)

This paper presents an economic model predictive control (EMPC) scheme for nonlinear affine systems employing the quadratic dissipativity constraint (QDC) previously introduced. The vector fields are included in the supply rate such that a dissipative condition based on linear matrix inequality (LMI) is rendered for nonlinear systems. Both storage function and supply rate are periodic and parameterized in this formulation. The closed-loop system stability is obtained as a result of having the QDC as an enforced stability constraint to the EMPC optimization. This is a constraint with respect to the current time control vector. In finding a stability condition suitable for systems that may not operate at the optimal steady state with EMPC, we have chosen the bounded-state stability (BSS) and derive a stabilizability condition with QDC in the discrete-time domain. The BSS is characterized by a non-monotonically decreasing storage function and the boundedness property.



Application of Partition-based Moving Horizon Estimation to Power System State Estimation

T-P Chen, A. Krishnan; Tri Tran

DOI: 10.1109/APPEEC.2015.7380907

The Partitioned-based Moving Horizon Estimation (PMHE), developed previously by others, is applied to the power system state estimation problem in this paper. The constraints on state variables and noises are taken into account in this scheme. In this distributed approach, the network is partitioned into several non-overlapping and observable areas. The global Jacobian matrix is required during the initial time before approaching the converged states. Only the estimated information data between neighboring areas are exchanged afterwards. The communication traffic is thus significantly reduced compared to a centralized solution. Meanwhile, each area estimates its local states by solving a smaller size optimization problem. The optimization problem is, therefore, scalable. PMHE converges to the centralized solution of moving horizon estimation (MHE) within finite time steps. Numerical simulation with the IEEE 14-bus system shows the convergence of PMHE. Further, the estimated states are better than those from the weighted least squares (WLS) with large outliers.

Dissipativity Constraint for Distributed Power System State Estimation

Tri Tran, T-P. Chen

DOI: 10.1109/ICCAIS.2015.7338693

The work in this paper deals with the intermittent communication broken-down in the distributed power system state estimation (PSSE) problem. The Partitioned-based Moving Horizon Estimation (PMHE), developed previously by others, is applied to PSSE here. In a PMHE scheme, the network is decomposed into several non-overlapping and observable areas, among which the estimated states are exchanged between neighbouring areas to assure the estimation performance and convergency. The solution of PMHE converges to the centralized solution of moving horizon estimation (MHE) within finite time steps. An additional constraint developed from the incrementally quadratic dissipativity constraint (iQDC) is imposed onto the PMHE optimization to prevent possible divergence of the algorithm during the converging time due to losses of data. An approximately time-invariant Jacobian matrix will be used once the PMHE approaches the steady states. Numerical simulation with the IEEE 14-bus system shows the convergence of PMHE with the iQDC.

A.1 Publications

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

A1.1 Joint IRP Publications

IRP1 and IRP3

- Amaniampong, Prince N., Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, and Samir H. Mushrif. 'Biomass Oxidation: Formyl C-H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves'. *Angewandte Chemie International Edition* 54, no. 31 (27 July 2015): 8928–33. doi:10.1002/anie.201503916.
- Amaniampong, Prince Nana, Amin Yoosefi Booshehri, Xinli Jia, Yihu Dai, Bo Wang, Samir H. Mushrif, and Armando Borgna. 'High-Temperature Reduction Improves the Activity of Rutile TiO2 Nanowires-Supported Gold-Copper Bimetallic Nanoparticles for Cellobiose to Gluconic Acid Conversion'. *Applied Catalysis A: General* 505 (September 2015): 16–27. doi:10.1016/j.apcata.2015.07.027.
- Azadi, Pooya, George Brownbridge, Immanuel Kemp, Sebastian Mosbach, John S. Dennis, and Markus Kraft. 'Microkinetic Modeling of the Fischer-Tropsch Synthesis over Cobalt Catalysts'. *ChemCatChem* 7, no. 1 (January 2015): 137–43. doi:10.1002/cctc.201402662.
- Li, Kaixin, Zhihong Yang, Jun Zhao, Junxi Lei, Xinli Jia, Samir H. Mushrif, and Yanhui Yang. 'Mechanistic and Kinetic Studies on Biodiesel Production Catalyzed by an Efficient Pyridinium Based Ionic Liquid'. *Green Chem.* 17, no. 8 (2015): 4271–80. doi:10.1039/C5GC00976F.

IRP1 and IRP2

- Xie, Ming Shi, Bao Yu Xia, Yawei Li, Ya Yan, Yanhui Yang, Qiang Sun, Siew Hwa Chan, Adrian Fisher, and Xin Wang. 'Amino Acid Modified Copper Electrodes for the Enhanced Selective Electroreduction of Carbon Dioxide towards Hydrocarbons'. *Energy Environ. Sci.*, 2016. doi:10.1039/C5EE03694A.
- Yan, Yibo, Jianwei Miao, Zhihong Yang, Fang-Xing Xiao, Hong Bin Yang, Bin Liu, and Yanhui Yang. 'Carbon Nanotube Catalysts: Recent Advances in Synthesis, Characterization and Applications'. *Chem. Soc. Rev.* 44, no. 10 (2015): 3295–3346. doi:10.1039/C4CS00492B.

IRP1 and IRP4

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

IRP3 and IRP4

- Chen, Tengpeng, Dexiang Zhou, Tri Tran, Catharine Kastner, K-V. Ling, K-J. Tseng, and Jan M. Maciejowski. 'Distributed Moving Horizon Estimation for Power Systems', 1–5. IEEE, 2015. doi:10.1109/PESGM.2015.7286281.

