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Biannual Research Report

May 2016 — October 2016

CAM.CREATE C4T

Cambridge Centre for Carbon Reduction in Chemical Technology

CREATE

Centre for Reseach Excellence and Technological Enterprise

University of Cambridge

Nanyang Technological University

National University of Singapore

Cover figure: CARES C4T members in the CREATE laboratories, July 2016. Photo credits: Joy Haughton

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3 Foreword

Prof. Markus Kraft,

CARES Director.

October 2016

I am very pleased to present the 5th 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).

Since our last report, we have welcomed our international Scientific Advisory Committee to Singapore to conduct the mid-term review of the programme's activities and progress. I am delighted to say that the event was a great success and the programme acquitted itself very well. Over three days in July 2016, the seven members of the Scientific Advisory Committee received presentations from all of the IRPs on the current work and future plans, viewed laboratory demonstrations and posters from the C4T researchers and had an opportunity to meet many of the programme members. Following the visit, the Scientific Advisory Committee's report described the current state of the programme as 'very impressive' and noted several areas where they felt we are capable of making a world-class contribution to carbon footprint reduction. The Committee were also able to offer the programme some useful guidance to support us in focussing our energies towards Phase 2. We hope to build on this excellent foundation as we consolidate the early successes of Phase 1.

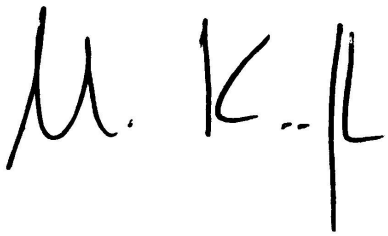
Alongside the efforts put into the mid-term review, CARES C4T researchers have continued to publish rapidly – we are now looking forward to the publication of our 200th paper in peer-reviewed journals and conference proceedings. The programme members have also had a number of opportunities to present their work to the wider Singapore community, including a very well-attended stakeholder event in May 2016 where the J-Park Simulator was demonstrated publically in Singapore for the first time to an audience of seventy representatives of local government agencies and industry. Readers in Singapore will be aware of the country's Smart Nation strategy – an ambitious national evolution aimed at harnessing the power of technology to improve living, create economic opportunity and build a closer community. CARES C4T hopes that the J Park Simulator, alongside a number of the other technologies being developed in the programme, can contribute a unique piece to the Smart Nation journey.

As may be obvious from the high productivity, the CARES C4T talent pipeline continues to flow well. We have recently welcomed ten new PhD students across the programme, including three Cambridge students who are about to start their residency in Singapore. Three interns, one from each of the collaborating institutions, joined the programme for two months. All three reported that the internships gave them insight into academic research and encouraged them to pursue a career in chemical engineering – we wish them very well and hope they stay in touch! Other members also left the programme to take the next steps in their careers. We would like to thank them all and wish them success. We are particularly pleased for Dr Paul Wen LIU to start his new post of Assistant Professor with the University of Newcastle in Singapore. Paul has contributed substantially to IRP1 and we shall miss his expertise and important contributions. We very much hope to continue collaborating with him in his new role at the University of Newcastle in Singapore. Dr Eddy FOO has also climbed the next step on the career ladder becoming a lecturer in the School of Electrical and Electronic Engineering at NTU. Eddy played a pivotal role in the collaborations between IRP3 and IRP4. He had a key involvement in the coupling of the real-time electrical network simulator OPAL-RT with the J-Park Simulator. We are optimistic that Eddy can continue to be involved in C4T as a co-investigator.

Finally, I am very pleased to report that our move into our permanent home at CREATE earlier in the

year has already started to generate some exciting inter-disciplinary collaborations among our scientists. As you will see from this report, there are many excellent examples. However, I'd like to highlight a few that have caught my attention recently. I was impressed by the good work by researchers in IRP3 and 4 to link the Opal RT simulator based at NTU into the J Park Simulator, which has allowed us for the first time to perform cross-domain simulations covering both the chemical and electrical engineering aspects. In the labs, IRP1,2 and 3 are starting to explore the synergetic potential of the work being done in the various groups on electrode development, combining their range of expertise to optimise not only for effectiveness but also cost and safety. All of this work is only just starting to hit the publication pipeline, so we may look forward to seeing far more about it in the next report.

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.



Prof. Markus Kraft, CARES Director

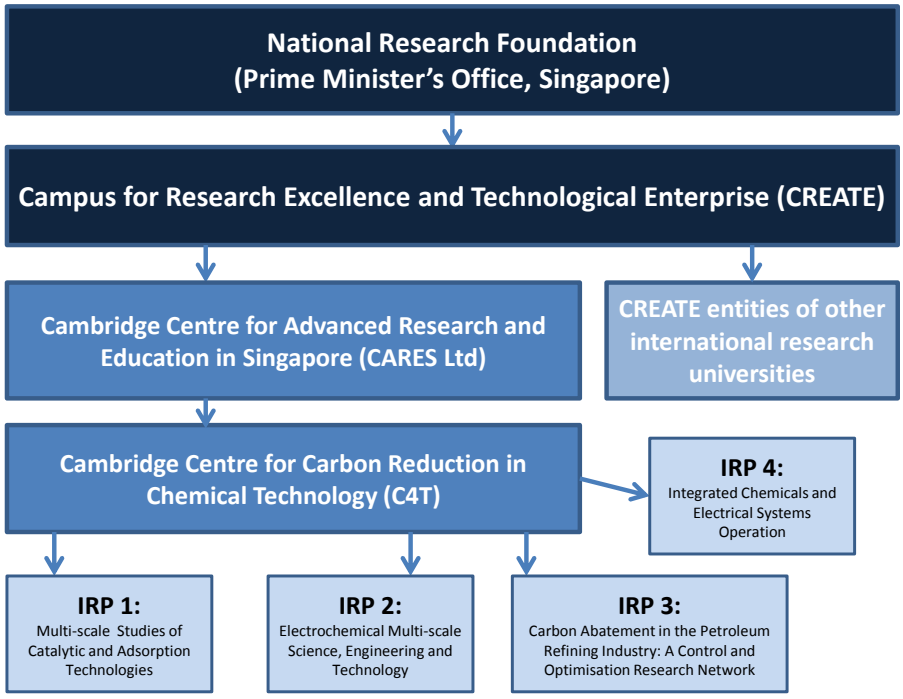
September 2016

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)

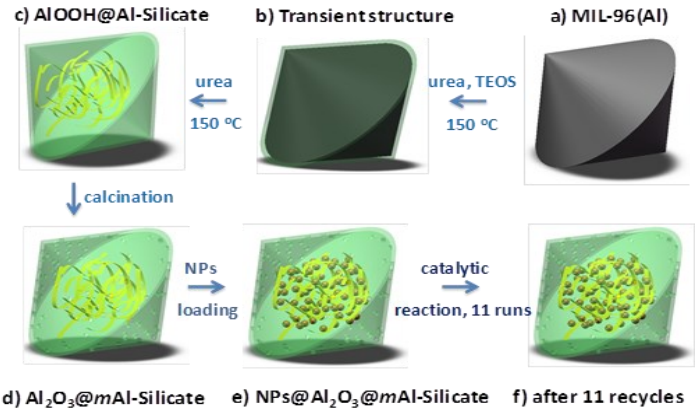
2.1 IRP1: 'Alumina-Supported Metal Catalysts inside a Mesoporous Aluminum-Silicate Shell: Nanoscale Reactors Prepared through Transformation of MIL-96(Al) Nanocrystals'.

Zhou, Yao; Zeng, Huachun

DOI: 10.1002/cctc.201600062

Highlights:

- Permeable mesoporous shells with a hollow interior are an important class of materials for heterogeneous catalysis.
- A transformative method has been developed for the preparation of submicron reactors, starting from MIL-96(Al) nanocrystals.
- Metal and metal-oxide nanoparticles are supported by gamma Al_2O_3 nanosheets and confined within a thin shell of mesoporous Al-silicate.
- Such robust catalyst nanoreactors promise a broad range of applications for heterogeneous catalysis.



Process flowchart of this work: (a,b,c,d) stepwise synthesis of Al_2O_3@mAl-silicate, (e) introduction of multiple catalytic NPs into Al_2O_3 nanosheets and formation of NPs/Al_2O_3@mAl-silicate nanoreactors, and (f) the NPs/Al_2O_3@ mAl-silicate after reused in Suzuki coupling reaction for 11 times.

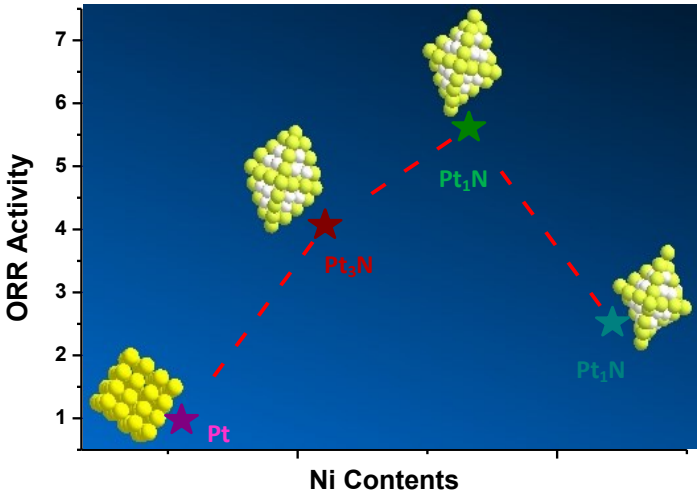
Abstract:

Permeable mesoporous shells with a hollow interior are an important class of materials for the design and synthesis of nanoscale reactors and delivery vehicles. We started from Al-based metal–organic framework MIL-96(Al) nanocrystals, and herein we report a transformative method to prepare submicron reactors in which metal and metal oxide nanoparticles (NPs) are supported by ?-Al2O3 nanosheets and confined within a thin shell of mesoporous Al-silicate (i.e., NPs/Al2O3@mAl-silicate). As an example, such Pd/Al2O3@mAl-silicate nanoreactors demonstrate a much higher catalytic stability than Pd protected within the hollow mAl-silicate nanoshell and Pd supported on commercial Al2O3. As ?-Al2O3 is an important catalyst support, such robust catalyst devices promise broad applications in catalysis.

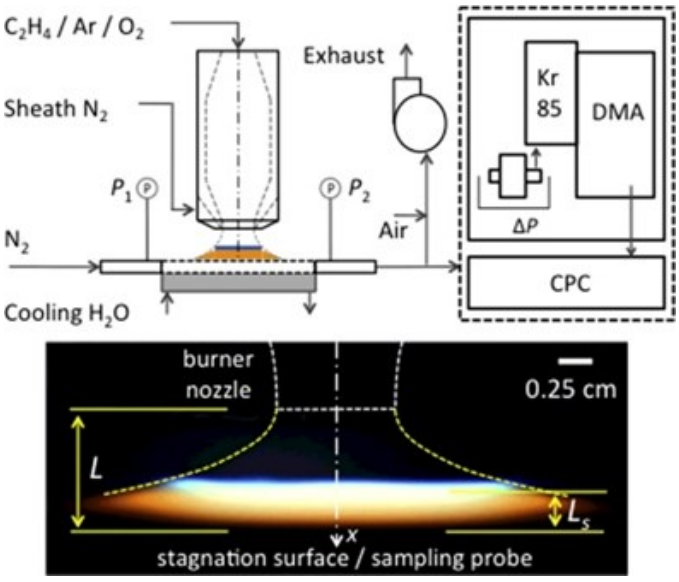
2.2 IRP2:

Dr Yizhong LU's (RF, NTU, IRP2) research demonstrated a generalized strategy to synthesize highly monodisperse, surfactant-free octahedral Pt_xNi_{1-x} nanoparticles with tunable surface structure and composition. With increasing Ni content in the bulk composition, the degree of concaveness of octahedral Pt_xNi_{1-x} nanoparticles increases. His research systematically studies the correlation between their surface structure/composition and their observed oxygen reduction activity. Electrochemical studies have shown that all octahedral Pt_xNi_{1-x} nanoparticles exhibit enhanced oxygen reduction activity relative to the state-of-the-art commercial Pt/C catalyst. More importantly, it was found that the surface structure and composition of octahedral Pt_xNi_{1-x} have significant effect on their oxygen reduction activity. Among the studied Pt_xNi_{1-x} nanoparticles, the octahedral Pt_1Ni_1 nanoparticles

with slight concaveness in its (111) facet show the highest activity. At 0.90 V vs RHE, the Pt mass and specific activity of the octahedral Pt_1Ni_1 nanoparticles are 7.0 and 7.5-fold higher than that of commercial Pt/C catalyst, respectively.



2.3 IRP3: 'Soot particle size distributions in premixed stretch-stabilized flat ethylene–oxygen–argon flames'.



Joaquin Camacho, Ajay V. Singh, Weijing Wang, Ruiqin Shan, Edward K.Y. Yapp, Dongping Chen, Markus Kraft, Hai Wang

DOI: http://dx.doi.org/10.1016/j.proci.2016.06.170

Abstract

Evolution of particle size distribution function (PSDF) was studied in premixed stretch-stabilized flat flames for the first time. The purpose is to demonstrate that stretch-stabilized flames can broaden the experimental flame condition space for studying soot formation in a pseudo-one dimensional flow configuration. PSDFs were measured in three series of atmospheric-pressure ethylene–oxygen–argon flames with maximum temperatures around 1980, 2000, and 2160 K. The measured PSDFs show a strong effect of flame temperature as nucleation and growth of soot is found to be suppressed towards high temperatures. Simulations using a population balance soot model show reasonably good agreement with the 1980 and 2000 K series of flames, but it significantly overpredicts the number density and size of soot in the highest temperature flame. Numerical tests suggest that the discrepancy can be caused by high-temperature reversibility in surface growth and other processes.

2.4 IRP4: 'Harmonic load modeling for smart microgrids'

Krishnanand, K.R, Moiranghtem, J, Bhandari, S. and Panda, S.K,

DOI: 10.1109/PCITC.2015.7435867

Abstract:

The study on modern microgrids implicitly comes with the concern of quality of power and its impact on the electrical network. That is the result of the accumulated impact of nonlinear processes, many of which include switching elements. To perform microgrid studies, especially simulations which test smart control techniques and strategies, the ideal of sinusoidal AC waveforms is no more

a valid assumption and the harmonic components must be correctly represented. This paper intends to present voltage and current signals based lumped models of harmonic electrical loads suitable for a simulation environment. The corresponding computations required for harmonic powers of the load are also presented. The calculations done could be used to obtain quantitative estimation of harmonics in contexts such as large built-environments, or microgrids with significant nonlinear processes such as chemical loads.

Yuan SHENG obtained B.Eng (1 st Hons.) in Chemical Engineering at the National University of Singapore and continued with PhD study supported by the President's Graduate Fellowship in the same university. His thesis is on synthesis of hierarchically porous nanocatalysts for CO 2 utilisation. He has recently joined CARES C4T as a Project Officer in IRP3.

2.5 Focus on Impact: How combustion could realize a carbon-neutral industry.

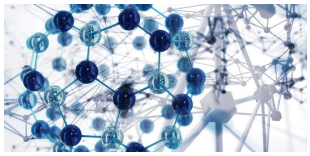
In the second of a CARES C4T series of short articles focusing on the potential real world impact of the programme's research, Yuan SHENG (Project Officer, IRP3, NTU), explores the benefits of developing flame synthesis methods to prepare low-cost, high-performance catalysts for water splitting.

Hydrogen is a major feedstock for the chemical industry and consumed in large scales by heavy oil hydrocracking, ammonia and methanol syntheses processes. Today it is produced almost exclusively from fossil fuels, accompanied by enormous CO_2 emission. If hydrogen from renewable sources, for example, solar-powered water splitting, were to feed the chemical processes, dramatic reduction in carbon footprint is then expected. Unfortunately high price of the "green hydrogen" has prevented its commercial success so far, but there do seem to be chances to change the situation, fortunately.

Some of the most important problems in the electrolytic production of green hydrogen are inefficient electricity-to-hydrogen conversion, high capital cost and poor durability of electrocatalysts. To overcome the activation barrier of the electrolysis reaction, an extra voltage beyond thermodynamic requirements, or overpotential, needs to be applied for any meaningful rate of water splitting. State-of-the-art precious metal catalysts including Pt, RuO_2 and IrO_2 can lower the overpotential to ~0.4 V, which still translates into at least 25% loss of energy as heat. With fast advance in nanotechnology, non-precious nanocatalysts achieving even better performance have been developed in research labs. However, largely wet-chemistry-based syntheses of the nanocatalysts are lengthy and costly, producing significant amount of hazardous waste at the same time. In addition, stability issues of the catalysts remain unresolved.

In CARES C4T, we are developing flame synthesis methods to prepare low-cost, high-performance catalysts for water splitting. During flame synthesis, vapours of precursors for the catalysts are introduced to a burning flame (H_2/O_2 for example) where catalyst nanoparticles form. Advantages of this method are 1) fast speed, 2) almost 100% yield from catalyst precursors, 3) negligible waste production, 4) ability to coat catalyst *in situ* on various substrates to prepare ready-to-use electrodes, 5) possibility of synthesizing different materials using the same process, and 6) suitability for continuous, large-scale production. It is hence expected to significantly reduce production as well as R&D costs of water splitting electrodes, which may ultimately lead the green hydrogen technology to commercialization.

Applications of the flame synthesis method are not limited to preparing water splitting catalysts. Since composition and morphology of flame-synthesized particles/films can be conveniently tuned, other low-carbon-footprint technologies such as photovoltaics, electrochemical CO_2 utilization and fuel cells may also benefit from these low-cost electrodes. In the end, combustion, which most people will consider as the very source of CO_2 emission, could actually help realize a carbon-neutral industry.