A.1.1 IRP1— MUSCAT

- Chen, Hong, Yihu Dai, Xinli Jia, Hao Yu, and Yanhui Yang. 'Highly Selective Gas-Phase Oxidation of Ethanol to Ethyl Acetate over Bi-Functional Pd/zeolite Catalysts'. *Green Chemistry*, February 2016. doi:10.1039/C5GC02593A.
- Dai, Yihu, Ye Wang, Bin Liu, and Yanhui Yang. 'Metallic Nanocatalysis: An Accelerating Seamless Integration with Nanotechnology'. *Small* 11, no. 3 (January 2015): 268–89. doi:10.1002/smll.201400847.
- Dai, Yihu, Xinping Wu, Yu Tang, Yanhui Yang, Xueqing Gong, and Jie Fan. 'Selectivity Switching Resulting in the Formation of Benzene by Surface Carbonates on Ceria in Catalytic Gas-Phase Oxidation of Benzyl Alcohol'. *Chemical Communications* 52, no. 13 (December 2015): 2827–30. doi:10.1039/C5CC08904B.
- Dunstan, Matthew T., Anubhav Jain, Wen Liu, Shyue Ping Ong, Tao Liu, Jeongjae Lee, Kristin A. Persson, Stuart A. Scott, John S. Dennis, and Clare P. Grey. 'Large Scale Computational Screening and Experimental Discovery of Novel Materials for High Temperature CO2 Capture'. *Energy & Environmental Science*, 4 February 2016. doi:10.1039/C5EE03253A.
- González, B., W. Liu, D. S. Sultan, and J. S. Dennis. 'The Effect of Steam on a Synthetic Ca-Based Sorbent for Carbon Capture'. *Chemical Engineering Journal* 285 (1 February 2016): 378–83. doi:10.1016/j.cej.2015.09.107.
- He, Chao, Ke Wang, Apostolos Giannis, Yanhui Yang, and Jing-Yuan Wang. 'Products Evolution during Hydrothermal Conversion of Dewatered Sewage Sludge in Sub- and near-Critical Water: Effects of Reaction Conditions and Calcium Oxide Additive'. *International Journal of Hydrogen Energy* 40, no. 17 (May 2015): 5776–87. doi:10.1016/j.ijhydene.2015.03.006.
- He, Chao, Ke Wang, Yanhui Yang, Prince Nana Amaniampong, and Jing-Yuan Wang. 'Effective Nitrogen Removal and Recovery from Dewatered Sewage Sludge Using a Novel Integrated System of Accelerated Hydrothermal Deamination and Air Stripping'. *Environmental Science & Technology* 49, no. 11 (2 June 2015): 6872–80. doi:10.1021/acs.est.5b00652.
- He, Chao, Jun Zhao, Yanhui Yang, and Jing-Yuan Wang. 'Multiscale Characteristics Dynamics of Hydrochar from Hydrothermal Conversion of Sewage Sludge under Sub- and near-Critical Water'. *Bioresource Technology* 211 (July 2016): 486–93. doi:10.1016/j.biortech.2016.03.110.
- Ismail, Mohammad, Wen Liu, Matthew T. Dunstan, and Stuart A. Scott. 'Development and Performance of Iron Based Oxygen Carriers Containing Calcium Ferrites for Chemical Looping Combustion and Production of Hydrogen'. *International Journal of Hydrogen Energy* 41, no. 7 (23 February 2016): 4073–84. doi:10.1016/j.ijhydene.2015.11.066.
- Liu, Wen, Belén González, Matthew T. Dunstan, D. Saquib Sultan, Adriano Pavan, Chris D. Ling, Clare P. Grey, and J. S. Dennis. 'Structural Evolution in Synthetic, Ca-Based Sorbents for Carbon Capture'. *Chemical Engineering Science* 139 (12 January 2016): 15–26. doi:10.1016/j.ces.2015.09.016.

- Liu, Wen, Mohammad Ismail, Matthew T. Dunstan, Wenting Hu, Zili Zhang, Paul S. Fennell, Stuart A. Scott, and J. S. Dennis. ‘Inhibiting the Interaction between FeO and Al_2O_3 during Chemical Looping Production of Hydrogen’. *RSC Adv.* 5, no. 3 (2015): 1759–71. doi:10.1039/C4RA11891J.
- Sheng, Yuan, and Hua Chun Zeng. ‘Monodisperse Aluminosilicate Spheres with Tunable Al/Si Ratio and Hierarchical Macro-Meso-Microporous Structure’. *ACS Applied Materials & Interfaces* 7, no. 24 (24 June 2015): 13578–89. doi:10.1021/acsami.5b03011.
- ———. ‘Structured Assemblages of Single-Walled 3d Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts’. *Chemistry of Materials* 27, no. 3 (10 February 2015): 658–67. doi:10.1021/cm502691s.
- Xi, Baojuan, Ying Chuan Tan, and Hua Chun Zeng. ‘A General Synthetic Approach for Integrated Nanocatalysts of Metal-Silica@ZIFs’. *Chemistry of Materials* 28, no. 1 (15 December 2015): 326–36. doi:10.1021/acs.chemmater.5b04147.
- Yang, Shiliang, Ke Zhang, and Jia Wei Chew. ‘Computational Study of Spout Collapse and Impact of Partition Plate in a Double Slot-Rectangular Spouted Bed’. *AIChE Journal*, August 2015, n/a – n/a. doi:10.1002/aic.14973.
- Yan, Yibo, Yihu Dai, Shuchao Wang, Xinli Jia, Hao Yu, and Yanhui Yang. ‘Catalytic Applications of Alkali-Functionalized Carbon Nanospheres and Their Supported Pd Nanoparticles’. *Applied Catalysis B: Environmental* 184 (March 2016): 104–18. doi:10.1016/j.apcatb.2015.11.024.
- Yan, Yibo, Jianwei Miao, Zhihong Yang, Fang-Xing Xiao, Hong Bin Yang, Bin Liu, and Yanhui Yang. ‘Carbon Nanotube Catalysts: Recent Advances in Synthesis, Characterization and Applications’. *Chem. Soc. Rev.* 44, no. 10 (2015): 3295–3346. doi:10.1039/C4CS00492B.
- Zhan, Guowu, Christopher C. Yec, and Hua Chun Zeng. ‘Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts’. *Chemistry - A European Journal* 21, no. 5 (26 January 2015): 1882–87. doi:10.1002/chem.201405697.
- Zhao, Jun, Chunmei Zhou, Chao He, Yihu Dai, Xinli Jia, and Yanhui Yang. ‘Efficient Dehydration of Fructose to 5-Hydroxymethylfurfural over Sulfonated Carbon Sphere Solid Acid Catalysts’. *Catalysis Today*, August 2015. doi:10.1016/j.cattod.2015.07.005.
- Zhou, Chunmei, Zhen Guo, Yihu Dai, Xinli Jia, Hao Yu, and Yanhui Yang. ‘Promoting Role of Bismuth on Carbon Nanotube Supported Platinum Catalysts in Aqueous Phase Aerobic Oxidation of Benzyl Alcohol’. *Applied Catalysis B: Environmental* 181 (February 2016): 118–26. doi:10.1016/j.apcatb.2015.07.048.
- Zhou, Yao, and Hua Chun Zeng. ‘Kinetically Controlled Growth of Fine Gold Nanofractals from Au(I) via Indirect Galvanic Replacement Reaction’. *ACS Applied Materials & Interfaces* 7, no. 38 (11 September 2015): 21552–61. doi:10.1021/acsami.5b06818.

A.1.2 IRP2— EMSET

- Ahn, Sunyhik D., Paul E. Frith, Adrian C. Fisher, Alan M. Bond, and Frank Marken. ‘Mass Transport and Modulation Effects in Rocking Dual-Semi-Disc Electrode Voltammetry’. *Journal of Electroanalytical Chemistry* 722–23 (May 2014): 78–82. doi:10.1016/j.jelechem.2014.02.018.

- Chen, Rong, Gengzhi Sun, Cangjie Yang, Liping Zhang, Jianwei Miao, Huabing Tao, Hongbin Yang, Jiazang Chen, Peng Chen, and Bin Liu. ‘Achieving Stable and Efficient Water Oxidation by Incorporating NiFe Layered Double Hydroxide Nanoparticles into Aligned Carbon Nanotubes’. *Nanoscale Horiz.* 1, no. 2 (2016): 156–60. doi:10.1039/C5NH00082C.
- Chen, Rong, Hsin-Yi Wang, Jianwei Miao, Hongbin Yang, and Bin Liu. ‘A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional NiCo2O4 Core-Shell Nanowires’. *Nano Energy* 11 (January 2015): 333–40. doi:10.1016/j.nanoen.2014.11.021.
- Dai, Chencheng, Chun-Wai I. Chan, William Barrow, Anna Smith, Peng Song, Francois Potier, Jay D. Wadhawan, Adrian C. Fisher, and Nathan S. Lawrence. ‘A Route to Unbuffered pH Monitoring: A Novel Electrochemical Approach’. *Electrochimica Acta* 190 (February 2016): 879–86. doi:10.1016/j.electacta.2016.01.004.
- Dai, Chencheng, Lynne P. Crawford, Peng Song, Adrian C. Fisher, and Nathan S. Lawrence. ‘A Novel Sensor Based on Electropolymerized Substituted-Phenols for pH Detection in Unbuffered Systems’. *RSC Advances* 2015, no. 5 (n.d.): 104048–53. doi:10.1039/c5ra22595g.
- Dai, Chencheng, Peng Song, Jay D. Wadhawan, Adrian C. Fisher, and Nathan S. Lawrence. ‘Screen Printed Alizarin-Based Carbon Electrodes: Monitoring pH in Unbuffered Media’. *Electroanalysis* 27, no. 4 (April 2015): 917–23. doi:10.1002/elan.201400704.
- Gu, Yunfeng, and Adrian C. Fisher. ‘An Ac Voltammetry Approach for the Detection of Droplets in Microfluidic Devices’. *The Analyst* 138, no. 16 (2013): 4448. doi:10.1039/c3an00822c.
- Huang, Bicheng, Hongyuan Shao, Naiqiang Liu, Zhichuan J. Xu, and Yaqin Huang. ‘From Fish Scales to Highly Porous N-Doped Carbon: A Low Cost Material Solution for CO_2 Capture’. *RSC Adv.* 5, no. 107 (2015): 88171–75. doi:10.1039/C5RA16745K.
- Hu, Nantao, Liling Zhang, Chao Yang, Jian Zhao, Zhi Yang, Hao Wei, Hanbin Liao, et al. ‘Three-Dimensional Skeleton Networks of Graphene Wrapped Polyaniline Nanofibers: An Excellent Structure for High-Performance Flexible Solid-State Supercapacitors’. *Scientific Reports* 6 (22 January 2016): 19777. doi:10.1038/srep19777.
- Inglesby, Alister E., and Adrian C. Fisher. ‘Downstream Application of a Microbial Fuel Cell for Energy Recovery from an Arthrospira Maxima Fed Anaerobic Digester Effluent’. *RSC Advances* 3, no. 38 (2013): 17387. doi:10.1039/c3ra42277a.
- Khezri, B., Y. Y. Chan, L. Y. D. Tiong, and R. D. Webster. ‘Annual Air Pollution Caused by the Hungry Ghost Festival’. *Environ. Sci.: Processes Impacts*, 2015. doi:10.1039/C5EM00312A.
- Latiff, Naziah Mohamad, Wei Zhe Teo, Zdenek Sofer, Adrian C. Fisher, and Martin Pumera. ‘The Cytotoxicity of Layered Black Phosphorus’. *Chemistry - A European Journal*, 20 August 2015, n/a – n/a. doi:10.1002/chem.201502006.
- Latiff, Naziah, Wei Zhe Teo, Zdenek Sofer, Štěpán Huber, Adrian C. Fisher, and Martin Pumera. ‘Toxicity of Layered Semiconductor Chalcogenides: Beware of Interferences’. *RSC Adv.* 5, no. 83 (2015): 67485–92. doi:10.1039/C5RA09404F.
- Lee, Jazreen H.Q., Sherman J.L. Lauw, and Richard D. Webster. ‘The Electrochemical Reduction of Carbon Dioxide (CO2) to Methanol in the Presence of Pyridoxine (vitamin B6)’. *Electrochemistry Communications* 64 (March 2016): 69–73. doi:10.1016/j.elecom.2016.01.016.
- Liao, Hanbin, Adrian Fisher, and Zhichuan J. Xu. ‘Surface Segregation in Bimetallic Nanoparticles: A Critical Issue in Electrocatalyst Engineering’. *Small* 11, no. 27 (July 2015): 3221–46. doi:10.1002/smll.201403380.
- Lim, Rern Jern, Mingshi Xie, Mahasin Alam Sk, Jong-Min Lee, Adrian Fisher, Xin Wang, and Kok

Hwa Lim. ‘A Review on the Electrochemical Reduction of CO2 in Fuel Cells, Metal Electrodes and Molecular Catalysts’. *Catalysis Today* 233 (September 2014): 169–80. doi:10.1016/j.cattod.2013.11.037.