3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

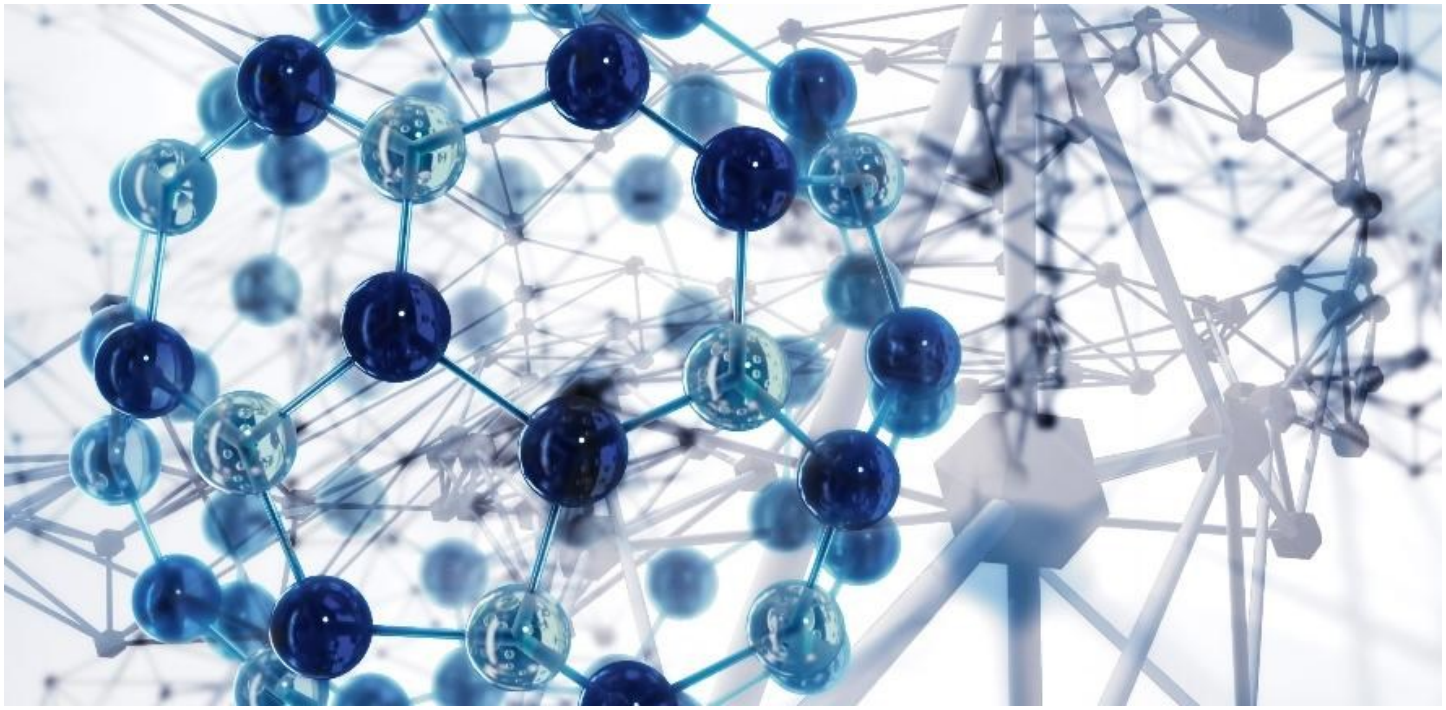
Electrochemical Multi-scale Science, Engineering and Technology

3.3 IRP3 — CAPRICORN

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

3.4 IRP4 — ICESO

Integrated Chemicals and Electrical Systems Operation



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

MUSCAT is led by PIs:

Prof Alexei LAPKIN (Cambridge)

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

Prof. Alexei Lapkin,

University of Cambridge

PI, IRP1,

October 2016

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:

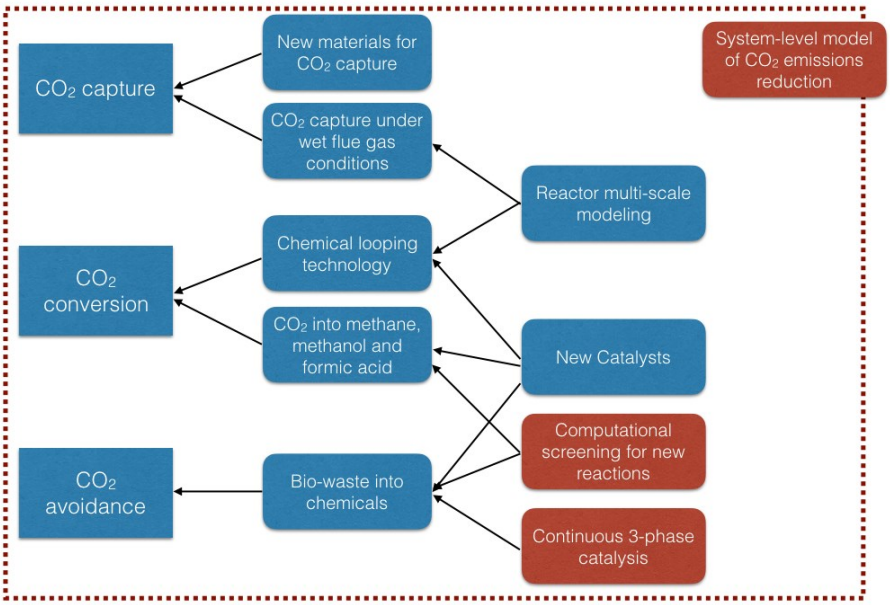
Chemical looping with advanced oxide carriers

· CO2 methanation and biomass conversion

· New materials and MOFs

· Multi-scale modelling

· Fundamentals of adsorption and PSA

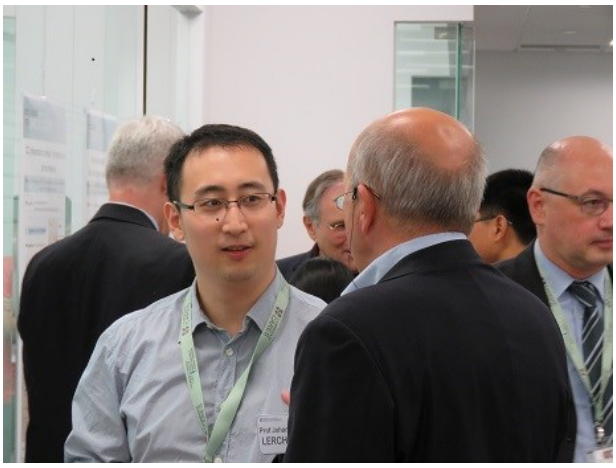


Over the reporting period to October 2016 a number of significant advances were made by IRP1 researchers and a foundation for further work was laid out. The nanomaterials group supervised by Prof. Hua Chun ZENG (PI, NUS, IRP1) developed several new approaches to synthesis of hybrid structured nanomaterials, such as tri-porous MOFs, core-shell particles with semi-permeable shells, or very small allow nanoparticles. These classes of materials are highly important in modern heterogeneous catalysis. The modeling group supervised by Prof. CHEW Jia Wei (Co-I, NTU, IRP1) have completed the development of DEM model for simulation of behaviour of solids flow in different reactor configurations. This model now enables the group to explore design of reactor components for chemical looping reaction system design. The development of novel chemical looping materials is continuing with several new materials reported in this period: for hydrogen production and high temperature CO2 capture/storage.

During this period IRP1 has decided to start several new projects, which will commence during the last quarter of 2016: study of early phases of formation of nanostructures for controlled and scalable synthesis of nano-structured catalysts, identification of active reaction mechanisms for scaling catalytic processes and study of interplay between reaction, diffusion and adsorption in liquid-phase catalytic reactions. These projects are directed at enhancing the fundamental understanding of catalytic processes and first principles design of catalytic materials for specific applications.

3.1.2 Update on work packages

Work package 1: Chemical looping with advanced oxide carriers



Dr Paul Wen LIU (SRF, NTU, IRP1) presenting his work to Prof Johannes LERCHER (SAC member)

Dr Wen LIU (SRF, NTU, IRP1) *et al.* developed a steam feed system for high temperature hydrogen production and is planning to complete and submit a paper shortly.

Dr Jijiang HUANG (PhD student, NTU, IRP1) has been focussing on the development of oxygen carriers for chemical looping processes. In his research, layered double hydroxides (LDH) were applied as the precursors for the preparation of Ni-based, MgO modified and Al_2O_3 supported oxygen carriers, because of the unique nanoplate structure, high surface area of LDH precursors, molecular level dispersion of Ni species, as well as the scalable syntheses. It was found that the synthesized oxygen carriers showed excellent performance over chemical looping cycles. The formation of solid solutions of $Mg_xNi_{1-x}O$ and $Mg_yNi_{1-y}Al_2O_4$ during the calcination resulted in the necessity of an activation period over a few redox cycles before the majority of the NiO became available for chemical looping. X-ray diffraction measurements and analysis revealed a semi-reversible migration of Ni^{2+} from the $Mg_yNi_{1-y}Al_2O_4$ phase to the $Mg_xNi_{1-x}O$ phase over cycling. Based on these experimental results and analysis, a manuscript has been prepared and submitted to Industrial & Engineering Chemistry Research for publication.

In addition, Dr Jijiang HUANG (PhD student, NTU, IRP1) prepared a series of Ni-Cu LDH via hydrothermal syntheses. The derived material after heat treatment will be investigated for chemical looping combustion of methane, with interests on their property of carbon formation resistance.

Work Package 2: CO_2 methanation and biomass conversion

CO_2 methanation

Dr Wen LIU (SRF, NTU, IRP1) has commissioned a flow chemistry system in the new lab and developed a palletisation method for sewage sludge powders. In addition, Dr Wen LIU (SRF, NTU, IRP1) has been working on the development of a continuous feed system and a batch feed system for the fluidised bed sewage sludge system.

Chunmiao JIA (PhD student, NTU, IRP1) conducted a comprehensive thermodynamics analysis of CO_2 hydrogenation to chemicals using the Gibbs free energy minimization method. The reaction systems with more than one product were also studied. This resulted into one paper being submitted. In addition, the fluidized bed modelling for CO_2 methanation was also demonstrated. The concentration profile of each component along the fluidized bed was obtained, and also the effect of some parameters including temperature, inlet flow rate and fluidized bed size. The CO_2 conversion, bubble size and reaction rate under corresponding condition along the fluidized bed height were also calculated.

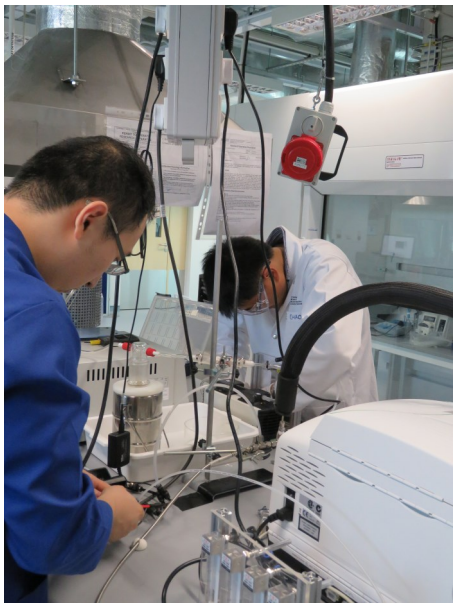
Biomass Conversion

Dr Yihu DAI (SRF, NTU, IRP1) et al. performed the selective oxidation of glucose to gluconic acid, which is a representative biomass conversion reaction, on a continuous flow reactor. Their previous works demonstrated that the CuO nanoleave catalyst revealed the superior activity and selectivity in single-batch conversion process, compared with supported Au nanoparticles and bimetallic Au-M (M=Ru, Cu, …) nanoparticles. However, the deactivation problem needs to be solved. By employing

continuous flow reactor, the oxidation of glucose and the regeneration of Cu sites into active CuO lattice can be coupled and controlleded. It can greatly boost the conversion rate of glucose-to-gluconic acid oxidation process. Several critical parameters such as retention time, sampling ratio were carefully investigated.

In addition, Dr DAI Yihu (SRF, NTU, IRP1) has been developing a design of novel CuO-based catalysts via doping Ce, Cr et al. to enhance the redox ability. The flow reactions and the catalysts can also be expanded to the direct oxidation of cellobiose and polymeric cellulose as biomass substances.

Dr HE Chao (RF, NTU, IRP1) *et al*. established and tested the catalytic CO_2 gasification setup fo simultaneous carbon reduction and sustainable energy generation for Cambridge CARES IRP1. In addition, Dr.HE Chao (RF, NTU, IRP1) contributed significantly to CARES - E2S2 joint proposal on gasification entitled “An Integrated Gasification - Carbon Abatement System for Manures and Municipal Solid Waste Management and Utilisation”.



Dr Paul Wen LIU (SRF, NTU, IRP1) and Dr HE Chao (RF, NTU, IRP1) at work in the C4T lab.

Furthermore, Dr HE Chao (RF, NTU, IRP1) conducted experiments pertaining to catalytic wet oxidation of humic substances using highly efficient Ni/ZrO_2 catalyst and prepared 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, NTU, IRP1) also performed experiments on conversion of wet biomass waste streams using Low-Carbon Technologies, which contributes to Carbon Reduction in IRP1. Based on the achievement, 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.

Dr HE Chao (RF, NTU, IRP1) developed one PCT patent (Application No: PCT/SG2016/050259) entitled “Method And System For Converting Biomass To Fuel Products”. A spin-off company ,Go Catalyst Pte Ltd , has been established in July. It mainly provides technical solutions to catalytic conversion. Currently, it is using patented catalysts to convert food wastes into fuels.

Work Package 3: New materials and MOFs

Project 1. Hierarchically structured graphene-based nanocomposites for CO_2 capture:

Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1) have been working on the development of a simple two-step strategy involving a self-assembly process and the subsequent thermal annealing treatment under inert gas is being developed for the synthesis of a class of hierarchically structured sandwich-like reduced graphene oxide (rGO)-based nanocomposites for high-performance CO_2 uptake. Benefitting from designed chemical and structural properties, including sandwich-like sheet-on-sheet architecture, sheets with abundant nanopores, high surface area, and monodisperse ultrafine MgO nanocrystallites, the as-obtained optimised rGO-based nanocomposites are able to display high CO_2 capture capacity, fast sorption rate, and long durability and recyclability.

Project 2. Porous carbon material for CO_2 adsorption:

Prof ZENG Hua Chun (PI, NUS, IRP1) and Dr LI Ping (RF, NUS, IRP1) have been working on the development of a class of heteroatom-doped porous carbon materials derived from metal-organic frameworks (MOFs)-based precursors via a facile synthetic route. The high specific surface area, nanoporous structure, and heteroatom doping effect endow the as-synthesised materials with abundant fully-exposed adsorption active sites, giving great potential for CO_2 uptake application. The work on the CO_2 uptake performance test is currently in progress.

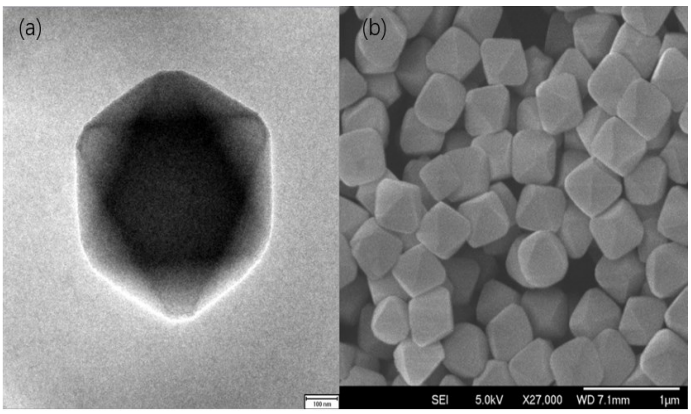


Figure 1. UiO-66 synthesized (a) TEM image of UiO-66 (b) FESEM image of UiO-66

In addition, QIN Runze (PhD student,NUS, IRP1) has been working on Metal-Organic Framework (MOF) materials. Metal-Organic Framework (MOF) materials have been hot research spot for many years for their tunable porosity, active catalytic site and high specific surface area. Among which UiO-66 raised much attention for its high capacity to store hydrogen and high tolerance for high temperature up to 400 ℃. As oxide of zirconium which constitutes the framework of UiO-66 can serve as excellent support for catalysts and meanwhile function as solid superacid which can be used to catalyze many common reactions such as Friedel-Craft alkylation, esterification and hydrolysis. We utilize UiO-66 to construct a nanoreactor which can both act as support for other valuable metals as catalysts and function as solid superacids. Moreover, the performance of solid superacid can be reinforced by addition of yttrium to form yttrium stabilized zirconia (YSZ).

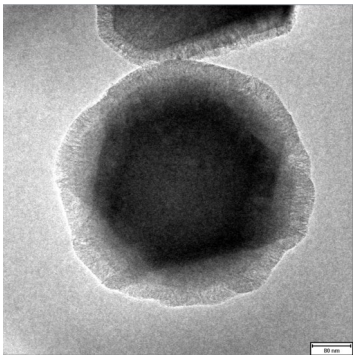


Figure 2. TEM image of UiO-66@mSiO₂

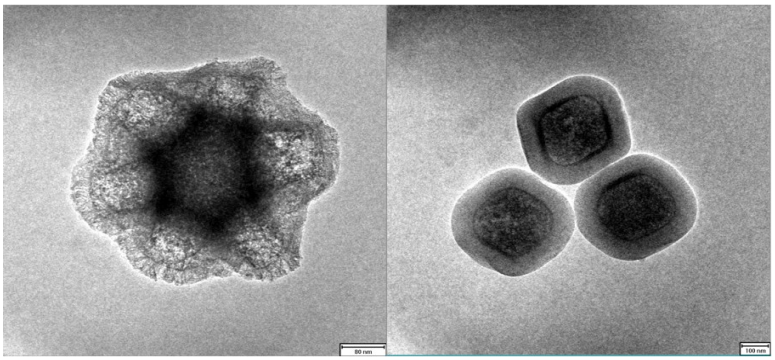
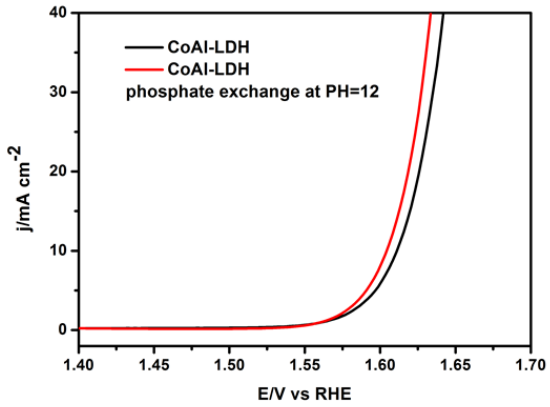
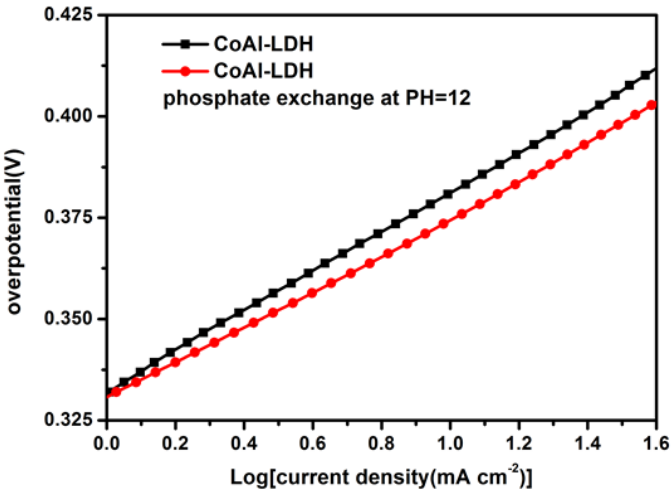


Figure 3. TEM images of two morphologies of YSZ@mSiO₂ formed

Firstly, UiO-66 is synthesized according to a previous paper after slight modifications to form octahedron morphology as shown in Figure. 1. Afterwards, a shell of silica is formed outside the original UiO-66 as Figure 2 shows. After that, calcination in Argon (20 mL/min) was conducted to remove the residual reactants in pores of UiO-66@mSiO2 with ramping rate of 1.5 ℃. After impregnation with yttrium nitrate, further calcination is conducted in air at 700 ℃ for 2 h. According to quantities of silica that wraps the UiO-66, two morphologies can be formed as shown in Figure 3. QIN Runze (PhD student,NUS, IRP1) is now testing the performance of this support as solid superacid. Moreover, some other metal can be loaded on our support to catalyze reactions to realize carbon dioxide reduction. Moreover, another project trying to develop a novel support for different MOFs as catalysts based on Dr. Sheng Yuan's work is also in progress.