- Li, Nan, Larissa Thia, and Xin Wang. ‘A CO2-Responsive Surface with an Amidine-Terminated Self-Assembled Monolayer for Stimuli-Induced Selective Adsorption’. *Chemical Communications* 50, no. 30 (2014): 4003. doi:10.1039/c4cc00412d.
- Li, Nan, Hai-Bo Wang, Larissa Thia, Jing-Yuan Wang, and Xin Wang. ‘Enzymatic-Reaction Induced Production of Polydopamine Nanoparticles for Sensitive and Visual Sensing of Urea’. *The Analyst* 140, no. 2 (2015): 449–55. doi:10.1039/C4AN01900H.
- Li, Nan, Ya Yan, Bao-Yu Xia, Jing-Yuan Wang, and Xin Wang. ‘Novel Tungsten Carbide Nanorods: An Intrinsic Peroxidase Mimetic with High Activity and Stability in Aqueous and Organic Solvents’. *Biosensors and Bioelectronics* 54 (April 2014): 521–27. doi:10.1016/j.bios.2013.11.040.
- Liu, Ying, Hanbin Liao, Ye Zhou, Yonghua Du, Chao Wei, Jian Zhao, Shengnan Sun, Joachim S. C. Loo, and Zhichuan J. Xu. ‘Fe2O3 Nanoparticle/SWCNT Composite Electrode for Sensitive Electrocatalytic Oxidation of Hydroquinone’. *Electrochimica Acta* 180 (2015): 1059–67. doi:10.1016/j.electacta.2015.09.046.
- Ng, Fong-Lee, Muhammad Musoddiq Jaafar, Siew-Moi Phang, Zhijian Chan, Nurul Anati Salleh, Siti Zulfikriyah Azmi, Kamran Yunus, Adrian C. Fisher, and Vengadesh Periasamy. ‘Reduced Graphene Oxide Anodes for Potential Application in Algae Biophotovoltaic Platforms’. *Scientific Reports* 4 (22 December 2014): 7562. doi:10.1038/srep07562.
- Ng, Fong-Lee, Siew-Moi Phang, Vengadesh Periasamy, Kamran Yunus, and Adrian C. Fisher. ‘Evaluation of Algal Biofilms on Indium Tin Oxide (ITO) for Use in Biophotovoltaic Platforms Based on Photosynthetic Performance’. Edited by Nikolai Lebedev. *PLoS ONE* 9, no. 5 (29 May 2014): e97643. doi:10.1371/journal.pone.0097643.
- Sun, Shengnan, and Zhichuan J. Xu. ‘Composition Dependence of Methanol Oxidation Activity in Nickel–cobalt Hydroxides and Oxides: An Optimization toward Highly Active Electrodes’. *Electrochimica Acta* 165 (May 2015): 56–66. doi:10.1016/j.electacta.2015.03.008.
- Sun, Shengnan, Ye Zhou, Benlin Hu, Qichun Zhang, and Zhichuan J. Xu. ‘Ethylene Glycol and Ethanol Oxidation on Spinel Ni-Co Oxides in Alkaline’. *Journal of The Electrochemical Society* 163, no. 2 (1 January 2016): H99–104. doi:10.1149/2.0761602jes.
- Sunyhik D. Ahn, Karthik Somasundaram, Erik Birgersson H.Viet Nguyen, Xiangming Gao Jim Yang Lee, Paul E. Frith Adrian C. Fisher, and Frank Marken. ‘Hydrodynamic Voltammetry at a Rocking Disc Electrode: Theory versus Experiment’. *Electrochimica Acta* 188, no. - (12 March 2015): 837–44. doi:10.1016/j.electacta.2015.11.143.
- Vengadesh, P., G. P. M. K. Ciniciato, C. Zhijian, M. Musoddiq, A. C. Fisher, and K. Yunus. ‘Capillary Force Assisted Fabrication of DNA Templated Silver Wires’. *RSC Adv.* 5, no. 11 (7 January 2015): 8163–66. doi:10.1039/C4RA16448B.
- Wang, Haibo, Larissa Thia, Nan Li, Xiaoming Ge, Zhaolin Liu, and Xin Wang. ‘Pd Nanoparticles on Carbon Nitride–Graphene for the Selective Electro-Oxidation of Glycerol in Alkaline Solution’. *ACS Catalysis* 5, no. 6 (5 June 2015): 3174–80. doi:10.1021/acscatal.5b00183.
- ———. ‘Selective Electro-Oxidation of Glycerol over Au Supported on Extended poly(4-Vinylpyridine) Functionalized Graphene’. *Applied Catalysis B: Environmental* 166–67 (May 2015): 25–31. doi:10.1016/j.apcatb.2014.11.009.
- Wang, Haibo, Mingshi Xie, Larissa Thia, Adrian Fisher, and Xin Wang. ‘Strategies on the De-

sign of Nitrogen-Doped Graphene’. *The Journal of Physical Chemistry Letters* 5, no. 1 (2 January 2014): 119–25. doi:10.1021/jz402416a.

- Wang, Hsin-Yi, Ying-Ya Hsu, Rong Chen, Ting-Shan Chan, Hao Ming Chen, and Bin Liu. ‘Ni^{3+}-Induced Formation of Active NiOOH on the Spinel Ni-Co Oxide Surface for Efficient Oxygen Evolution Reaction’. *Advanced Energy Materials* 5, no. 10 (May 2015): n/a – n/a. doi:10.1002/aenm.201500091.
- Wang, Hsin-Yi, Sung-Fu Hung, Han-Yi Chen, Ting-Shan Chan, Hao Ming Chen, and Bin Liu. ‘In Operando Identification of Geometrical-Site-Dependent Water Oxidation Activity of Spinel Co_3O_4’. *Journal of the American Chemical Society* 138, no. 1 (13 January 2016): 36–39. doi:10.1021/jacs.5b10525.
- Wang, Luyuan Paul, Linghui Yu, Rohit Satish, Jixin Zhu, Qingyu Yan, Madhavi Srinivasan, and Zhichuan Xu. ‘High-Performance Hybrid Electrochemical Capacitor with Binder-Free Nb_2O_5 @graphene’. *RSC Advances* 4, no. 70 (14 August 2014): 37389. doi:10.1039/C4RA06674J.
- Wang, Luyuan Paul, Linghui Yu, Xin Wang, Madhavi Srinivasan, and Zhichuan J. Xu. ‘Recent Developments in Electrode Materials for Sodium-Ion Batteries’. *J. Mater. Chem. A* 3, no. 18 (2015): 9353–78. doi:10.1039/C4TA06467D.
- Wang, Luyuan Paul, Yi Zhao, Chao Wei, Chuiling Wong, Madhavi Srinivasan, and Zhichuan J. Xu. ‘Polycrystalline Zinc Stannate as an Anode Material for Sodium-Ion Batteries’. *J. Mater. Chem. A* 3, no. 26 (2015): 14033–38. doi:10.1039/C5TA02734A.
- Wei, Chao, Pooi See Lee, and Zhichuan Xu. ‘A Comparison of Carbon Supports in MnO_2/C Supercapacitors’. *RSC Advances* 4, no. 59 (8 July 2014): 31416. doi:10.1039/C4RA04914D.
- Xia, Bao Yu, Hao Bin Wu, Nan Li, Ya Yan, Xiong Wen David Lou, and Xin Wang. ‘One-Pot Synthesis of Pt-Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties’. *Angewandte Chemie International Edition* 54, no. 12 (16 March 2015): 3797–3801. doi:10.1002/anie.201411544.
- Xiao, Peng, Xiaoming Ge, Haibo Wang, Zhaolin Liu, Adrian Fisher, and Xin Wang. ‘Novel Molybdenum Carbide-Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution’. *Advanced Functional Materials* 25, no. 10 (March 2015): 1520–26. doi:10.1002/adfm.201403633.
- Xiao, Peng, Mahasin Alam Sk, Larissa Thia, Xiaoming Ge, Rern Jern Lim, Jing-Yuan Wang, Kok Hwa Lim, and Xin Wang. ‘Molybdenum Phosphide as an Efficient Electrocatalyst for the Hydrogen Evolution Reaction’. *Energy Environ. Sci.* 7, no. 8 (29 May 2014): 2624–29. doi:10.1039/C4EE00957F.
- Yan, Ya, Larissa Thia, Bao Yu Xia, Xiaoming Ge, Zhaolin Liu, Adrian Fisher, and Xin Wang. ‘Construction of Efficient 3D Gas Evolution Electrocatalyst for Hydrogen Evolution: Porous FeP Nanowire Arrays on Graphene Sheets’. *Advanced Science*, June 2015, n/a – n/a. doi:10.1002/advs.201500120.
- Yan, Ya, Bao Yu Xia, Xiaoming Ge, Zhaolin Liu, Adrian Fisher, and Xin Wang. ‘A Flexible Electrode Based on Iron Phosphide Nanotubes for Overall Water Splitting’. *Chemistry - A European Journal* 21, no. 50 (7 December 2015): 18062–67. doi:10.1002/chem.201503777.
- Yan, Ya, BaoYu Xia, Xiaoming Ge, Zhaolin Liu, Jing-Yuan Wang, and Xin Wang. ‘Ultrathin MoS_2 Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution’. *ACS Applied Materials & Interfaces* 5, no. 24 (26 December 2013): 12794–98. doi:10.1021/am404843b.
- Yan, Ya, BaoYu Xia, Nan Li, Zhichuan Xu, Adrian Fisher, and Xin Wang. ‘Vertically Oriented

MoS_2 and WS_2 Nanosheets Directly Grown on Carbon Cloth as Efficient and Stable 3-Dimensional Hydrogen-Evolving Cathodes'. *J. Mater. Chem. A* 3, no. 1 (2015): 131–35. doi:10.1039/C4TA04858J.

- Yan, Ya, BaoYu Xia, Zhichuan Xu, and Xin Wang. 'Recent Development of Molybdenum Sulfides as Advanced Electrocatalysts for Hydrogen Evolution Reaction'. *ACS Catalysis* 4, no. 6 (6 June 2014): 1693–1705. doi:10.1021/cs500070x.
- Yu, Linghui, Luyuan Paul Wang, Shibo Xi, Ping Yang, Yonghua Du, Madhavi Srinivasan, and Zhichuan J. Xu. 'β-FeOOH: An Earth-Abundant High-Capacity Negative Electrode Material for Sodium-Ion Batteries'. *Chemistry of Materials* 27, no. 15 (11 August 2015): 5340–48. doi:10.1021/acs.chemmater.5b01747.
- Yu, Linghui, Chao Wei, Qingyu Yan, and Zhichuan J. Xu. 'Controlled Synthesis of High-Performance β-FeOOH Anodes for Lithium-Ion Batteries and Their Size Effects'. *Nano Energy* 13 (April 2015): 397–404. doi:10.1016/j.nanoen.2015.03.003.
- Yu, Linghui, Shibo Xi, Chao Wei, Wenyu Zhang, Yonghua Du, Qingyu Yan, and Zhichuan Xu. 'Superior Lithium Storage Properties of β-FeOOH'. *Advanced Energy Materials* 5, no. 6 (March 2015): n/a – n/a. doi:10.1002/aenm.201401517.
- Zhao, Yi, Zhenxing Feng, and Zhichuan J. Xu. 'Yolk–shell Fe_2O_3 ⊙ C Composites Anchored on MWNTs with Enhanced Lithium and Sodium Storage'. *Nanoscale* 7, no. 21 (2015): 9520–25. doi:10.1039/C5NR01281C.
- Zhao, Yi, Chao Wei, Shengnan Sun, Luyuan Paul Wang, and Zhichuan J. Xu. 'Reserving Interior Void Space for Volume Change Accommodation: An Example of Cable-Like MWNTs@SnO_2@C Composite for Superior Lithium and Sodium Storage'. *Advanced Science* 2, no. 6 (June 2015): n/a – n/a. doi:10.1002/advs.201500097.
- Zhao, Yi, Wangliang Wu, Jiaxin Li, Zhichuan Xu, and Lunhui Guan. 'Encapsulating MWNTs into Hollow Porous Carbon Nanotubes: A Tube-in-Tube Carbon Nanostructure for High-Performance Lithium-Sulfur Batteries'. *Advanced Materials* 26, no. 30 (August 2014): 5113–18. doi:10.1002/adma.201401191.

A.1.3 IRP3 — CAPRICORN

- Azadi, Pooya, George Brownbridge, Sebastian Mosbach, Oliver Inderwildi, and Markus Kraft. 'Simulation and Life Cycle Assessment of Algae Gasification Process in Dual Fluidized Bed Gasifiers'. *Green Chem.* 17, no. 3 (2015): 1793–1801. doi:10.1039/C4GC01698J.
- Azadi, Pooya, George Brownbridge, Sebastian Mosbach, Andrew Smallbone, Amit Bhave, Oliver Inderwildi, and Markus Kraft. 'The Carbon Footprint and Non-Renewable Energy Demand of Algae-Derived Biodiesel'. *Applied Energy* 113 (January 2014): 1632–44. doi:10.1016/j.apenergy.2013.09.027.
- Azadi, Pooya, George P.E. Brownbridge, Sebastian Mosbach, Oliver R. Inderwildi, and Markus Kraft. 'Production of Biorenewable Hydrogen and Syngas via Algae Gasification: A Sensitivity Analysis'. *Energy Procedia* 61 (2014): 2767–70. doi:10.1016/j.egypro.2014.12.302.
- Botero, Maria L., Erin M. Adkins, Silvia González-Calera, Houston Miller, and Markus Kraft. 'PAH Structure Analysis of Soot in a Non-Premixed Flame Using High-Resolution Transmission Electron Microscopy and Optical Band Gap Analysis'. *Combustion and Flame* 164 (February 2016): 250–58. doi:10.1016/j.combustflame.2015.11.022.
- Botero, Maria L., Dongping Chen, Silvia González-Calera, David Jefferson, and Markus Kraft.