Jingjing WANG (PhD student, NUS, RP1) has been working on making catalysts with more efficient performance in OER application through synthesizing nanoflower-like CoAl-LDH (Layered Double Hydroxide). It presents great potential for OER application due to its stable chemical property, large surface area and low cost. Then by simple liquid method, the anion of CoAl-LDH can easily be exchanged to phosphate, which significantly enhance its OER performance. More interestingly, it was discovered that this method can only enhance the performance of Co-based LDH. Jingjing WANG





(PhD student, IRP1, NUS) will continue to do more detailed research to find the inner mechanism for this.

Work Package 4: Multi-scale modelling

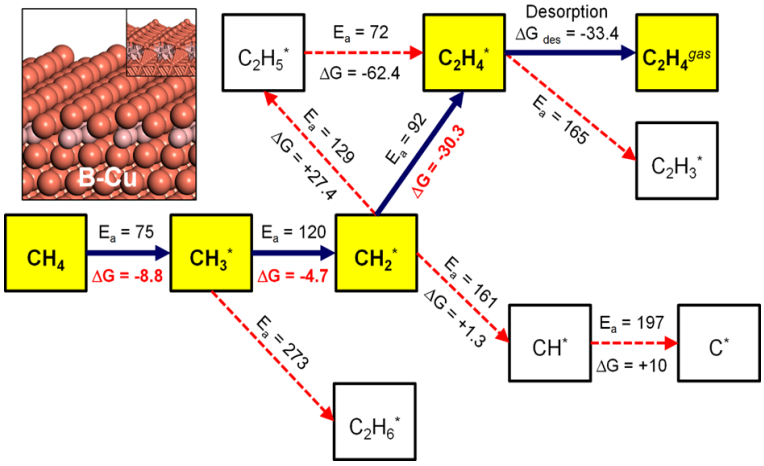
Dr. Liangqi ZHANG, (RF, NTU, IRP1), under the supervision of Prof. Jiawei CHEW (C0-PI, NTU, IRP1), has been dedicated to the mathematical description of the fluid dynamics with the coupling of the chemical reactions. Firstly, the application of the lattice Boltzmann method on the incompressible axisymmetric flow, which is widely encountered in engineering practices, has been investigated, and alternative axisymmetric LB models are proposed with better numerical performances. Secondly, various ways of describing the fluid structure interaction has been studied, such as the immerse boundary method, the CFD-DEM method, and the direct boundary conditions at the solid walls, and try to add the surface reaction processes into the CFD framework. Thirdly, application of the continuum hydrodynamic framework to the micro-scale and nano-scale gaseous flows, as well as the mass and heat transfer phenomenon, has also been investigated, the numerical description of the adsorption processes of CO2 in micro- and nano- channels is the further extension.

In addition, TRINH Quang Thang (RF, NTU, IRP1) *et al.* (including IRP1 NTU PI YANG Yanhui and IRP3 NTU Co-PI Samir H. MUSHRIF) have performed Density Functional theory calculations to guide the design of effective catalyst for methane conversion to bulk chemicals. In particular, motivated from recent studies using transition metals doped with boron, the structure and activity of a novel catalyst – Boron doped Copper (called B-Cu) was comprehensively evaluated in methane activation. In details, using first principles calculations, they predict that Copper catalyst, when doped with a monolayer of subsurface Boron (Cu-B), can efficiently activate the C-H bond of Methane and can facilitate the C-C coupling reaction, resulting in high selectivity towards C_2 hydrocarbons. The presence of the monolayer subsurface B creates corrugated step-like structure on Cu surface and significantly brings down the methane C-H activation barrier from 174 kJ/mol on Cu(111) to only 75 kJ/mol on Cu-B. Further analysis on Bader charge and Density of states reveal that there is a charge transfer from B to Cu, which synergistically promotes the C-H activation together with the geometrical/corrugation effect and makes the B-Cu as active for C-H activation as other expensive transition metals (Rh, Ru, Ir and Ni). The paper based on those results has been submitted and the abstract of this work has been accepted for oral presentation at the 2016 AIChE Annual meeting.

Furthermore, Dr Wen LIU (SRF, NTU, IRP1) has carried out methane dry reforming studies using novel catalysts as well as TPD and DRIFT studies of CO_2 adsorption on novel sorbents.

Challenges regarding to the reliable solids transport system and efficient heat integration still exist in the chemical looping combustion (CLC), which is mainly due to the complex geometry adopted, the multi-scale flow characteristics of gas-solid phase involved in the process. By resolving the gas and solid motion at different scale level, Dr. Shiliang YANG (RF, NTU, IRP1) *et al.* has numerically studied the dense gas-solid reactive flow involved in the spout-fluid bed, which is a kind of apparatus adopted in the CLC, to get a deep understanding on the particle transport phenomenon in this fluid-particle system and to understand the overall performance and cost potential of the spout-fluid bed so that the reactor performance and cost goals could be established. Specifically, the gas and solid flow is tracked using the computational fluid dynamics in combination with discrete ele-

ment method in the Eulerian and Lagrangian framework, respectively. Results regarding to the effect of draft plates on improving the flow stability of the gas-solid flow in this reactor have been analysed.



Work Package 5: Fundamentals of adsorption and PSA

Dr Mark John PURDUE (RF, NUS,I RP1) has completed a chemical engineering equipment design for a multi-purpose experimental vacuum swing adsorption rig in the pilot room of the CARES laboratory to investigate post-combustion CO_2 capture and concentration from wet flue gas. The ordering of equipment components from vendors has been completed with the administrative assistance of Ms. Janos Santos in CARES. A local engineering firm, assigned to construct the rig, visited CARES with representatives from mechanical, electrical and software control engineering. Various components to be used in the construction have begun to arrive in the pilot room. Additional time is required for all of the rig components to be delivered.

In the meantime, work is underway to establish a computationally inexpensive non-linear multicomponent adsorption isotherm model to characterize the behaviour of wet flue gas ($CO_2/N_2/H_2O$) on zeolite 13X using data points obtained from molecular simulation. Process simulation studies have begun to be implemented using Fortran programming and NAG mathematical libraries. A non-isothermal non-isobaric linear driving force model of a two-stage process involving separate moisture and carbon capture packed columns is being developed. The process model incorporates the finite volume method with the weighted essential non-oscillatory scheme to ensure rapid and robust solution of the resultant ODEs. Transient solutions are sought for ternary gas and adsorbent phase compositions, system temperatures and pressure in both the moisture capture and carbon capture columns. The process metrics include purity, recovery, energy consumption and productivity that are depicted in two Pareto curves for given process conditions.

Simulated results shall be experimentally investigated using the aforementioned rig, in addition to experimental validation of the adsorption isotherm data points using dynamic column breakthrough measurements.

Dr Mark PURDUE (RF, NUS, IRP1) discusses his work with Prof Claire ADJIMAN (SAC member)

A techno-economic optimization study of the process is in preparation to minimize the levelized cost of electricity associated with power plants equipped with the proposed VSA technology, while targeting regulatory constraints of 95% purity and 90% recovery with respect to CO_2. The process modelling aims to establish a parameterized VSA process cost benchmark that is further planned to be parameterized by a variation in future fuel prices, CO_2 storage cost, potential CO_2 feedstock

price, weighted average cost of capital and taxation policies.

Other Activities and Achievements

- IRP1 prepared one Technology Disclosure (NTU Ref: TD/312/15) on "Nickel Catalyst for High Efficient Destruction of Humic Substances Using Catalytic Wet Oxidation". A further Singapore Patent entitled " Efficient Energy Recovery from Wet Biomass Waste Streams Using a Two-Stage Hydrothermal Conversion System" is under further conversion and commercialisation .
- IRP1 filed one PCT Patent (2 June 2016) entitled "Method And System For Converting Biomass To Fuel Products". A spin off company has also been founded.
- IRP1 work has been presented at the 16th International Congress on Catalysis, July 3—8 Beijing, P.R. China and at Energy Innovation 2016, Suntec Singapore Convention and Exhibition Centre, Singapore.

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.

An Alternative Synthetic Approach for Macro-Meso-Microporous Metal–Organic Framework via 'Domain Growth' Mechanism

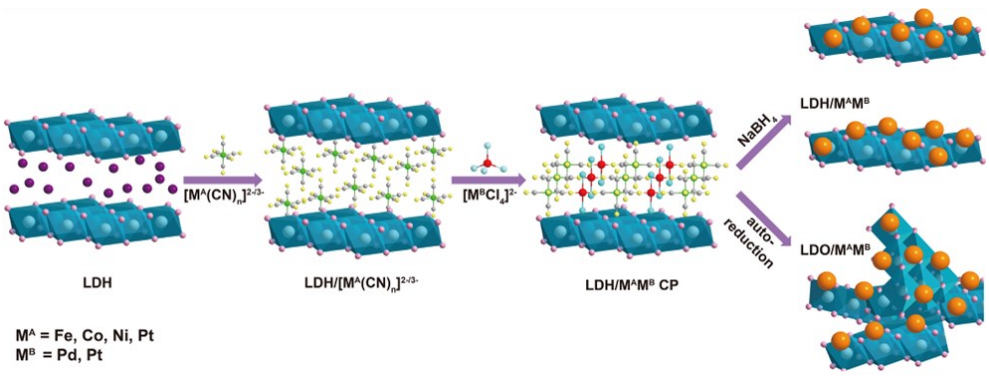
Zhan, Guo Wu; Zeng, Hua Chun

DOI: 10.1039/C6CC03555H

Abstract:

A nanoscale "domain growth" mechanism was proposed based on experimental facts to describe the formation process of macro-meso-microporous HKUST-1 with 3-dimensional networks. Metal-organic frameworks (MOFs) have shown vast potential in adsorption and catalysis applications, especially when larger pores (> 2 nm) are introduced into their matrices. Herein, we report our recent synthesis of 3-dimensional networks of HKUST-1 via an one-pot chemical and structural transformation of cuprite nanocubes in the presence of 1,3,5-benzenetricarboxylic acid ligands under mild conditions (room temperature, ambient pressure, and short time). Different from soluble metal salts in homogeneous solution, the sacrificial cuprite nanocubes in solid-phase act as isolated domains and provide copper cations in spatially and temporally controlled ways. A nanoscale "domain growth" mechanism was proposed based on experimental facts to describe the formation process of macro-meso-microporous HKUST-1 with 3-dimensional networks. Importantly, effective accessibility and high Lewis acidity of the hierarchically porous HKUST-1 matrices have been verified by organic dye adsorption and catalytic synthesis of quinoxaline, respectively.

Ultrafine Alloy Nanoparticles Converted from 2D Intercalated Coordination Polymers for Catalytic Application



Synthesis procedure for LDH/LDO-supported multimetallic alloy NPs.

Li, Ping; Zeng, Hua Chun

DOI: 10.1002/adfm.201601174

Highlights:

- Two-dimensional (2D) cyanide bridged coordination polymers (CP) are formed in the confined space of layered materials.
- Ultrafine alloy NPs can be prepared with high particulate uniformity and compositional tailorability.
- Supported binary alloy NPs and ternary alloy NPs have been successfully synthesized with this approach.
- The above new catalysts have shown excellent activity for carbon-carbon cross coupling reactions.

Abstract:

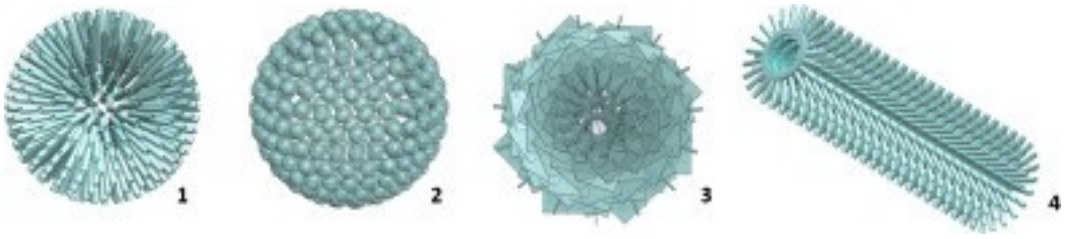
Supported multimetallic alloy nanoparticles (NPs) have shown great potential for applications owing to combined functions of constituent metals, and more remarkably, enhanced physicochemical

properties and even novel synergistic effects that are not possessed by their parent metals. Nevertheless, synthesizing this kind of nanocomposites has been a long-standing challenge using conventional wet chemistry. Here, this study reports an efficient, versatile strategy for the preparation of multimetallic alloy NPs supported by layered double hydroxides (LDH) and/or layered double oxides (LDO). In this approach, different metal precursors are intercalated stepwise into the gallery space of LDH. Along with the coordination reaction between the metal precursors, 2D cyanide bridged coordination polymers (CP) are formed in the confined space. Afterward, supported multimetallic alloy NPs can be obtained via either liquid-phase reduction or thermal autoreduction. Due to the homogeneous mixing of metals in the 2D CP, ultrafine alloy NPs can be obtained with high particulate uniformity and compositional tailorability. A large series of supported binary alloy NPs (FePd, FePt, CoPd, CoPt, NiPd, NiPt, and PtPd) and ternary alloy NPs (FePdPt, FeNiPt, FeCoPt, and NiCoPt) are successfully synthesized with this approach. The resulting supported multimetallic alloy NPs present great potential in numerous applications. To demonstrate their workability, one class of LDH/NiPd nanocomposite is explored as a model heterogeneous catalyst with respect to the carbon –carbon cross-coupling reactions (Suzuki–Miyaura, Heck, and Sonogashira cross-coupling reactions).

Integrated Nanocatalysts with Mesoporous Silica/Silicate and Microporous MOF Materials

Zhan, Guowu; Zeng, Huachun

DOI: 10.1016/j.ccr.2016.03.003



Typical hierarchically structured metal silicates: (1) "tubes in a sphere", (2) "bubbles in a bubble", (3) "sheets in a sphere", and (4) "tubes in a tube", where hollow cavities are in the center of each assembled structure.

Abstract:

Integrated nanocatalysts (INCs) with multicomponent and hierarchically complex structures have recently drawn extensive research attention in terms of their fundamental sciences and industrial applications. To date, many innovative strategies have been established for the synthesis of INCs by thoughtful design. The aim of this review is to highlight the state-of-the-art of INCs with different porous materials for catalyst technology and heterogeneous catalysis. In the first part of this review, we briefly introduce catalytic active components (mainly metal, metal oxide, and hybrid nanoparticles) that are commonly used in INCs. Combining such active components with various porous materials provides us a huge array of architectural designs for INCs that can be used in chemical reactions. In choosing host materials for INCs, we focus on the mesoporous siliceous materials (viz., silica and metal silicates) and microporous metal-organic frameworks (MOFs), since they represent the two most attractive classes of porous materials known today. In the latter parts of this article, therefore, we review the recent developments of INCs which comprise these mesoporous and microporous solids with special emphasis on their roles as supports, encapsulating shells, and metal sources. Examples described here are drawn from our group and others; future research directions are also discussed.

DEM Study of Granular Flow Characteristics in the Active and Passive Regions of a Three-dimensional Rotating Drum

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

DOI: http://dx.doi.org/10.1002/aic.15315

Abstract:

Three-dimensional modeling of the solid motion in a lab-scale rotating drum has been conducted via

the discrete element method (DEM). After validating the simulated results with available experimental data, the active-passive interface was identified, following which particle-scale information in these two regions, in particular the influences of fill level and rotating velocity, were obtained. The results demonstrate that: (i) the total number of particles in the passive region is three times that in the active, (ii) the transverse and axial velocities span a wider range in the active region, with the transverse values being greater, (iii) the collision force is much higher in the active region, with the greatest magnitudes in the y-direction relative to that in the x- and z-directions, (iv) particle displacements are generally lower and have a narrower distribution in the active region, (v) the local solid residence time (SRT) distribution profiles are similar axially in that the highest SRT magnitudes are at the center region of the bed, while the other parts of the bed have uniform SRT magnitudes.