‘HRTEM Evaluation of Soot Particles Produced by the Non-Premixed Combustion of Liquid Fuels’. *Carbon* 96 (January 2016): 459–73. doi:10.1016/j.carbon.2015.09.077.

- Botero, Maria L., Sebastian Mosbach, Jethro Akroyd, and Markus Kraft. ‘Sooting Tendency of Surrogates for the Aromatic Fractions of Diesel and Gasoline in a Wick-Fed Diffusion Flame’. *Fuel* 153 (August 2015): 31–39. doi:10.1016/j.fuel.2015.02.108.
- Botero, Maria L., Sebastian Mosbach, and Markus Kraft. ‘Sooting Tendency and Particle Size Distributions of N-Heptane/toluene Mixtures Burned in a Wick-Fed Diffusion Flame’. *Fuel* 169 (April 2016): 111–19. doi:10.1016/j.fuel.2015.12.014.
- ———. ‘Sooting Tendency of Paraffin Components of Diesel and Gasoline in Diffusion Flames’. *Fuel* 126 (June 2014): 8–15. doi:10.1016/j.fuel.2014.02.005.
- Brownbridge, George, Pooya Azadi, Andrew Smallbone, Amit Bhave, Benjamin Taylor, and Markus Kraft. ‘The Future Viability of Algae-Derived Biodiesel under Economic and Technical Uncertainties’. *Bioresource Technology* 151 (January 2014): 166–73. doi:10.1016/j.biortech.2013.10.062.
- Buerger, Philipp, Daniel Nurkowski, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. ‘First-Principles Thermochemistry for the Thermal Decomposition of Titanium Tetraisopropoxide’. *The Journal of Physical Chemistry A* 119, no. 30 (30 July 2015): 8376–87. doi:10.1021/acs.jpca.5b01721.
- Chen, Dongping, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. ‘Surface Reactivity of Polycyclic Aromatic Hydrocarbon Clusters’. *Proceedings of the Combustion Institute* 35, no. 2 (2015): 1811–18. doi:10.1016/j.proci.2014.06.140.
- Chen, Dongping, Jethro Akroyd, Sebastian Mosbach, Daniel Opalka, and Markus Kraft. ‘Solid–liquid Transitions in Homogenous Ovalene, Hexabenzocoronene and Circumcoronene Clusters: A Molecular Dynamics Study’. *Combustion and Flame* 162, no. 2 (February 2015): 486–95. doi:10.1016/j.combustflame.2014.07.025.
- Chen, Dongping, Tim S. Totton, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. ‘Phase Change of Polycyclic Aromatic Hydrocarbon Clusters by Mass Addition’. *Carbon* 77 (October 2014): 25–35. doi:10.1016/j.carbon.2014.04.089.
- Chen, Dongping, Tim S. Totton, Jethro W.J. Akroyd, Sebastian Mosbach, and Markus Kraft. ‘Size-Dependent Melting of Polycyclic Aromatic Hydrocarbon Nano-Clusters: A Molecular Dynamics Study’. *Carbon* 67 (February 2014): 79–91. doi:10.1016/j.carbon.2013.09.058.
- Han, Jianyu, Danping Wang, YongHua Du, Shibo Xi, Zhong Chen, Shengming Yin, Tianhua Zhou, and Rong Xu. ‘Polyoxometalate Immobilized in MIL-101(Cr) as an Efficient Catalyst for Water Oxidation’. *Applied Catalysis A: General*, December 2015. doi:10.1016/j.apcata.2015.10.015.
- Kastner, Catharine A., Raymond Lau, and Markus Kraft. ‘Quantitative Tools for Cultivating Symbiosis in Industrial Parks; a Literature Review’. *Applied Energy* 155 (October 2015): 599–612. doi:10.1016/j.apenergy.2015.05.037.
- Lee, Kok Foong, John F. Davidson, Jethro Akroyd, and Markus Kraft. ‘Lifting a Buried Object: Reverse Hopper Theory’. *Chemical Engineering Science* 105 (February 2014): 198–207. doi:10.1016/j.ces.2013.11.002.
- Lee, Kok Foong, Sebastian Mosbach, Markus Kraft, and Wolfgang Wagner. ‘A Multi-Compartment Population Balance Model for High Shear Granulation’. *Computers & Chemical Engineering* 75 (April 2015): 1–13. doi:10.1016/j.compchemeng.2015.01.009.