Transition Ions Induced Coalescence: Stitching Au Nanoclusters into Tubular Au-Based Nanocomposites

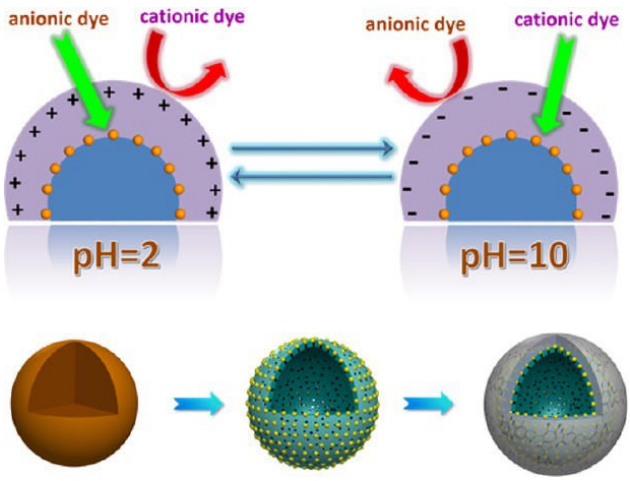
Zhou, Yao; Zeng, Hua Chun

DOI: 10.1002/smll.201503881

Abstract:

Rod-shaped assemblages of Au nanoclusters (AuNCs) can serve as self-templating solid precursors to produce tubular Au-based nanocomposites via the coalescence induced by transition metal ions. Specifically, when the AuNC assemblages react with transition metal ions with relatively high standard oxidation potentials such as Cu(II), Ag(I), Pd(II), and Au(III), a series of polycrystalline and ultrathin Au and AuxMy (where M = Cu, Ag, and Pd) alloy hollow nanorods (HNRs) can be obtained with further reduction; these metallic products are evaluated for electrooxidation of methanol. Alternatively, the above transition metal ions-induced transformations can also be carried out after coating the AuNC assemblages with a layer of mesoporous SiO2 (mSiO2), giving rise to many mSiO2-coated Au-based HNRs. Onto the formed AuPd0.18 alloy HNRs, furthermore, a range of transition metal oxides such as TiO2, Co3O4, and Cu2O nanocrystals can be deposited easily to prepare metal oxide–AuPd0.18 HNRs nanocomposites, which can be used as photocatalysts. Compared with those conventional galvanic replacement reactions, the controlled coalescence of AuNCs induced by transition metal ions provides a novel and efficient chemical approach with improved element efficiency to tubular Au-based nanocomposites.

Charge-Switchable Integrated Nanocatalysts for Substrate-Selective Degradation in Advanced Oxidation Processes



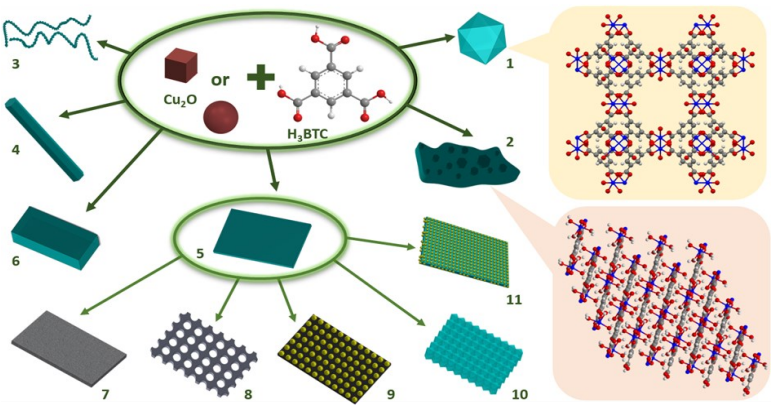
Zhan, Guowu; Zeng, Hua Chun

DOI: 10.1021/acs.chemmater.6b01128

Abstract:

Substrate-selective catalysis is highly desirable in pharmaceutical and petrochemical industries. To pursue the goal, basically, catalysts should have the ability to recognize and screen their substrates by shape, size, charge, or hydrophobicity/hydrophilicity matching. In this contribution, we design a new type of integrated nanocatalyst, which shows selective catalytic activities toward substrates carrying different charges. More significantly, such “smart” catalysts possess switchable surface charges under different pH environments, and thus, the catalytic performance with controllable substrate selectivity can be achieved. These integrated nanocatalysts encompass three basic components: (i) metal nanoparticles serving as catalytically active centers for chemical reactions (i.e., 4

nm Pt); (ii) charge-switchable polymer shell (i.e., polydopamine layer, PDA) working as dual-function membrane (i.e., screening substrates and protecting metal catalysts underneath); and (iii) carrier material providing large reaction area/space (i.e., hollow mesoporous support, such as Mn, Fe, Co, Ni silicates) for immobilization of metal catalysts. Importantly, in a typical advanced oxidation process (AOP), the exemplary nanocatalyst Pt/MnSi@PDA shows selective degradation of cationic dyes (e.g., rhodamine 6G, methylene blue) at pH values higher than the isoelectric point (IEP = 3.1), whereas anionic dyes (e.g., Congo red, methyl orange, thymol blue) were degraded preferably at pH values lower than the IEP.



Schematic illustrations of controlled syntheses of MOF-based functional materials, starting with cubic or spherical Cu_2O particles as a metal source and H_3BTC as ligands: (1) octahedral HKUST-1, (2) shape-uncontrolled Cu (HBTC)-1, (3) 1D Cu(HBTC)-1 nanofibers, (4) 1D Cu (HBTC)-1 nanorods, (5) 2D Cu(HBTC)-1 nanosheets, (6) doped 2D Cu(HBTC)-1 nanocuboids, (7) 2D assemblage of CuO nanoparticles, (8) 2D assemblage of CuO-Cu_2O, (9) carbon-supported 2D nanocatalysts of copper, (10) 2D assemblage of HKUST-1, and (11) Cu (HBTC)-1 supported 2D nanocatalysts of noble metals. Ball and sticks models of HKUST-1 (right top) and Cu(HBTC)-1 (right bottom) structures, viewed from the [010] direction. Blue, red, gray, and white spheres represent Cu, O, C and H atoms, respectively.

Synthesis and Functionalization of Oriented Metal-Organic Framework Nanosheets: Toward a Series of Two-dimensional Catalysts

Zhan, Guowu; Zeng, Huachun

DOI: 10.1002/adfm.201505380

Highlights:

- A facile route at room temperature and ambient pressure has been developed for the preparation of low dimensional copper based MOFs.
- The as-prepared 2D MOF nanosheets provide a material platform to the fabrication of 2D supported metal nanocatalysts.
- The copper MOF nanosheets can serve as a self-templating solid precursor to prepare different oxide nanocomposites.
- Ultrafine transition metal and noble metal nanoparticles can be anchored on the surfaces of the MOF nanosheets.
- Catalytic activities of the derived catalysts have been evaluated for CO_2 hydrogenation and 4-nitrophenol reduction in gas phase and liquid phase, respectively.

Abstract:

Synthesis of metal–organic frameworks (MOFs) is based on coordination-driven self-assembly of metal ions and organic ligands. However, to date, it remains difficult to adjust the coordination behaviors of MOFs and then control geometric shapes of nanostructures; especially their morphologies in 1D nanofibers or 2D nanosheets have seldom been explored. Here, a facile route at room temperature and ambient pressure is reported for the preparation of copper-based MOFs with low-dimensional shapes (i.e., nanofibers, nanorods, nanosheets, and nanocuboids), via thermodynamic and kinetic controls over the anisotropic growth. Importantly, the as-prepared 2D MOF nanosheets with monocrystalline nature (100% exposed {010} facets) provide a material platform to the fabrication of 2D supported metal nanocatalysts. First, the MOF nanosheets can serve as a self-templating solid precursor to prepare different CuO and CuO-Cu2O nanocomposites, or even Cu metals via thermolysis or reduction under controlled atmospheres. Upon their formation, second, ultrafine noble metal nanoparticles (e.g., Au, Ag, Pt, Pd, Au0.4Pt0.6, Au0.4Pd0.6, and Au0.3Pt0.3Pd0.4) can be exclusively anchored on the external surfaces of the MOF nanosheets. To show their open accessibility, catalytic activities of the derived catalysts have been evaluated using CO2 hydrogenation and 4-nitrophenol reduction in gas phase and liquid phase, respectively.

In situ studies of materials for high temperature CO2 capture and storage

Dunstan, Matthew; Maugeri, Serena; Liu, Wen; Tucker, Matthew; Taiwo, Oluwadamilola; Gonzalez, Belen; Allan, Phoebe; Gaultois, Michael; Shearing, Paul; Keen, David; Philips, Anthony; Dove, Martin; Scott, Stuart; Dennis, John; Grey, Clare

DOI: 10.1039/C6FD00047A

Abstract:

Carbon capture and storage (CCS) offers a possible solution to curb the CO2 emissions from stationary sources in the coming decades, considering the delays in shifting energy generation to carbon neutral sources such as wind, solar and biomass. The most mature technology for post-combustion capture uses a liquid sorbent, amine scrubbing. However, with the existing technology, a large amount of heat is required for the regeneration of the liquid sorbent, which introduces a substantial energy penalty. The use of alternative sorbents for CO2 capture, such as the CaO-CaCO3 system, has been investigated extensively in recent years. However there are significant problems associated with the use of CaO based sorbents, the most challenging one being the deactivation of the sorbent material. When sorbents such as natural limestone are used, the capture capacity of the solid sorbent can fall by as much as 90 mol % after the first 20 carbonation-regeneration cycles. In this study a variety of techniques were employed to understand better the cause of this deterioration from both a structural and morphological standpoint. X-ray and neutron PDF studies were employed to understand better the local surface and interfacial structures formed upon reaction, finding that after carbonation the surface roughness is decreased for CaO. In situ synchrotron X-ray diffraction studies showed that carbonation with added steam leads to faster and more complete conversion of CaO than under conditions without steam, as evidenced by the phases seen at different depths within the sample. Finally, in situ X-ray tomography experiments were employed to track the morphological changes in the sorbents during carbonation, observing directly the reduction in porosity and increase in tortuosity of the pore network over multiple calcination reactions.

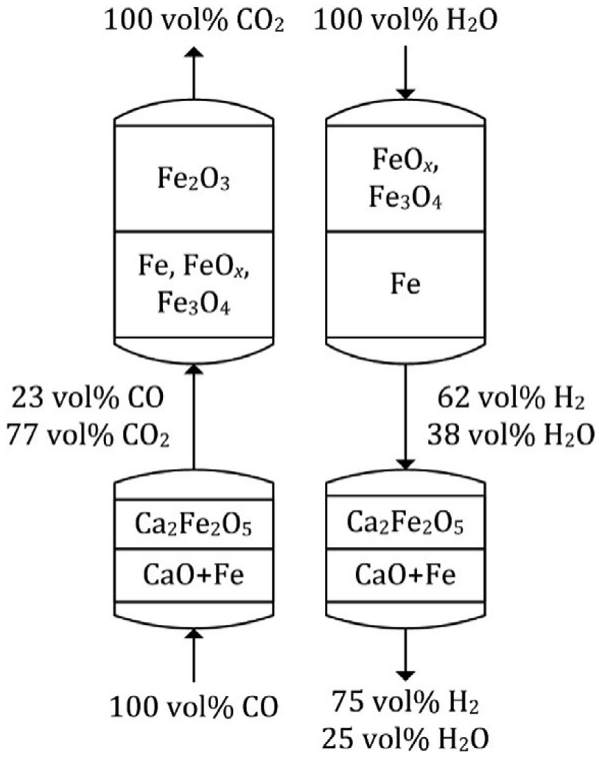


Illustration of the polishing concept in combination with reversal of the flows operating at 1123 K. The flow direction during reduction (left) and oxidation (right) are reversed in order to maximise the conversion of the feed gases.

Improving hydrogen yields, and hydrogen: steam ratio in the chemical looping production of hydrogen using Ca 2 Fe 2 O 5

Chan, Martin SC; Liu, Wen; Ismail, Mohammad; Yang, Yanhui; Scott, Stuart; Dennis, John

DOI: 10.1016/j.cej.2016.03.132

Abstract:

A thermodynamic property of Ca2Fe2O5 was exploited to improve the efficiency of the steam-iron process to produce hydrogen. The ability of reduced Ca2Fe2O5 to convert a higher fraction of steam to hydrogen than chemically unmodified Fe was demonstrated in a packed bed. At 1123 K, the use of Ca2Fe2O5 achieved an equilibrium conversion of steam to hydrogen of 75%, in

agreement with predicted thermodynamics and substantially higher than that theoretically achievable by iron oxide, viz. 62%. Furthermore, in Ca2Fe2O5, the full oxidation from Fe(0) to Fe(III) can be utilised for hydrogen production – an improvement from the Fe to Fe3O4 transition for unmodified iron. Thermodynamic considerations demonstrated in this study allow for the rational design of oxygen carriers in the future. Modifications of reactors to capitalise on this new material are discussed.

Numerical investigation on the effect of draft plates on spouting stability and gas–solid characteristics in a spout-fluid bed

Yang, Shiliang; Sun, Yuhao; Zhang, Liangqi; Zhao, Ya; Chew, Jia Wei

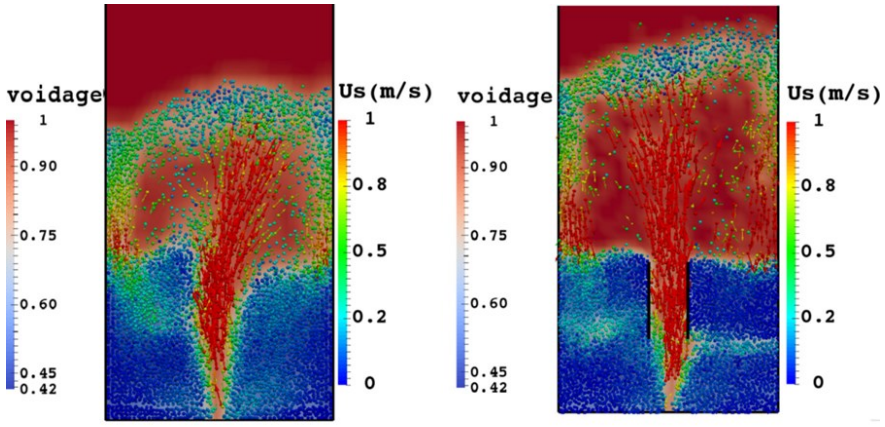
DOI: http://dx.doi.org/10.1016/j.ces.2016.03.010

Highlights:

- Spouting stability in a spout-fluid bed was investigated via CFD–DEM.
- Impact of draft plate with different lengths on improving spouting stability.
- Draft plates affect gas–solid hydrodynamics in spout, annulus and fountain.
- Cause of the dancing spout rooted in bubbles merging with spouting channel.
- Draft plate length optimized by balancing spout stability and solid circulation rate.

Abstract:

Numerical simulation of dense gas–solid motion in a spout-fluid bed was carried out using the computational fluid dynamics coupled with discrete element method (CFD–DEM), in which the gas and solid motion are solved in the Eulerian and Lagrangian framework, respectively. After validating the simulated results with experimental data, the main cause of spouting instability was first identified, followed by evaluating the effect of draft plate length on spouting stability, pressure signals, and gas–solid hydrodynamics in the system. The results demonstrate that the onset of spout dancing, which is a type of spouting instability, is primarily due to the merging of the rising bubbles in the annulus with the spouting channel, which can be circumvented by the presence of draft plates. Increasing the draft plate length diminishes the mean pressure in the spouting inlet and the corresponding peak value of the power spectrum, and the correlation coefficient of pressure signals in the spout and background inlets. Regarding effect on the gas–solid hydrodynamics, a longer draft plate length leads to a more dilute upper spout, a higher spoutable height, higher voidage in the central fountain region, higher vertical gas flux (Fgz) and solid velocity (Usz) in the central axis, lower Fgz and Usz near the wall, and lower vertical solid flux (Fsz) overall. The optimization of the draft plate length depends on a balance between spout stability and solid circulation rate, since the former increases but the latter decreases with draft plate length.



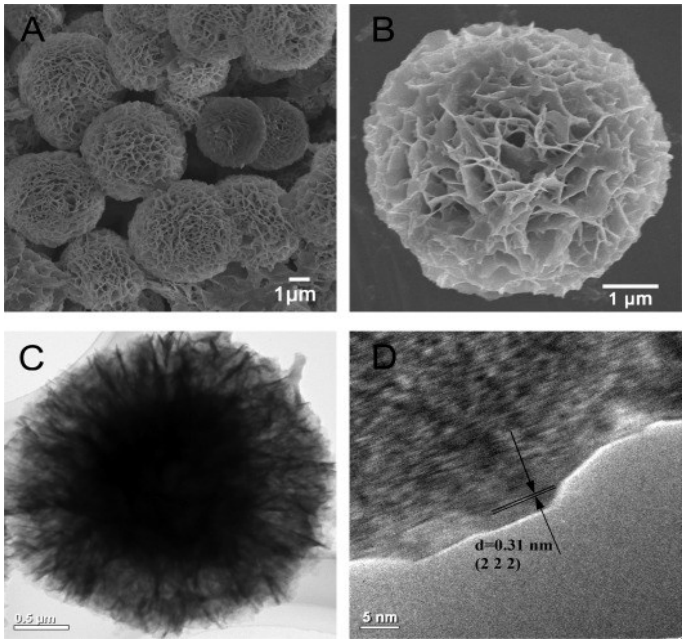
Synthesis, Application, and Carbonation Behavior of Ca2Fe2O5 for Chemical Looping H2 Production

Ismail, Mohammad; Liu, Wen; Chan, Martin S.C.; Dunstan, Matthew T.; Scott, Stuart A.

DOI: 10.1021/acs.energyfuels.6b00631

Abstract:

Chemical looping hydrogen production uses the oxidation and reduction of metal oxides, typically iron, to produce hydrogen. This work focuses on the modification of iron oxide with calcium oxide to form an oxygen carrier containing dicalcium ferrite (Ca2Fe2O5), which presents favorable thermodynamics for achieving higher conversions of steam to hydrogen, compared to chemically unmodified iron oxide. Different methods of synthesis, viz. mechanochemical synthesis and coprecipitation, were used to produce Ca2Fe2O5, and their resulting performances were compared. Consistent with thermodynamic predictions, it was found that CO2, or steam, was sufficient to fully regenerate the reduced carriers to Ca2Fe2O5. The cyclic stability of the oxygen carriers were studied in fluidized bed reactors and by thermogravimetric analysis (TGA). Good stability of the materials was observed for up to 50 cycles, with no evidence of agglomeration, even up to 950 °C. The rate of deactivation was found to correlate with the purity of Ca2Fe2O5 and the presence of impurity phases such as CaFe2O4, which had a tendency to segregate into its constituent elemental oxides. Carbonation of the oxygen carriers was examined by TGA, and it was found to occur appreciably only for the reduced carrier (a mixture of CaO and Fe) between temperatures of 500–700 °C and 0.1–0.5 atm of CO2, whereas the oxidized carrier (viz. Ca2Fe2O5) did not carbonate. Fresh and cycled materials were characterized by XRD, SEM, and BET analysis. Ca2Fe2O5 is a potentially viable material as an oxygen carrier for hydrogen production; however, because of thermodynamic limitations, it cannot be used for complete fuel oxidation.



Synthesis of 3D mesoporous samarium oxide hydrangea microspheres for enzyme-free sensor of hydrogen peroxide

Yibo Yan; Kaixin Li; Yihu Dai; Xiaoping Chen; Jun Zhao; Yanhui Yang; Jong-Min Lee

DOI: 10.1016/j.electacta.2016.05.037

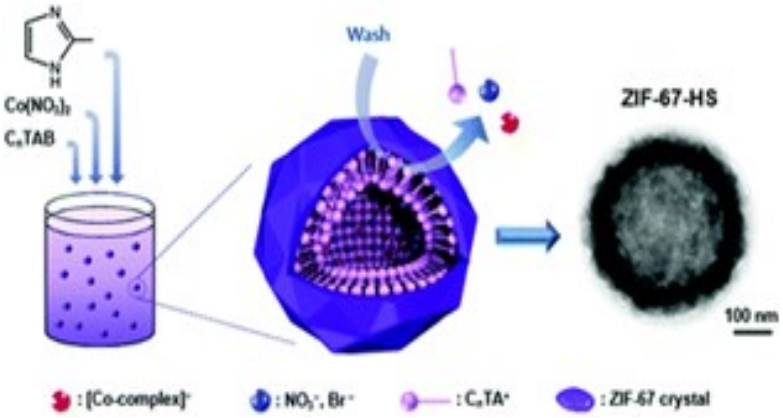
Abstract

A novel 3D mesoporous Sm2O3 hierarchical hydrangea microspheres sensor has been developed and investigated for highly sensitive electrochemical detection of hydrogen peroxide (H2O2). Their morphology and structure were observed by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) isotherms and the Barret-Joyner-Halenda (BJH) measurements. This stable non-enzymatic sensor was found to capable of implementing H2O2 detection in a wide linear range from 1 to 320 mu M with a linear correlation coefficient (R) of 0.997. It presents an ultrahigh sensitivity of 20.5 mu A mM(-1), a remarkably low detection limit of similar to 1 mu M (signal/noise = 4), as well as a prompt response attaining 95% of steady current within 3s. As such, the Sm2O3 hierarchical hydrangea microspheres are considered one of the remarkably prominent sensors for the detection of hydrogen peroxide in biological diagnosis, food and environmental monitoring.

Consistent lattice Boltzmann methods for incompressible axisymmetric Flows

Liangqi ZHANG, Shiliang Yang; Jia Wei Chew

DOI: http://dx.doi.org/10.1103/PhysRevE.94.023302



Abstract:

In this work, consistent lattice Boltzmann (LB) methods for incompressible axisymmetric flows are developed based on two efficient axisymmetric LB models available in the literature. In accordance with their respective original models, the proposed axisymmetric models evolve within the framework of the standard LB method, and the source terms contain no gradient calculations. Moreover, the incompressibility conditions are realized with the Hermite expansion, thus the compressibility errors arising in the existing models are expected to be reduced by the proposed incompressible models. Besides, an extra relaxation parameter is added to the BGK collision operator to suppress the effect of the ghost variable, and thus the numerical stability of the present models is significantly improved. Theoretical analyses, based on the Chapman-Enskog expansion and the equivalent moment system, are performed to derive the macroscopic equations from the LB models, and the resulting truncation terms (i.e., the compressibility errors) are investigated. In addition, numerical validations are carried out based on four well-acknowledged benchmark tests, and the accuracy and applicability of the proposed incompressible axisymmetric LB models are verified.

Self-templating Synthesis of Hollow Spheres of MOFs and Their Derived Nanostructures

Tan, Ying Chuan; Zeng, Hua Chun

DOI: 10.1039/C6CC05699G

Abstract:

An aqueous one-pot self-templating synthesis method to prepare highly uniform ZIF-67 hollow spheres (ZIF-67-HS) and their transition metal-doped derivatives (M/ZIF-67-HS, M = Cu and/or Zn) was developed. Extension of this approach to another important class of MOFs (metal carboxylates; *e.g.*, HKUST-1) and facile design of derived nanostructures with complex architectures were also achieved.

Controlled Synthesis of 3D Nanoplate-Assembled La2O3 Hierarchical Microspheres for Enzyme-Free Detection of Hydrogen Peroxide

Yibo Yan; Kaixin Li; Yihu Dai; Jun Zhao; Xiaoping Chen; Yong Yan; Jijiang Huang; Yanhui Yang; Jong-Min Lee

DOI: 10.1002/admi.201500833

Abstract:

Novel 3D mesoporous La2O3 hierarchical microspheres for the enzyme-free electrochemical detection of hydrogen peroxide are developed via 3D nanoplate-assembling for a novel electrode architecture.

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

October 2016

3.2.1 IRP2 Research Overview

The electrochemistry programme is focused on the prevention of CO_2 emissions in process industries through the exploitation of a key reagent, the electron, from renewable, clean electricity supplies. Electrochemical processes which can harness these clean electron supplies have been employed successfully in a selected range of chemical and energy storage industries (eg the chloroalkali industry). It is well established that electrochemical technologies can provide cost-effective, environmentally friendly and highly controllable industrial processes for chemical production and in recent years there has been a considerable renewal in the development of industrial pilot plant scale production of a range of commodity chemicals.

The IRP2 programme has a tight focus in three core areas; (i) the development of methods and tools which can provide a clearer and quantitative understanding of the processes which limit efficient electrical conversion, with the target of improving the overall efficiency of a given chemical production route. (ii) the development of improved catalysts, electrode architectures and electrical connectivity to ensure optimal conversion rates for a process of interest and (iii) the development of integrated reactor systems which explore new routes and processes for the synthesis of chemical products.

In the current reporting period significant developments have been reported throughout the core activities. In collaboration with Prof Erik BIRGERSSON at NUS, new protocols are under development to investigate electrical waveforms which can be used to study in a more discriminating manner the pathways of electrochemical reactions. These are linked closely to concepts such as identifiability which are more commonly found in the area of predictive electrical control. This work has led to advanced discussions with members of the IRP4 team and we will be exploring potential collaborations in this area.

In the catalyst design and reactor development, Dr Yizhong LU's (RF, NTU, IRP2) recent work has developed a generalized strategy to synthesize highly monodisperse, surfactant-free octahedral PtxNi1-x nanopar-ticles with tunable surface structure and composition. By exploring the increasing Ni content in the bulk composition, the degree of concaveness of octahedral PtxNi1-x nanoparticles increases. Currently this research has been systematically used to study the correlation between their surface structure/composition and their observed oxygen reduction activity.

Participants of the Masterclass: Advanced Electrochemical Techniques Programme (AETP)

In an ongoing industrial collaboration Dr Peng SONG (RF, Cambridge IRP2) has been working in the area of electrochemical monitoring using an advanced strategy by exploiting the catalytic EC' mechanism. The work has detailed the potential sensitivity of the strategy and led to a joint industrial publication in RSC Advances. Dr Peng SONG ((RF, Cambridge IRP2).

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 outreach activities have been further extended. In July 2016 a Masterclass programme was delivered in the CREATE C4T laboratories. This programme attracted stakeholders from local industry, CREATE programmes, local universities and international visitors from Thailand and the Philippines. We are already in advanced discussions to extend this series on 2016 in the UK and develop further activities in 2017 in Singapore.

3.2.2 Update on work packages

Work Package 2.1 Numerical Multi-Scale Electrochemical Modelling and Analysis

It is essential that the design of an electrochemical reactor has to be evaluated and optimised in order to be scaled from a lab scale to a commercial production scale. An understanding of the mechanism of various electrochemical processes that happen within the reactor may help in the optimisation of the reactor design. The reaction mechanisms of such electrochemical processes can be studied with greater confidence by employing various electroanalytical tools such as rotating disk electrode, rocking disk electrode and so on. It has been established that the comprehension of the mechanisms is more effective employing an alternating current (of a specific frequency ω) superimposed on to a DC wave than employing just an aperiodic wave. Whence, AC voltammetry is an important technique that is exercised to investigate such mechanisms. AC voltammetry when performed with large- amplitudes brings to light about eight AC harmonic responses in addition to the fundamental AC frequency and aperiodic (DC) response. Though the experimental existence of such responses were validated through numerical simulations, to our knowledge, there is no analytical proof available. We attempt to elucidate the analytical solution for such studies by approaching the system through simple test cases with increasing order of complexity. The mathematical approach involves the transformation of the system to frequency domain by the introduction of a phasor. The test cases are formulated by considering a simple diffusion equation and the intricacy of the problem is included by the manipulation of the boundary condition. We consider a definite length of the electrode surface L for all our analyses.

Test Case 1- Introduction of phasors:

1 Mathematical Formulation

We consider the following system of equations:

$$c_t = Dc_{xx}, \tag{1a}$$

$$c(0,t) = 0 \tag{1b}$$

$$c(L,t) = c_0 cos(\omega t + \varphi) \tag{1c}$$

$$c(x,0) = 0 \tag{1d}$$

Note: Here, we may get negative concentrations during the simulation since the initial concentration is taken as 0. But this test case is purely to experiment with the mathematics; hence this can be ignored.

2 Analysis

By postulating that the solution for the concentration, c is sinusoidal in nature, we write

Defining a phasor, *C(x)*, for the concentration as

$$c(x,t) = \mathfrak{M}_c(x) cos(\omega t + \varphi + \mathfrak{P}_c(x)) \tag{2}$$

$$= \Re\left(\mathfrak{M}_c(x) e^{i(\omega t+\varphi)} e^{i\mathfrak{P}_c(x)}\right)$$

$$C(x) = \mathfrak{M}_c(x)e^{i\mathfrak{P}_c(x)} \tag{2a}$$

and introducing it into Eq. 2, we obtain

$$c(x,t) = \Re\left(C(x)e^{i(\omega t+\varphi)}\right) \tag{2b}$$

$$\frac{dc}{dt} = i\omega\Re\left(Ce^{i(\omega t+\varphi)}\right) = i\omega c \tag{2c}$$

We further note that we can now introduce complex conjugate (c.c) and rewrite Eq.2 as

$$c(x,t) = \frac{1}{2}C(x)e^{i(\omega t+\varphi)} + \frac{1}{2}C(x)e^{-i(\omega t+\varphi)} \tag{2d}$$

$$= \frac{1}{2}C(x)e^{i(\omega t+\varphi)} + c.c$$

$$\frac{dc}{dt} = \frac{1}{2}i\omega C(x)e^{i(\omega t+\varphi)} - i\omega(c.c) = i\omega c - i\omega(c.c) \tag{2e}$$

Here the equation with the complex conjugate (c.c) is redundant and hence can be dropped. The governing equation now becomes

$$i\omega c = Dc_{xx} \tag{3a}$$

$$c(0) = 0 \tag{3b}$$

$$c(L) = c_0 \tag{3c}$$

The key advantage here is that we have reduced a one dimensional partial differential equation to an ordinary one. Solving Eqns. 3(a)- 3(c) analytically as:

$$\mathbf{c} = \boldsymbol{c_1 e^{(\sqrt{\Theta}x)} - e^{(-\sqrt{\Theta}x)}} \tag{5}$$

where

$$\boldsymbol{c_1} = \frac{\boldsymbol{c_0}}{\boldsymbol{e^{(\sqrt{\Theta}L)} - e^{(-\sqrt{\Theta}L)}}} \tag{5a}$$

$$\Theta = \frac{i\omega}{D} \tag{5b}$$

3 Validation

Validation is carried out in COMSOL Multiphysics by solving the time- dependent system of equations and frequency- formulated counterpart numerically and then comparing them with the analytical solution; see Fig. 1 and Fig. 2.

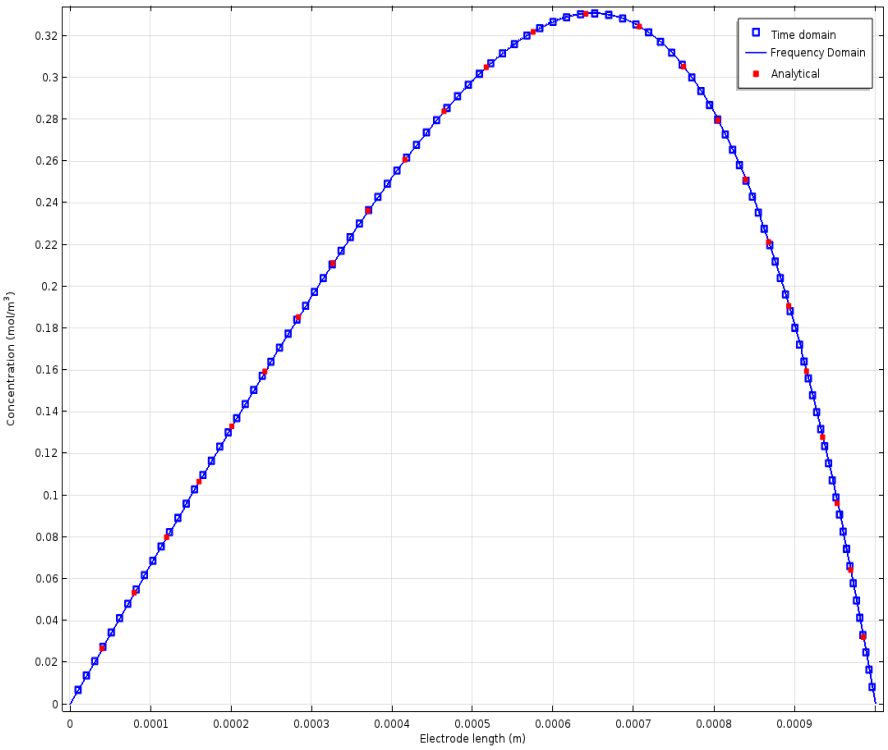
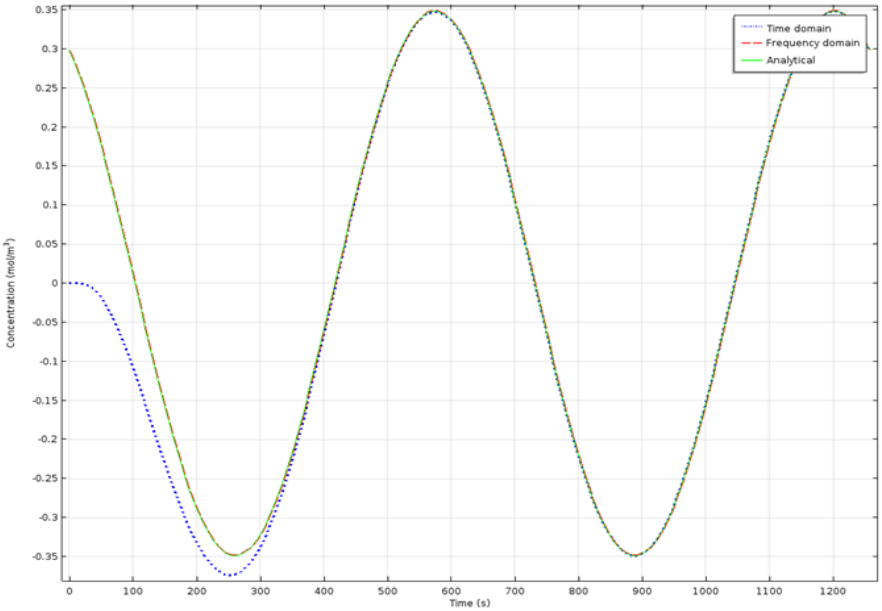


Figure 1. (right) Validation for test case 1

Figure 2. (below) Concentration vs time plot for test case 1



The introduction of phasors works fine with this test case, which has been successfully validated. Now we can add complexity to the system by introducing a constant offset to the sinusoidal term at one of the boundaries.

Test Case 2- Decoupling the system:

1 Mathematical Formulation

We consider the following system of equations:

$$c_t = Dc_{xx}, \tag{1a}$$

$$c(0,t) = c_0 \tag{1b}$$

$$c(L,t) = c_1 + c_2 cos(\omega t + \varphi) \tag{1c}$$

$$c(x,0) = 0 \tag{1d}$$

2 Analysis

In this case we can decouple the system in to a steady linear part and a transient (sinusoidal) part around it. This can be represented as

$$\begin{aligned} c(x,t) &= C^{(0)}(x,t) + \mathfrak{M}_c(x)\cos(\omega t + \varphi + \mathfrak{V}_c(x)) \\ &= C^{(0)}(x,t) + \Re\left(C(x)e^{i(\omega t+\varphi)}\right) \end{aligned} \tag{2}$$

Where the phasor, *C(x)*, for the concentration is

$$C(x) = \mathfrak{M}_c(x)e^{i\mathfrak{V}_c(x)} \tag{2a}$$

$$c(x,t) = \Re\left(C(x)e^{i(\omega t+\varphi)}\right) \tag{2b}$$

$$\frac{dc}{dt} = i\omega\Re\left(Ce^{i(\omega t+\varphi)}\right) = i\omega c \tag{2c}$$

We note that we can also introduce complex conjugate (c.c) and rewrite Eq.2 as

$$\begin{aligned} c(x,t) &= \frac{1}{2}C(x)e^{i(\omega t+\varphi)} + \frac{1}{2}C(x)e^{-i(\omega t+\varphi)} \\ &= \frac{1}{2}C(x)e^{i(\omega t+\varphi)} + c.c \end{aligned} \tag{2d}$$

$$\frac{dc}{dt} = \frac{1}{2}i\omega C(x)e^{i(\omega t+\varphi)} - i\omega(c.c) = i\omega c - i\omega(c.c) \tag{2e}$$

As discussed in the previous test case, the equation with the complex conjugate (c.c) is redundant and hence can be dropped. The governing equations now become

$$0 = D\frac{\partial^2 C^{(0)}(x)}{\partial x^2} \quad (3a)$$

$$C^{(0)}(0,t) = c_0 \quad (3b)$$

$$C^{(0)}(L,t) = c_1 \quad (3c)$$

For the steady linear part, and

$$i\omega C^{(1)} = D\frac{\partial^2 C^{(1)}(x)}{\partial x^2} \quad (3d)$$

$$C^{(1)}(0,t) = 0 \quad (3e)$$

$$C^{(1)}(L,t) = c_2 \quad (3f)$$

For the transient part

2.1 Analytical solution for $C^{(0)}$

Solving Eqs. 3(a) - 3(c) analytically, we obtain the solution for the steady linear part as

$$C^{(0)}(x) = \frac{c_0 - c_1}{L}x + c_0 \quad (4)$$

2.2 Analytical solution for $C^{(1)}$

Eqs.3 (d)- 3(f) when solved analytically, give

$$C^{(1)} = \psi(e^{(\sqrt{\Theta}x)} - e^{(-\sqrt{\Theta}x)}) \quad (5)$$

where

$$\psi = \frac{c_0}{e^{(\sqrt{\Theta}L)} - e^{(-\sqrt{\Theta}L)}} \quad (5a)$$

$$\Theta = \frac{i\omega}{D} \quad (5b)$$

3. Validation

The validation for this Test case was also carried out in a similar way to the previous test case.