- Lee, Kok Foong, Robert Patterson, Wolfgang Wagner, and Markus Kraft. 'Stochastic Weighted Particle Methods for Population Balance Equations with Coagulation, Fragmentation and Spatial Inhomogeneity'. *Journal of Computational Physics* 303 (2015): 1–18. doi:10.1016/j.jcp.2015.09.031.
- Li, Jing, Wenming Yang, Hui An, Dezhi Zhou, and Markus Kraft. 'Application of Dynamic φ–T Map: Analysis on a Natural Gas/Diesel Fueled RCCI Engine'. *Journal of Engineering for Gas Turbines and Power* 138, no. 9 (22 March 2016): 092803. doi:10.1115/1.4032712.
- Menz, William J., George P.E. Brownbridge, and Markus Kraft. 'Global Sensitivity Analysis of a Model for Silicon Nanoparticle Synthesis'. *Journal of Aerosol Science* 76 (October 2014): 188–99. doi:10.1016/j.jaerosci.2014.06.011.
- Mosbach, Sebastian, Je Hyeong Hong, George P. E. Brownbridge, Markus Kraft, Soumya Gudiyella, and Kenneth Brezinsky. 'Bayesian Error Propagation for a Kinetic Model of N-Propylbenzene Oxidation in a Shock Tube'. *International Journal of Chemical Kinetics* 46, no. 7 (July 2014): 389–404. doi:10.1002/kin.20855.
- Mosbach, Sebastian, and Markus Kraft. 'Influence of Experimental Observations on N-Propylbenzene Kinetic Parameter Estimates'. *Proceedings of the Combustion Institute* 35, no. 1 (2015): 357–65. doi:10.1016/j.proci.2014.05.061.
- Nurkowski, Daniel, Philipp Buerger, Jethro Akroyd, and Markus Kraft. 'A Detailed Kinetic Study of the Thermal Decomposition of Tetraethoxysilane'. *Proceedings of the Combustion Institute* 35, no. 2 (2015): 2291–98. doi:10.1016/j.proci.2014.06.093.
- Nurkowski, Daniel, Philipp Buerger, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. 'Skeletal Chemical Mechanism of High-Temperature TEOS Oxidation in Hydrogen–oxygen Environment'. *Combustion and Flame* 166 (April 2016): 243–54. doi:10.1016/j.combustflame.2016.01.025.
- Nurkowski, Daniel, Stephen J. Klippenstein, Yuri Georgievskii, Marco Verdicchio, Ahren W. Jasper, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. 'Ab Initio Variational Transition State Theory and Master Equation Study of the Reaction (OH)3SiOCH2 + CH3 ⇌ (OH)3SiOC2H5'. *Zeitschrift Für Physikalische Chemie* 229, no. 5 (28 January 2015). doi:10.1515/zpch-2014-0640.
- Pan, Ming, Janusz Sikorski, Catharine A. Kastner, Jethro Akroyd, Sebastian Mosbach, Raymond Lau, and Markus Kraft. 'Applying Industry 4.0 to the Jurong Island Eco-Industrial Park'. *Energy Procedia* 75 (August 2015): 1536–41. doi:10.1016/j.egypro.2015.07.313.
- Wang, Buyu, Sebastian Mosbach, Sebastian Schmutzhard, Shijin Shuai, Yaqing Huang, and Markus Kraft. 'Modelling Soot Formation from Wall Films in a Gasoline Direct Injection Engine Using a Detailed Population Balance Model'. *Applied Energy* 163 (2016): 154–66. doi:10.1016/j.apenergy.2015.11.011.
- Wenbin Yu, Wenming Yang, Balaji Mohan, Kunlin Tay, Feiyang Zhao, Yunpeng Zhang, Siawkiang Chou, et al. 'Numerical and Experimental Study on Internal Nozzle Flow and Macroscopic Spray Characteristics of a Kind of Wide Distillation Fuel (WDF) - Kerosene'. *SAE Internationa* 2016–01–0839 (2016). doi:10.4271/2016-01-0839.
- Yang, Wenming, Hui An, Jing Li, Dezhi Zhou, and Markus Kraft. 'Impact of Urea Direct Injection on NOx Emission Formation of Diesel Engines Fueled by Biodiesel', V002T04A005. ASME, 2015. doi:10.1115/ICEF2015-1059.
- Yapp, Edward K.Y., Dongping Chen, Jethro Akroyd, Sebastian Mosbach, Markus Kraft, Joaquin

Camacho, and Hai Wang. ‘Numerical Simulation and Parametric Sensitivity Study of Particle Size Distributions in a Burner-Stabilised Stagnation Flame’. *Combustion and Flame* 162, no. 6 (June 2015): 2569–81. doi:10.1016/j.combustflame.2015.03.006.

- Yapp, Edward, Robert Patterson, Jethro Akroyd, Sebastian Mosbach, Erin Adkins, Houston Miller, and Markus Kraft. ‘Numerical Simulation and Parametric Sensitivity Study of Optical Band Gap in a Laminar Co-Flow Ethylene Diffusion Flame’. *Combustion and Flame*, n.d. doi:10.1016/j.combustflame.2016.01.033.
- You Xu, Markus Kraft, and Rong Xu. ‘Metal-Free Carbonaceous Electrocatalysts and Photocatalysts for Water Splitting’. *Chemical Society Reviews*, 2016.
- Zhang, Wei, Tianhua Zhou, Jindui Hong, and Rong Xu. ‘MoS3 Loaded TiO2 Nanoplates for Photocatalytic Water and Carbon Dioxide Reduction’. *Journal of Energy Chemistry*, January 2016. doi:10.1016/j.jechem.2016.01.016.
- Zhang, Wei, Tianhua Zhou, Jianwei Zheng, Jindui Hong, Yunxiang Pan, and Rong Xu. ‘Water-Soluble MoS_3 Nanoparticles for Photocatalytic H_2 Evolution’. *ChemSusChem* 8, no. 8 (24 April 2015): 1464–71. doi:10.1002/cssc.201500067.
- Zhou, Dezhi, Wenming Yang, Hui An, Jing Li, and Markus Kraft. ‘An Enhanced Primary Reference Fuel Mechanism Considering Conventional Fuel Chemistry in Engine Simulation’. *Journal of Engineering for Gas Turbines and Power* 138, no. 9 (22 March 2016): 092804. doi:10.1115/1.4032713.

A.1.4 IRP4— ICESO

- Dang, T-V, K-V. Ling. ‘Moving Horizon Estimation on a Chip’. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)*, 431–37. Singapore: IEEE, 2014. doi:10.1109/ICARCV.2014.7064344.
- Dang, T-V, K-V. Ling, and J. Maciejowski. ‘Embedded ADMM-Based Quadratic Programming Solver for Model Predictive Control with Polytopic Constraints’. In *Proceedings of European Control Conference (ECC’15)*, 3451–56. Linz, Austria: IEEE, 2015. doi:10.1109/ECC.2015.7331067.
- Dang, Thuy V., Keck Voon Ling, and Daniel E. Quevedo. ‘Event-Triggered Anytime Control with Two Controllers’. In *2015 54th IEEE Conference on Decision and Control (CDC)*, 4157–62. Osaka, Japan: IEEE, 2015. doi:10.1109/CDC.2015.7402867.
- Foo. Eddy, Y. S., H. B. Gooi, and S. X. Chen. ‘Multi-Agent System for Distributed Management of Microgrids’. *IEEE Transactions on Power Systems* 30, no. 1 (January 2015): 24–34. doi:10.1109/TPWRS.2014.2322622.
- Lynn, Nandar, Rammohan Mallipeddi, and Ponnuthurai Nagaratnam Suganthan. ‘Differential Evolution with Two Subpopulations’. In *Swarm, Evolutionary, and Memetic Computing*, edited by Bijaya Ketan Panigrahi, Ponnuthurai Nagaratnam Suganthan, and Swagatam Das, 8947:1–13. Cham: Springer International Publishing, 2015. http://link.springer.com/10.1007/978-3-319-20294-5_1.
- Qiu, Xueheng, Le Zhang, Ye Ren, P. Suganthan, and Gehan Amaratunga. ‘Ensemble Deep Learning for Regression and Time Series Forecasting’. In *2014 IEEE Symposium on Computational Intelligence in Ensemble Learning (CIEL)*, 1–6. Orlando, FL: IEEE, 2014. doi:10.1109/CIEL.2014.7015739.

- Ren, Ye, Xueheng Qiu, and P. Suganthan. ‘Empirical Mode Decomposition Based Adaboost-Backpropagation Neural Network Method for Wind Speed Forecasting’. In *2014 IEEE Symposium on Computational Intelligence in Ensemble Learning (CIEL)*, 1–6. Orlando, FL: IEEE, 2014. doi:10.1109/CIEL.2014.7015741.
- Ren, Ye, Zhang, Le, and P. N. Suganthan. ‘Ensemble Classification and Regression-Recent Developments, Applications and Future Directions’. *IEEE Computational Intelligence Magazine* 11, no. 1 (February 2016): 41–53. doi:10.1109/MCI.2015.2471235.
- Ren Y., X. Qiu, and Gehan Amaratunga P. N. Suganthan. ‘Detecting Wind Power Ramp with Random Vector Functional Link (RVFL) Network’. In *Proceedings of 2015 IEEE Symposium Series on Computational Intelligence*, 687–94. Cape Town, South Africa: IEEE, 2015. doi:10.1109/SSCI.2015.105.
- T-P Chen, A. Krishnan, and Tri Tran. ‘Application of Partition-Based Moving Horizon Estimation to Power System State Estimation’. In *Proceedings of the 7th IEEE PES Asia-Pacific Power and Energy Engineering Conference (PES APPEEC’15)*, 1–5. Brisbane, Australia: IEEE, 2015. doi:10.1109/APPEEC.2015.7380907.
- T-P. Chen, Tri Tran, W-K. Ho D. Zhou, and K-V. Ling. ‘Iterated Moving Horizon Estimation for Power Systems’. In *2014 International Conference on Control, Automation and Information Sciences (ICCAIS)*, 81–86. IEEE, 2014. doi:10.1109/ICCAIS.2014.7020573.
- Tri Tran. ‘Periodic Economic Model Predictive Control with Bounded-State Stability’. In *Proceedings of the 5th Australian Control Conference (AUCC’15)*, 253–58. Gold Coast, Australia: IEEE, 2015. http://ieeexplore.ieee.org/xpl/articleDetails.jsp?arnumber=7361943&newsearch=true&queryText=Periodic%20Economic%20Model%20Predictive%20Control%20with%20Bounded-State%20Stability.
- ———. ‘State Feedback Control of Explicitly-Bounded Nonlinearly-Coupled Interconnected Systems’. In *2014 International Conference on Control, Automation and Information Sciences (ICCAIS)*, 30–35. IEEE, 2014. doi:10.1109/ICCAIS.2014.7020563.
- Tri Tran, D-X. Zhou, and J. Maciejowski K-V. Ling. ‘Multiplexed Model Predictive Control of Interconnected Systems’. In *Proceedings of IEEE Conference on Decision and Control (CDC’14)*, 15–17. Los Angeles, CA: IEEE, 2015. doi:10.1109/CDC.2014.7040439.
- Tri Tran, Eddy Y. S. Foo., and J. Maciejowski K-V. Ling. ‘Application of Quadratically-Constrained Model Predictive Control in Power Systems’. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)*, 193–98. IEEE, 2014. doi:10.1109/ICARCV.2014.7064303.
- Tri Tran, K-V. Ling, and J. Maciejowski. ‘Closed-Loop Development for Dissipativity Constraint’. In *2014 International Conference onControl, Automation and Information Sciences (ICCAIS)*, 24–29. IEEE, 2014. doi:10.1109/ICCAIS.2014.7020562.
- ———. ‘Economic Model Predictive Control - A Review’. In *Proceedings of the 31st ISARC, Sydney, Australia*, 35–42. Accessed 27 July 2015. http://www.iaarc.org/publications/2014_proceedings_of_the_31st_isarc_sydney_australia/economic_model_predictive_control_a_review.html.
- ———. ‘Model Predictive Control of Nonlinear Input-Affine Systems with Feasibility and Stability Constraints’. In *2014 13th International Conference on Control Automation Robotics & Vision (ICARCV)*, 992–97. IEEE, 2014. doi:10.1109/ICARCV.2014.7064441.
- ———. ‘Model Predictive Control via Quadratic Dissipativity Constraint’. In *2014 IEEE 53rd Annual Conference on Decision and Control (CDC)*, 6689–94. IEEE, 2014. doi:10.1109/

CDC.2014.7040439.

- Tri Tran, Q. P. Ha. 'Dependable Control Systems with Internet of Things'. *ISA Transactions*, August 2015. doi:10.1016/j.isatra.2015.08.008.
- ———. 'Dependable Control Systems with Self-Recovery Constraint'. In *2014 International Conference onControl, Automation and Information Sciences (ICCAIS)*, 87–92. IEEE, 2014. doi:10.1109/ICCAIS.2014.7020574.
- Tri Tran, T-P. Chen. 'Dissipativity Constraint for Distributed Power System State Estimation'. In *Proceedings of the 4th International Conference on Control, Automation, and Information Science (ICCAIS'15)*, 360–65. Changshu, China: IEEE, 2015. doi:10.1109/ICCAIS.2015.7338693.
- X-B Chen, K-J Tseng, and G. Amaratunga. 'State Estimation for Distribution Systems Using Micro-Synchrophasors'. In *Proceedings of the 7th IEEE PES Asia-Pacific Power and Energy Engineering Conference (PES APPEEC'15)*, 1–5. Brisbane, Australia: IEEE, 2015. doi:10.1109/APPEEC.2015.7381051.
- Yu, Chao, Qing-Guo Wang, Dan Zhang, Lei Wang, and Jiangshuai Huang. 'System Identification in Presence of Outliers'. *IEEE Transactions on Cybernetics*, 2015, 1–1. doi:10.1109/TCYB.2015.2430356.

Conference papers given and to be published in proceedings

- Bhagyesh V. Patil. 'The Bernstein Branch-and-Prune Constrained Global Optimization Algorithm for MINLPs'. In *Proceedings of the 6th International Conference on Mathematical Aspects of Computer and Information Sciences (MACIS'15)*. Berlin, Germany, 2015.
- Krishnanand, KR, Moirangthem Joymala, and Panda Sanjib Kumar. 'Harmonic Load Modeling for Smart Microgrids'. In *2015 IEEE International Conference on Building Efficiency and Sustainable Technologies (ICBEST)*. Singapore, 2015.
- ———. 'Selective Harmonic Optimization for Flexible Single-Phase Operation of Cascaded H-Bridge Multilevel Inverters'. In *Proceedings of the 1st Power, Communication and Information Technology Conference (PCITC'15)*. Bhubaneswar, India, 2015.

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