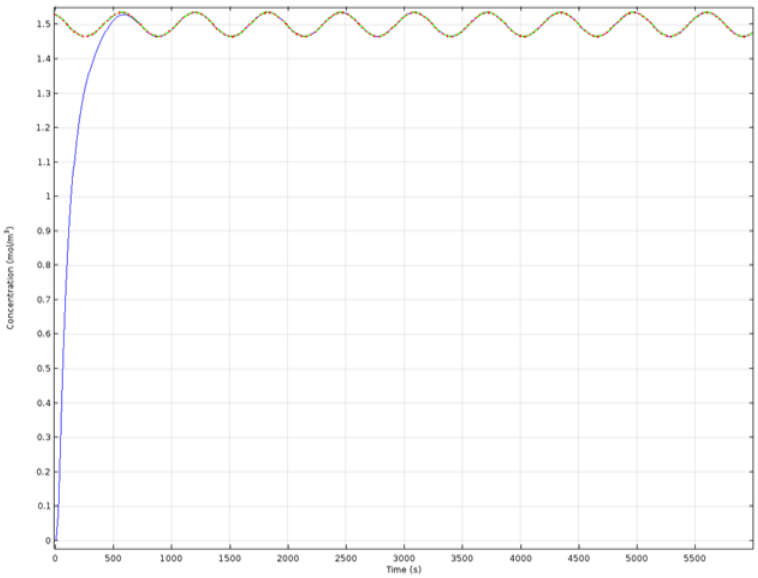


Figure 3. Concentration vs time plot for test case 2

The above test cases show the effectiveness of the introduction of a phasor and how the system can be decoupled in order to obtain the analytical solution. We further increase the complexity of the test cases by incorporating the current and voltages to the boundary conditions making the problem a galvanostatic or a potentiostatic one. We have extended the study to a two component system with higher AC harmonic components. The analyses for these test cases are in progress.

Dr Peng SONG (RF, Cambridge, IRP2) coordinated the installation of rocking disc system for numerical studies. The rocking disc system is now fully functional in CREATE Cambridge Lab 2. In addition, a lab demonstration took place during the mid-term review for the Scientific Advisory Committee.

Work Package 2.2 Electrode Development and Testing

Dr Peng SONG (RF, Cambridge IRP2) has been working on the area of electrochemical analysis for sensing of chemical products. He and colleagues developed a mechanistic study of the EC' mechanism and published a paper on RSC Advances. Dr Peng SONG ((RF, Cambridge IRP2) has been working with Dr. Nathan LAWRENCE from Schlumberger Gould Research (SGR) for EC' mechanism study electrodes. This work applies a range of aqueous ferrocene, for use as a EC' mechanism study tool via electrochemical response. An experimental phenomenon in EC' mechanism has been analyzed via CV and SWV by different redox reactants via glassy carbon electrode. A split wave is observed under certain conditions in these electrochemical techniques. This phenomenon reveals how kinetic and diffusion conditions influence the shape of experimental results in electron transfer process coupled with homogeneous chemical reaction.

Dr Bahareh KHERZI, (RF, NTU, IRP2), under the supervision of Prof Martin PUMERA, (Co-PI, NTU, IRP2) carried out a literature survey in Electrochemical CO_2 Reduction through heterogeneous catalysts. In this project Dr Bahareh KHERZI's, (RF, NTU, IRP2) will synthesize and work with new 2D materials as catalysts (mostly non-metallic or metal doped material (contain trace amount of metals)) for CO_2 conversion. After synthesis and characterization, the catalytic performance (activity, faradic efficiency and current density) will explore in CO_2 saturated aqueous solution. The product of CO_2 conversion will be detected with GC, HPLC and NMR. The electrochemical cell has been designed and required chemical and consumables have been ordered.

Dr Bahareh KHERZI's, (RF, NTU, IRP2), second project, under supervision of Prof Richard D. Webster (Co-Pi, NTU,IRP2) includes a literature survey in Electrochemical CO_2 Reduction through homogenous catalysts. The aim of this project is the study of kinetic and thermodynamic of CO_2 conversion since in many studies the mechanism is unknown or it is only hypothesized. The product of CO_2 con-

Dr Bahareh KHEZRI (RF, NTU, IRP2) and Naziah Binte MOHAMAD LATIFF (PhD student, NTU, IRP2)

version will be detected with GC, HPLC and NMR. The required electrochemical cell has been designed and required chemical and consumables have been ordered.

Naziah Binthe MOHAMAD LATIFF (PhD student, NTU, IRP2) has been working on a manuscript reporting how possible valence and oxide impurities of MoS_2 and WS_2 affect their performance towards electrocatalytic proton reduction has recently been accepted by Nanoscale. This study serves as a platform for better understanding of these materials as electrocatalysts for the hydrogen evolution reaction (HER). HER is a clean method to produce hydrogen gas as an alternative fuel with zero carbon emission. However, due to thermodynamic constraints, an electrocatalysts is needed to make the reaction more efficient. Thus far, platinum has been identified as the best catalyst for the reaction but its high cost impedes the widespread application of this technology. As such, there is much interest in developing alternative HER electrocatalysts from cheap and earth-abundant materials such as MoS_2 and WS_2.

Moreover, experiments to investigate the electrochemical capacitance of doped graphene prepared from different oxidation methods have been completed and its manuscript is under preparation. Energy storage devices such as capacitors are important to store the excess electrons produced from renewable sources of energy. However, better performance of these devices is required to meet the increasing demand for energy. Therefore, it is important to develop materials with better capacitive performance. Doped graphene has shown promising potential for this application. This study can aid our understanding on the capacitive behaviour of this family of materials.

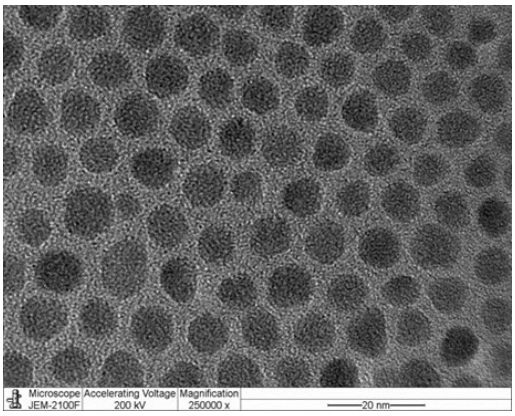
Feng ZHENG (PhD student, Cambridge, IRP2) has been working on the synthesis of Molybdenum trioxide and Molybdenum Disulfide embedded on mesoporous Carbon microspheres. Research on porous carbon material has attracted tremendous attention due to various important applications of the is novel materials in water treatment, gas separation and purification, heterogeneous catalysis and energy storage. However, there are only a few reports on metal and metal oxide nanoparticles embedded inside carbon spheres, which are also non-porous or relatively small surface area. As a consequence, preparing nanocatalysts with high loading of active components on porous carbon remain a challenge.

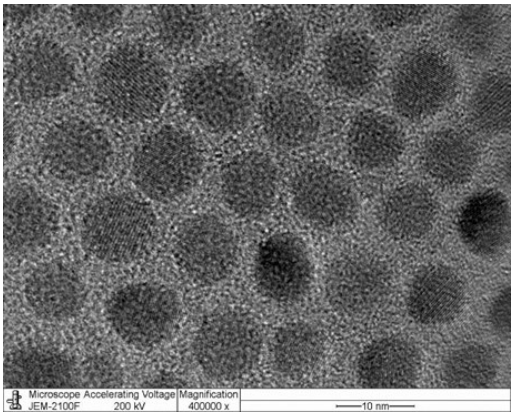
For the synthesis process, a precursor solid is first synthesized from a hydrothermal route to form highly dispersed molybdenum dioxide crystals. The sphere structure will then be strengthened by the carbonization of the solid precursor, micro and mesopores will also be generated within the resultant biphasic nanocomposite. After calcination in air at 300 °C, the oxidation states of encapsulated molybdenum can be tuned to Mo^{+6}, more mesopores can be geneareted, which increases specific surface area of the sample. Nano-composites surface is supposed to be amphiphilic due to the co-presence of hydrophilic and hydrophobic groups.

Work Package 2.3: Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

Dr Bahareh KHEZRI (RF, NTU, IRP2) has been working closely together with Dr Peng SONG from Prof Adrian FISHER's research Group at University of Cambridge to design and make the required reactors for her experiments.

Shengliang ZHANG (PhD student, NUS, IRP2) reported that his research project will focus on tunable plasmonic semiconductor nanocrystals for smart windows. His research aims to synthesis some semiconductor nanocrystals with specialized structure and morphology, and shift the surface plasmonic resonance (SPR) wavelength from 2000 nm to 800-1200 nm for blocking the near infrared light into our building and reducing the energy consumption for air conditioning. He has been working on the preparing and charactering methods of nanoparticles by synthesizing some nanoparticles such as (ITO, Au) and characterizing them by XRD, TEM and Vis-NIR. Up to now, ITO nanoparticles with different size and doping level have been synthesized successfully by controlling the experimental conditions. The gold nanoparticles with the uniform size of 5 nm are prepared with two different methods.





TEM images of 8nm ITO with 5% Sn doping (above)

Guo Xiong THAM (PhD Student, NTU, IRP2) reported on the development of a novel vitamin-based pH sensor using a novel electrochemical approach. Two vitamin compounds riboflavin and vitamin E analogue were dissolved together in dimethyl sulfoxide (DMSO) to give a 2 mM stock solution. Square wave voltammetry experiments were performed in buffered aqueous solutions from pH 2 to 13 with a Pt auxiliary electrode, a 10 µL stock solution coated on a 3-mm diameter planar glassy carbon disk working electrode, and an Ag/AgCl reference electrode in 3 M KCl. The results indicate that as pH increases, the oxidative peak potentials of the vitamin E analogue remain relatively constant while the reductive peak potentials of the riboflavin shift more negatively. Triple consecutive voltammetric scans reveal good precision, and also near Nernstian fashion with an average of 50.01 and 51.83 mV under oxygenated and deoxygenated conditions respectively. Currently, the project is adopting microfabrication techniques to use both vitamin compounds and develop into a pH sensor which is analogous to a lab-in-a-chip.

Other Activities and Achievements

- Dr Bahareh KHEZRI (RF, NTU, IRP2) has published two papers as a result of her joint projects with Prof PUMERA's research group (NTU) in collaboration with Prof FISHER's research group (Dr Peng SONG, Cambridge). In addition, she has submitted a journal paper and one review paper on microfluidic channels (microreactors) and is writing a book chapter for microfluidics.
- In July 2016, Dr Peng SONG (RF, CAM, IRP2) and colleagues, under the supervision of Dr Adrian FISHER (PI, CAM, IRP2) held a successful and well attended Masterclass Programme "Advanced Electrochemical Analysis & Sensor Development".

3.2.3 Scientific output of IRP2

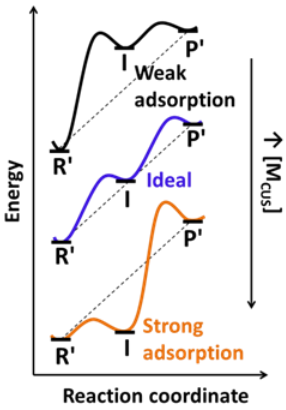
The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP2 during the reporting period. A full list of publications during the period may be found in Appendix A.

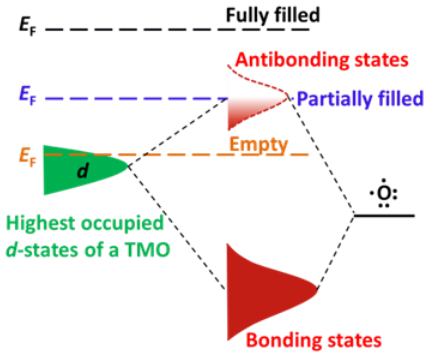
Identification of Surface Reactivity Descriptor for Transition Metal Oxides in Oxygen Evolution Reaction

Tao, Hua Bing; Fang, Liwen; Chen, Jiazang; Bin, Hong Yang; Gao, Jiajian; Miao, Jianwei; Chen, Shengli; Liu, Bin

DOI: 10.1021/jacs.6b05398

Abstract:





A number of important reactions such as the oxygen evolution reaction (OER) are catalyzed by transition metal oxides (TMOs), the surface reactivity of which is rather elusive. Therefore, rationally tailoring adsorption energy of intermediates on TMOs to achieve desirable catalytic performance still remains a great challenge. Here we show the identification of a general and tunable surface structure, coordinatively unsaturated metal cation (MCUS), as a good surface reactivity descriptor for TMOs in OER. Surface reactivity of a given TMO increases monotonically with the density of MCUS, and thus the increase in MCUS improves the catalytic activity for weak-binding TMOs but impairs that for strong-binding ones. The electronic origin of the surface reactivity can be well explained by a new model proposed in this work, wherein the energy of the highest-occupied d-states relative to the Fermi level determines the intermediates' bonding strength by affecting the filling of the antibonding states. Our model for the first time well describes the reactivity trends among TMOs, and would initiate viable design principles for, but not limited to, OER catalysts.

Identification of catalytic sites for oxygen reduction and oxygen evolution in N-doped graphene materials: Development of highly efficient metal-free bifunctional electrocatalyst

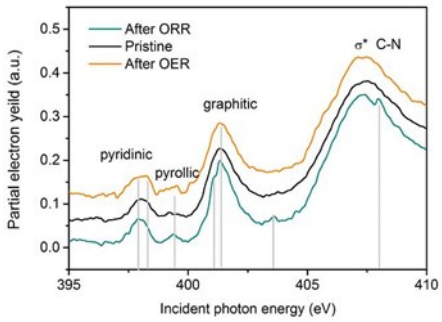
Yang, Hong Bin; Miao, Jianwei; Hung, Sung-Fu; Chen, Jiazang; Tao, Hua Bing; Wang, Xizu; Zhang, Liping; Chen, Rong; Gao, Jiajian; Chen, Hao Ming; Dai, Liming; Liu, Bin

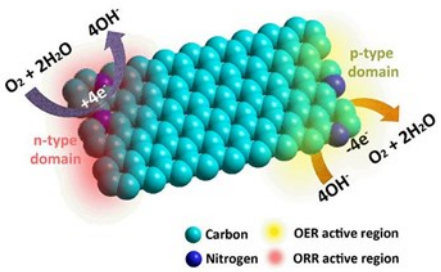
DOI: 10.1126/sciadv.1501122

Abstract:

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are critical to renewable energy conversion and storage technologies. Heteroatom-doped carbon nanomaterials have been reported to be efficient metal-free electrocatalysts for ORR in fuel cells for energy conversion, as well as ORR and OER in metal-air batteries for energy storage. We reported that metal-free three-dimensional (3D) graphene nanoribbon networks (N-GRW) doped with nitrogen exhibited superb bifunctional electrocatalytic activities for both ORR and OER, with an excellent stability in alkaline electrolytes (for example, KOH). For the first time, it was experimentally demonstrated that the electron-donating quaternary N sites were responsible for ORR, whereas the electron-withdrawing pyridinic N moieties in N-GRW served as active sites for OER. The unique 3D nanoarchitecture provided a high density of the ORR and OER active sites and facilitated the electrolyte and electron

transports. As a result, the as-prepared N-GRW holds great potential as a low-cost, highly efficient air cathode in rechargeable metal-air batteries. Rechargeable zinc-air batteries with the N-GRW air electrode in a two-electrode configuration exhibited an open-circuit voltage of 1.46 V, a specific capacity of 873 mAh g?1, and a peak power density of 65 mW cm?2, which could be continuously charged and discharged with an excellent cycling stability. Our work should open up new avenues for the development of various carbon-based metal-free bifunctional electrocatalysts of practical significance.





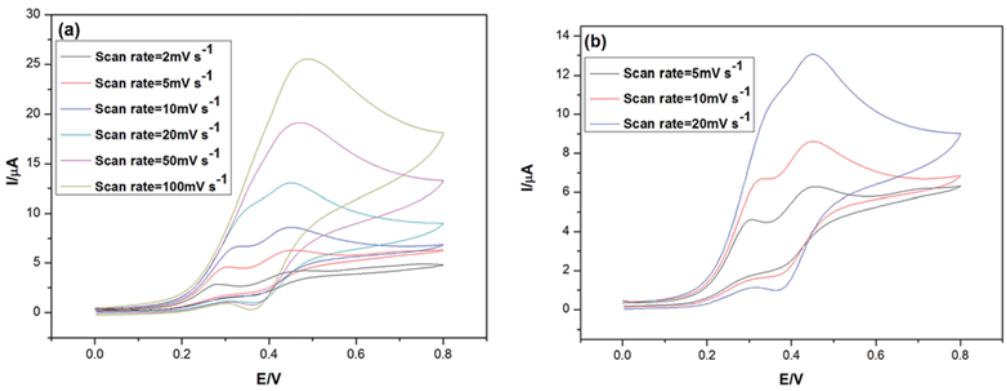


Figure (a) Cyclic voltammograms in 0.1 M borate buffer (pH 1⁄4 9) detailing the response of 2 mM FDA and 4 mM L-cysteine to increase the scan rate (2–100 mV s_1) at a glassy carbon electrode. (b) A zoom- in view of the voltammogram at scan rates of 5, 10 and 20 mV s_1.

A mechanistic study of the EC' mechanism – the split wave in cyclic voltammetry and square wave voltammetry

Peng Song; Adrian C. Fisher; Jay D. Wadhawan; Joshua J. Cooper; Haydn J. Ward; Nathan S. Lawrence

DOI: 10.1039/c6ra08723j

Abstract:

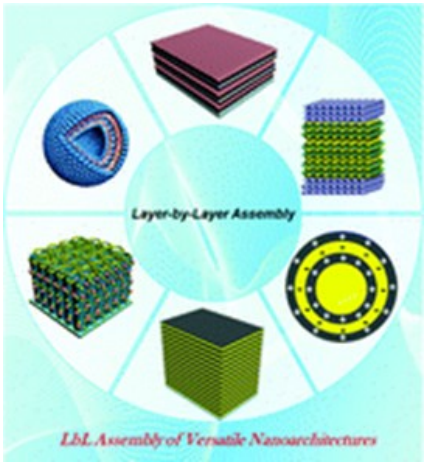
In this paper, a detailed investigation of electrochemical reactions coupled with homogenous chemical steps using cyclic voltammetry (CV) and square wave voltammetry (SWV) was carried out to study the electrocatalytic (EC') mechanism. In CV, parameters including scan rate, electrode material and redox reactant were investigated while in SWV, parameters including substrate concentrations and frequencies were altered to demonstrate the EC' mechanism. Mechanistic studies focused on the EC' mechanism using L-cysteine with ferrocenecarboxylic acid and 1,1'-ferrocenedicarboxylic acid respectively. Voltammetric responses were recorded and under conditions of high chemical rate constant and low substrate concentration, a split wave was observed in both CV and SWV studies. In CV, parameters including scan rate, electrode material and redox reactant are investigated to find the best conditions to demonstrate the split wave phenomenon. The phenomenon is highly depended on the experimental timescale, which is scan rate in cyclic voltammograms. For options of electrodes, the heterogeneous electron transfer process on the electrode substrate is highly depending on the electrode material. Also, the physical property of ferrocene derivatives illustrates how a carboxyl group shows its influence on the pre wave feature. The experimental result under SWV gives a convictive evidence on the study of EC0 reaction due to their special features to decouple non-faradic current.

Layer-by-layer assembly of versatile nanoarchitectures with diverse dimensionality: a new perspective for rational construction of multilayer assemblies

Xiao, Fang-Xing; Pagliaro, Mario; Xu, Yi-Jun; Liu, Bin

DOI: 10.1039/C5CS00781J

Abstract:



Over the past few decades, layer-by-layer (LbL) assembly of multilayer thin films has garnered considerable interest on account of its ability to modulate nanometer control over film thickness and its extensive choice of usable materials for coating planar and particulate substrates, thus allowing for the fabrication of responsive and functional thin films for their potential applications in a myriad of fields. Herein, we provide elaborate information on the current developments of LbL assembly techniques including different properties, molecular interactions, and assembly methods associated with this promising bottom-up strategy. In particular, we highlight the principle for rational design and fabrication of a large variety of multilayer thin film systems including multi-dimensional capsules or spatially hierarchical nanostructures based on the LbL assembly technique. Moreover, we discuss how to judiciously choose the building block pairs when exerting the LbL assembly buildup which enables the engineering of multilayer thin films with tailor-made physicochemical properties. Furthermore, versatile applications of the diverse LbL-assembled nanomaterials are itemized and elucidated in light of specific technological fields. Finally, we provide a brief perspective and potential future challenges of the LbL assembly technology. It is anticipated that our current review could provide a wealth of guided information on the LbL assembly technique and furnish firm grounds for rational design of LbL assembled multilayer assemblies toward tangible applications.

Bipolar Electrochemical Synthesis of WS2 Nanoparticles and Their Application in Magneto Immunosandwich Assay

*Carmen C. Mayorga-Martinez, Bahareh Khezri, Alex Yong Sheng Eng, Zdenek Sofer, Pavel Ulbrich, Martin Pumera**

DOI: 10.1002/adfm.201600961

Abstract:

WS2 nanoparticles are prepared using bipolar electrochemistry. Obtained material exhibits high activity for hydrogen evolution reaction (HER) and it is used as a label in standard magneto-immunosandwich assay for protein detection through HER. This new system shows high analytical performance in terms of a wide range, selectivity, sensitivity, and reproducibility.

Self-Propelled Supercapacitors for On-Demand Circuit Configuration Based on WS2 Nanoparticles Micromachines

Carmen C. Mayorga-Martinez, James Guo Sheng Moo, Bahareh Khezri, Peng Song, Adrian C. Fisher, Zdenek Sofer, and Martin Pumera

DOI: 10.1002/adfm.201601165

Abstract:

The miniaturization of energy storage microcapacitors to develop portable electronic devices has been of high recent interest. Here, microsupercapacitors microrobot is fabricated using membrane template-assisted electrodeposition of WS_2 nanoparticles (WS_2NPs)/polyaniline (PANI) and platinum

(Pt) layers. The microrobot navigates in the microchannel and attaches itself as part of the electrical circuit. The attached WS_2NPs-PANI/Pt microrobots enhance the capacitive behavior of the circuit significantly. The results presented in this work open the door for the development of smart and miniaturized functional micromotors that are able to self-assemble to on-demand circuits.

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

October 2016

3.3.1 IRP3 Research Overview

As part of the full review of the C4T programme conducted during their three-day visit in July, the Scientific Advisory Committee was very impressed with the current state of the programme in general, but also with IRP3 in particular. Specifically, the Committee recognised that the nanoparticles work-stream is a "world-leading activity of great societal relevance" and further that our presence in Singapore is "likely to develop the field locally in a way that would have been unlikely to happen without C4T".

Commissioning of our laboratory in the CREATE building has progressed very well. Four burner systems have been set up for investigations of soot formation in different flame configurations as well as for the synthesis of inorganic nanoparticles and composites for various engineering applications. Flame configurations we can study now include premixed stagnation flames, wick-fed liquid fuel flames, and co-flow diffusion flames, allowing a broad range of aspects of organic as well as inorganic nanoparticle formation to be investigated.

On the Cambridge side, the laboratory is in the process of being upgraded to enable a wider range of combustion experiments. Two new burners were acquired for studying in detail how soot and metal oxide nanoparticle are formed in flames. The instruments for operating the two burners are interchangeable building blocks, giving the system a high degree of flexibility and versatility. A custom-made fuel delivery system allows the use of a large number of liquid fuels/precursors and their mixtures. All instruments required for the flame operation can be controlled though a computer and a single graphical user interface developed in-house. As both burners operate under well-defined conditions, interrelating the experiments with particle formation models becomes feasible. The gained knowledge will find applications in areas such as pollutant control during hydrocarbon combustion and the fabrication of functional nanomaterials.

We are proud to have launched our new Media Lab in May this year, a state-of-the-art, energy-efficient, interactive visualisation system for the J-Park Simulator. It consists of a video wall which provides an immersive 3D-environment spread over a large touchscreen as well as a projector screen solution which includes radar touch, allowing it to be controlled by articulated hand gestures. The Media Lab forms an integrative part of our research and as such is shared with the other IRPs. The hardware capabilities providing real-time interactive control support the researchers in deepening their understanding of the vast data and complex models being handled in the programme's flagship research output, the J-Park Simulator, and thus will be pivotal in achieving our research goals.

Also in May this year, a Stakeholder Event was held, entitled "J-Park Simulator: The Roadmap to a Smart Industrial Park". With the emphasis on practical application, we presented a live demonstration how the virtual representation of smart factories within the J-Park Simulator links together the three concepts of Industry 4.0, Eco-Industrial Park (EIP), and cross-domain ontology and can be used for designing and optimising the EIP of Jurong Island in Singapore. The event was attended by all major Singapore government agencies as well as private sector companies, with a total of more than 70 participants.

CARES has been nominated as a finalist in the IChemE Global Awards 2016 for outstanding work in the education of chemical engineers. The IChemE Global Awards celebrate excellence, innovation, and achievement in the chemical, biochemical, and process industries. Running in the Training and Development category, we were selected for the Cambridge Weblab, a laboratory experiment controlled by a SIEMENS PCS 7 system and fully accessible through the internet, which exposes students to a real-world, modern, industrial-scale control system.

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.

J-Park Simulator is designed as a novel knowledge-based expert system, which can process all the associated information (data, information, mathematical models and solving approaches) and be able to seamlessly integrate mathematical modelling with information modelling to support model-based engineering work process. The main objective of the J-Park Simulator is to address the symbiosis of energy and resource management for enhancing energy efficiency, improving cost effectiveness, and increasing sustainability and environmental benefits in eco-industrial parks (EIPs). Furthermore, J-Park Simulator is conceived under the ongoing trend of realizing Industry 4.0, where the construction of a Cyber-Physical System (the convergence of the physical world and the virtual world) is the key.

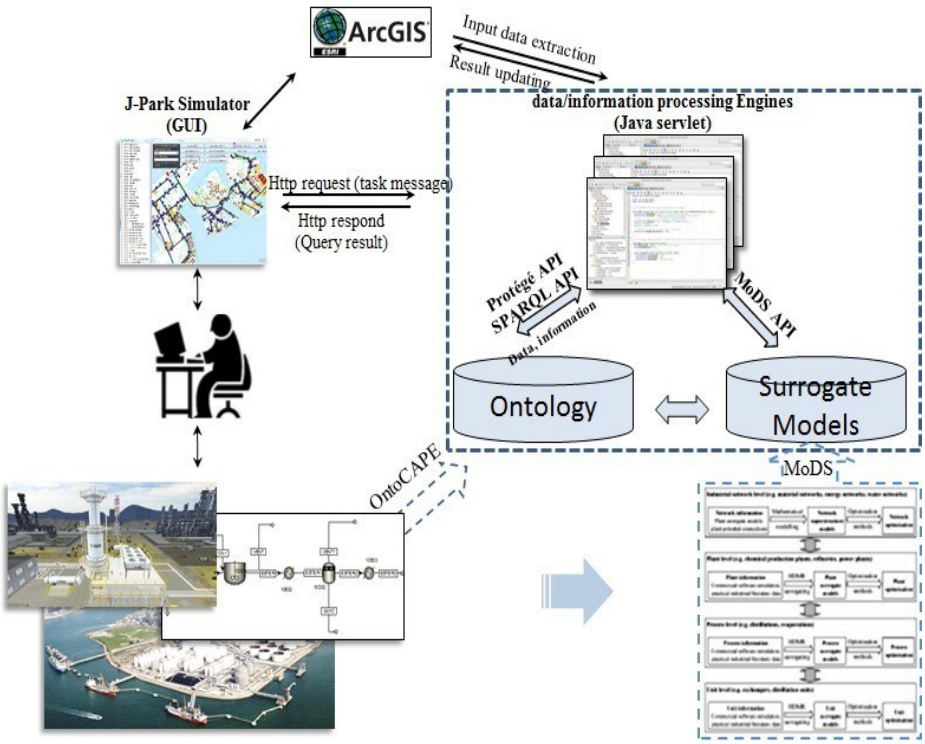


Figure 1 Proposed architecture for J-Park Simulator

In order to establish such a system, three basic components are considered as requisites: 1) an explicit knowledge base containing generic domain knowledge, concrete facts about the domain of interest; 2) an inference engine to interpret the knowledge and facts encoded in the knowledge base and derive solutions from it; 3) and a virtualized representation of the eco-industrial park of concern. Fig. 1 gives the proposed architecture for J-Park Simulator.

During the reporting period, the development team has made significant progresses on the three above mentioned aspects.

1) Development of OntoEIP, an ontology for eco-industrial park, which serves as the knowledge base for J-Park Simulator

Ontological technology is primarily considered as an efficient tool to build knowledge base for software systems, as it provides the means for describing explicitly the conceptualization behind the knowledge in a formal manner. Formal refers to the fact that the ontology is machine-readable. In such way, it provides a shared vocabulary for communication between interoperable agents (human and/or software applications).

Based on OntoCAPE, which is the most dominant and widely-accepted ontology framework for computer aided process engineering, we are in the process of establishing an ontology framework (OntoEIP) for eco-industrial parks, as shown in Fig. 2.

Currently, we have modified and extended OntoCAPE in order to represent the chemical engineering components as well as to fit into the framework of J-Park Simulator. Also, by reusing the Meta Layer and Upper Layer, we established a framework for electrical engineering domain, transportation network and industrial resource network. A research paper on this subject is under preparation.

Moreover, along with the developing process of ontologies, we are also under the process of migrating the J-Park Simulator database from ArcGIS database to local-hosted ontology based database.

2) Hierarchical modelling and representation of industrial parks

The major objective of establishing OntoEIP is to support the energy and resource management in EIPs for overall sustainability enhancement. The sustainability can be achieved through optimizing the performance at each operational level, including optimal unit operations with minimal utility consumption, optimal processes producing minimum waste, flexible plant planning and scheduling as well as optimal industrial resource networks with the lowest emission. To that end, it is proposed to model EIPs in a hierarchical structure, as shown in Fig. 3. At the bottom level lies the unit operations, which is considered as the basic technical component in an EIP system. On the second level resides the chemical processes which are aggregations of unit operations, while the third level is occupied by the companies which usually consist of several chemical processes. At the top is the industrial resource networks that manage the resource allocation for all the companies in the industrial park. At each level, it is proposed to associate the technical components with their own representation which include: 1) visualization information in order to realize virtual representation of the real entity in a graphical user interface (GUI), 2) executable models, and 3) its interconnection with the environment.

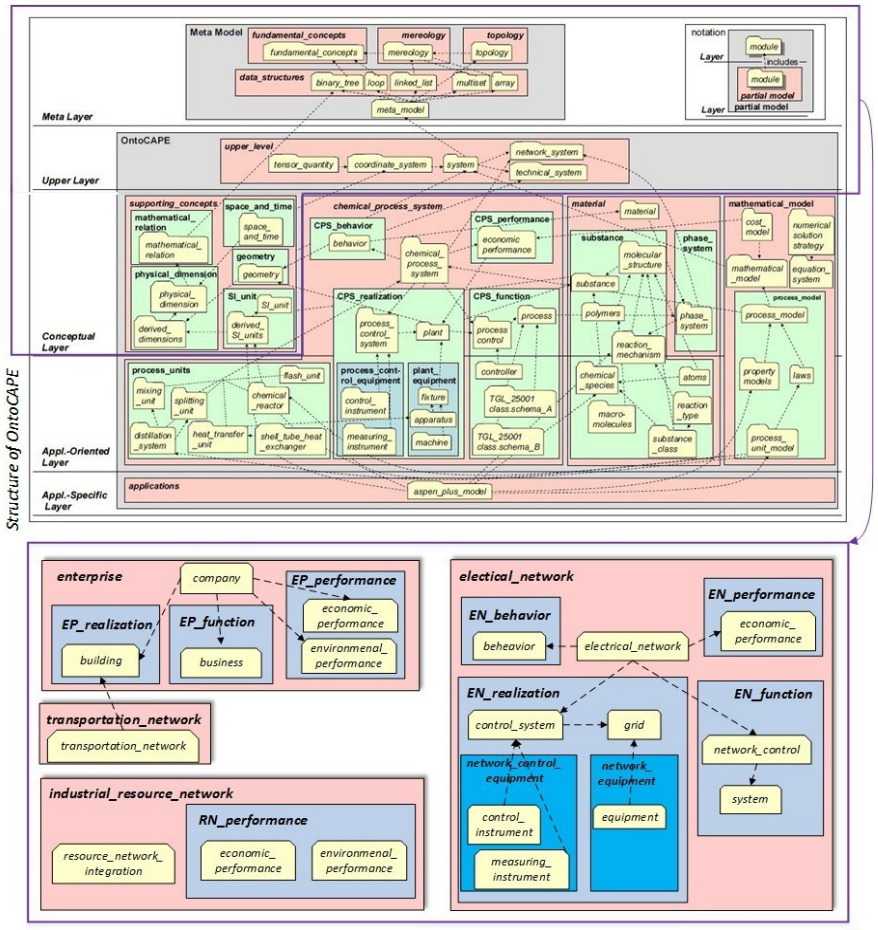


Figure 2 Proposed structure of OntoEIP by adding new partial models to OntoCAPE.

At current stage, we have modelled the chemical processes (operational level 2). The developing team is working on developing component surrogate models for each unit operation (operational level 1), expecting to realize process integration and optimization in the next step. Mathematical models for the upper two operational levels (company level and industrial network level) will be built in the future.

3) Establishment of 2D and 3D virtual representation of industrial parks

Establishment of virtualized representation for the eco-industrial park is crucial to the realization of Industry 4.0. In order to become independent from ArcGIS, we have started to construct a framework for the virtual visualization of J-Park, both for 2D representation and 3D representation. For the 2D version of J-Park Simulator, we will still use what we have built using the ArcGIS software, except that we will not rely on the service from ArcGIS any more in the near future. For the 3D version of J-Park Simulator, we started building 3D representation for the industrial entities by using AutoCAD and the Unity5 engine. Prototypes are available now, which proves to be more intuitive.

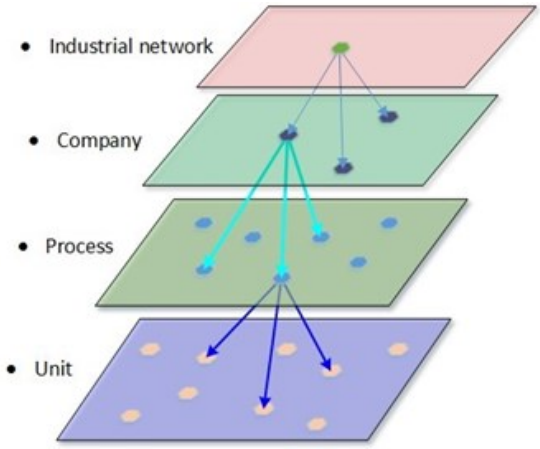


Figure 3 Hierarchical structure of the operational levels in EIPs.

In the future, the 3D version of J-Park Simulator will allow Virtual Reality (VR) walks through the industrial park.

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

The increasing concerns over climate change and urban pollution produced by the emission of greenhouse gases has become a driving force for the study of cleaner fuels and more efficient engines.

IRP3 work aims to tackle this issue from different yet interconnected and interdependent perspectives. On one side, experimental work is conducted on the formulation of cleaner, cheaper and high-performance fuels that can enhance the combustion in engines and reduce de emission of pollutants. Alongside, an intensive experimental and modelling study of the formation of pollutants during combustion aims to answer questions on how to circumvent this phenomena.

Fuel Formulation

Dr. Maria BOTERO (Research Fellow, NUS, IRP3) has been leading the experimental efforts in CARES to study new additives with the potential of reducing pollutant emissions in the combustion of commercial fuels. Together with Dr. Sheng YUAN, they are working on the synthesis of PODE: polyoxymethylene dimethyl ethers ($H_3CO(CH_2O)_nCH_3$) which are a promising "green" additive to diesel fuel. These compounds can be added to diesel without altering the current engine infrastructure and significantly reduce the emission of soot particles, CO and unburnt hydrocarbons. This work comprises the study of the sooting characteristics of the synthesized PODE different polymer fractions of PODE (n=3-5) and its mixtures with commercial fuels.

Experimental study of soot formation

In the past 6 months Dr. Maria BOTERO (Research Fellow, NUS, IRP3) and Dr. Weijing WANG (Research Fellow, NTU, IRP3) have being commissioning the lab and setting up the rigs for the study of soot formation in different flame configurations. Four burner systems have been assembled and commissioned, two premixed and two non-premixed: 1- The Burner Stabilised Stagnation Flame (BSSF), which is a premixed burner that can be used to study soot formation and oxidation; 2- The flame stabilized by a rotating surface burner (FSRS), which can be used for high temperature studies of soot formation; 3- The smoke point burner, that enables the study of a wide range of liquid hydrocarbon and their mixtures and 4- The Yale burner, a coflow diffusion flame system that allows better control of the flame conditions and a more detail characterisation of the soot particles. These burners are also used for the synthesis of inorganic nanoparticles and composites for various engineering applications (as described in WP3).

During the university summer break, we hosted Ms. Zhenyu SHI as an intern from the Chemical and Biomedical department at NTU. Under the supervision of Dr. BOTERO (Research Fellow, NUS, IRP3), Ms. Zhenyu SHI worked on the setting-up and commissioning of the smoke point lamp burner and the measurement of particle size distributions emitted from flames of heptane, decane, isooctane and toluene, which are surrogates of commercial fuels. Her work was aimed to reproduce previous experimental results obtained at the University of Cambridge in order to establish the validity of the experiments conducted at CARES.

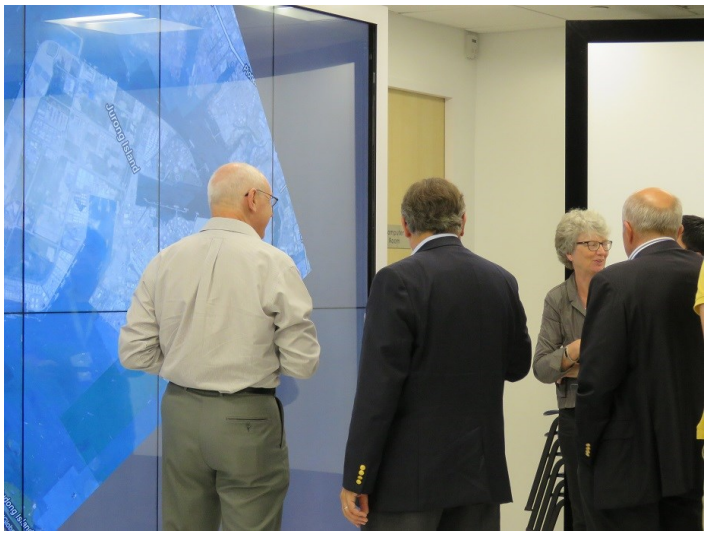
As part of a collaboration with Prof. Hai WANG at Stanford University, Dr. Weijing WANG (RF, NTU, IRP3, used the FSRS to study the soot sizes produced from the combustion of ethylene at high temperatures. This work broadens the experimental conditions typically used for the study of soot formation. The results from this investigation led to a publication and were also presented at the 36th International Symposium on Combustion held in Korea in August.

In May 2016, Dr. Jochen DREYER joined IRP3 at the University of Cambridge. Dr. DREYER (Research fellow, UCAM, IRP3) has achieved an impressive progress in the design, set-up and commissioning of different combustion systems for the study of soot formation. With the collaboration of Jacob MARTIN (PhD student, UCAM, IRP3) a system for plasma assisted combustion was set up.

Computational study of soot formation

Successful modelling of soot in flames could help us better understand the soot formation mechanism and help us to achieve the goal of reducing carbon emission. The development of simple, fast and accurate mathematical model to simulate the soot particle dynamics is fundamental for study on soot formation in flames. Shaohua WU (PhD Student, NUS, IRP3) is working towards the development of such model. During the reporting period he has developed a moment projection method which retains the advantages of the ease of implementation and numerical robustness of moment methods and at the same time is able to handle the oxidation process. The results of this project have been submitted for two publications and presented in a poster at the 36th International Symposium on Combustion. The method was tested using Matlab and shown very satisfactory results. It is now being implemented into the commercial software Kinetics and SRM engine suite in order to simulate the soot formation process in real flames, for example inside burners and combustion engines.

As a complement to this work, Dr. Edward YAPP (Project Officer, IRP3) is developing a detailed population balance code and improving the way in which particles are represented in the model. This could have important implications on the fragmentation process. He has recently submitted a paper to Combustion and Flame journal on the role of PAH curvature in soot formation, which have received positive feedback. This work was also presented as a poster at the 36th International Symposium on Combustion.



Dr Keith CARPENTER, Prof Johannes LERCHER, Prof Katharina KOHSE-HÖINGHAUS and other members of the SAC view the J-Park Simulator Demo

WP3: Nanoparticle/film flame synthesis – kinetics and application

Flame aerosol synthesis has proved to be one of the most scalable and economical method for producing well-controlled nanostructured materials in the past two decades. Compared with wet chemistry approach, flame synthesis method has more advantages on apparent simplicity (continuous one-step process), high-throughput production and less environmental harm.

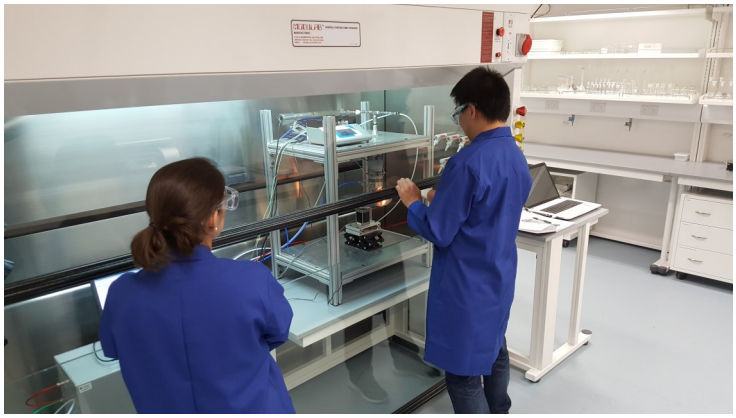
The research in this area is currently focused on the production of catalysts with improved properties for the capture of CO_2 in processes such as chemical looping performed within IRP1, and in the area of photocatalytic or electro-catalytic water splitting. In the past 6 months Dr. Weijing WANG (Research Fellow, NTU, IRP3) and Dr. Sheng YUAN (Research Fellow, NTU, IRP3) have been building the rigs for the synthesis of inorganic nanoparticles at the CARES laboratory. A flame stabilized by a rotating surface burner (FSRS), a burner stabilized stagnation flame (BSSF) and a co-flow diffusion flame burner (Yale) rigs were assembly to for the synthesis and application of novel metal oxide nanoparticles combining techniques of both flame synthesis and wet chemistry.

Suitable precursors and methods for flame synthesis of oxides of more than 10 different metal/metalloid elements have been identified, and purchase of relevant chemicals have started. To allow for synthesis of a wider range of materials from solid precursors using the current burners, a further modification of the FSRS burner has been designed and implemented. These include the proper

heating of liquid precursors as well as multiple precursor doping.

In addition to previous synthesized Titanium Dioxide nanoparticles using different flame conditions, Tin Dioxide nanoparticles have also been produced using lean flames. Diagnostics to the Tin Dioxide nanoparticles will be carried out regarding the size and morphology. Vanadium oxide/Titanium Oxide and Vanadium oxide/Tin Oxide nanocomposites will be the next target.

Shuyang WU recently joined IRP3 team as a PhD student at NTU under the supervision of Prof. Xu RONG (Co-PI, NTU, IRP3). He will be focused on fabrication of metal oxide and carbon material catalysts for the production of green renewable energy using flame synthesis method. This work includes coating the catalyst or co-catalyst directly on the electrode through flame synthesis with the assistance of Dr. WANG, and test and characterize the performance of catalysts for photocatalytic or electro-catalytic hydrogen generation. This loading method in high temperature may reduce the mass transfer resistance and facilitate charge localization and electron transfer process, hence improve the overall catalytic performance. This research also includes the optimization of catalysts and co-catalysts by varying their compositions. He will explore the performance of metal oxide such as TiO_2, ZnO, Ga_2O_3, In_2O_3 and NiO, non-noble metal sulfide and phosphide like CdS, MoP, and carbonaceous materials like g-C_3N_4.



Dr Maria BOTERO (RF, NUS, IRP3) and Dr WANG Weijing (RF, NTU, IRP3) working on one of the burner rigs

In the efforts of improving the electro-catalytic and photo-catalytic water-splitting process, Prof Xu RONG (Co-PI, NTU, IRP3) published a paper on the construction of a highly efficient system. She reports the construction of a highly efficient noble metal free photocatalytic hydrogen (H2) evolution system using CdS quantum dots and metallic MoP as the co-catalyst. Small clusters of MoP nanoparticles sized 10–30 nm synthesized by wet chemistry. The highest H2 evolution rate obtained is comparable to that when Pt was used as the co-catalyst. A high quantum efficiency of 45% is obtained at 460 nm irradiation.

To combine and complement our experimental efforts, extensive work on the simulation of the synthesis of inorganic nanoparticles has been carried out thorough the reporting period.

Casper LINDBERG (PhD student, UCAM,IRP3), funded by Huntsman Pigments and Additives, has been working on the effect of reactor conditions on the milling properties of flame synthesised titanium dioxide particles. A milling model is applied as post-process to a detailed population balance model that simulates the evolution of titanium dioxide particles in a reactor. He has developed particle breakage models which utilise the morphological data captured by our detailed particle model.

Astrid BOJE's (PhD student, UCAM, IRP3) PhD project involves developing a reactor model to study synthesis of pigmentary titanium dioxide in an industrial reactor. She has developed a reactor network model, using a sequence of ideal reactors. In the model, continuously stirred tank reactors (CSTRs) are used to model local mixing and variation in composition around the dosing points and plug flow reactors (PFRs) are used to model variation in temperature after the dosing zone, due to the exothermic nature of the reaction, and to model the cooler. The model uses a detailed population balance which is coupled to the gas-phase chemistry and solved using a stochastic method. The current model illustrates the potential to use a reactor network approach to model the industrial titania reactor and the outputs include a detailed description of the pigmentary particles. Information about the size and morphology of the particles is important to determining the product quality as well as the milling energy requirement in the industrial process. She has performed a preliminary sensitivity analysis, varying process parameters such as reactor temperature and residence time, in order to explore the effect on the particle structure. She then compared the observations from the current model with literature studies and is in the process of obtaining data/feedback from Huntsman Pigments and Additives, which sponsors the project. She is currently finalising a manuscript on the current model.

Jacob MARTIN (PhD student, UCAM, IRP3), since beginning his PhD in January 2016, started to study gas interactions with the nuclei of soot particles made up of clusters of flat aromatic molecules. This crucial stage of soot formation is dependent on gas interactions for further growth of the cluster through reactions with acetylene or breakdown with oxidation by molecular oxygen. Using nitrogen as a probe we found for collisions with the cluster two main scattering modes, specular or direct reflection and diffuse or sustained residence time on the surface of the cluster. For diffuse scattering we observed different interactions most importantly an 80-90% chance of interacting with hydrogen. The main growth and oxidation reaction rely in hydrogen abstraction and reaction with the edge of the molecules. This finding justifies the success of these methods as the hydrogen is the primary interaction site. Passing the melting point of the clusters led to the opening of the internal structure and we found one in a thousand collisions led to gas penetration into the cluster. This suggests the ability of liquid nascent soot particle to burn from the inside which is the title of the paper recently published in the Journal Carbon.

WP4: Modelling and optimisation of unit operations

As part of our investigation of CO_2 mitigation, conversion or avoidance, a CO_2 neutral scenario was outlined based on the exclusive utilisation of nuclear power across Jurong Island replacing all natural gas fired conventional power plants. A concept was developed that would involve between 10 and 20 modules of small -size Light Water Reactors (LWR) placed in convenient locations that would minimise the distance to the end consumer, and provide an opportunity to procure waste steam to chemical or refining processes in the vicinity of the reactor.

Pulkit CHHABRA, PhD Student, IRP3 discusses with Prof Lord Julian HUNT (SAC member)

As part of the finance module being developed, we started investigating the integration of blockchain technology and smart contracts into the architecture at object level of the J-Park Simulator. Under such a scenario, each object can be associated with a smart contract and interact autonomously without human intervention with other objects while all executed transactions would be verified and recorded by a decentralised community of processing units. Such a configuration would be able to accommodate new forms of price discovery between participating nodes at any level within the hierarchy of models of the J-Park Simulator. Towards that end a mini-network consisting of several nodes was set up and transactions were being executed.

The Semakau Simulator was modelled and implemented and is in the process of being tested. The Semakau Simulator is a smart grid simulation tool modelled first in PowerWorld, then parameterised, of real world, renewable energy generating assets being installed on the island. It includes a PV solar farm, wind turbine, battery storage, a smart grid power hub controlling load shifting and load balancing between the variable power sources and the cyclical power loads due to the relative unpredictability of the power generation. The Semakau Simulator forms an important simulation tool for our industry collaboration plans with ENGIE as indicated in the industry contact section below.

Five chemical plants were modelled in Protégé (ontology) and AutoCAD (3D visualisation) 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.

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 IRP4. 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.

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.

WP5: Automated model development and experimental design/decision support

Research into the parameterisation methods of high-dimensional models continued using the model development suite MoDS. The established standard parameterisation methodology for modelling and studying physical models of equipment, industrial processes, plants and parks 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. Modelling and investigation of superstructures was initiated involving the comparison of systems of simultaneous surrogate models each representing a single equipment unit of a chemical process plant, with a single surrogate model representing the chemical process plant as a whole.

Prof Markus KRAFT, Dr ZHOU Li and Kevin ADITYA present the J-Park Simulator to the SET conference, Singapore. July 2016.

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.

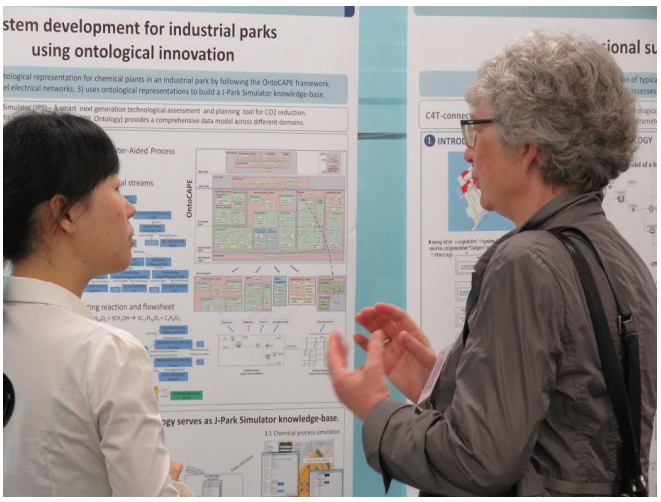
A paper on the “effects of dimensionality and surrogate type on the parameterisation accuracy of AspenPlus simulations of chemical processes” has been accepted for publication.

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

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.

OntoCAPE specifies them in the form of 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.



Dr ZHOU Li, RF, IRP3, presents her work to Prof Katharina KOHSE-HÖINGHAUS

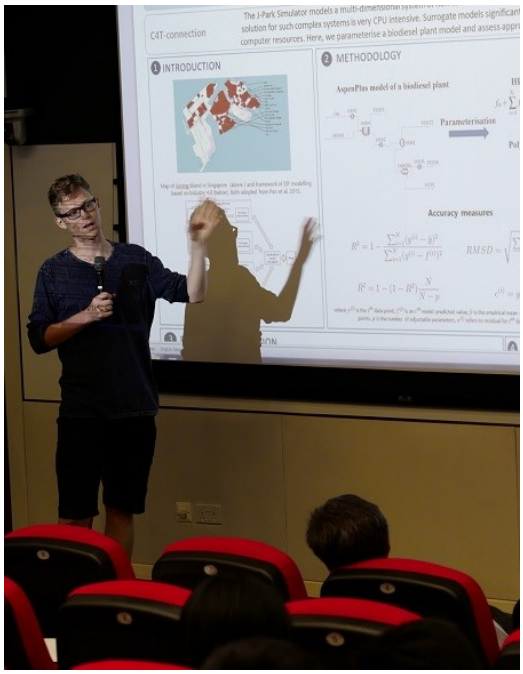
Other Activities and Achievements

- Industry contacts include a **stakeholder event** on 12 May 2016 titled "J-Park Simulator: The roadmap to a smart industrial park", attended by all major Singapore government agencies as well as private sector companies for a total of approx. 70 participants.

- Industry collaboration was started with the Enterprise Resource Planning (ERP) software vendor **SAP** within their University Alliance program. The objective of this collaboration is the integration of SAP into the J-Park Simulator.

- Industry contact to the French energy firm **ENGIE** was further developed in a meeting that took place in July 2016. The discussion was focussed on research collaboration with their R&D team that designs and implements a microgrid on Semakau Island as part of the REIDS project. This EDB supported project will see the construction and operation of a cluster of three micro-grids built and operated by three different companies and each consisting of a PV solar farm and a wind turbine as power sources, a power storage facility in the form of a battery or a hydrogen storage tank, and various power sinks (loads), for instance a desalination plant, a fish hatchery, or transportation trucks running on hydrogen powered fuel cells.

- **Potential collaboration with SIEMENS to bring the Weblabs to Singapore Education**. The recent publication of Prof. Markus KRAFT (PI, IRP3, Cambridge) Dr. Maria BOTERO (RF, IRP3, NUS) and Dr. Mukta BANSAL in the special issue 10th Anniversary of the Journal of Education for Chemical Engineers has attracted SIEMENS Automation attention. This paper reports the experience with the implementation of an experiment remotely controlled using a SIEMENS system for reactor engineering teaching at the University of Cambridge.



Janusz SIKORSKI (Phd Student, Cambridge, IRP3) presents at the C4T Poster Competition, June 2016

- There has been an ongoing discussion with SIEMENS regarding the potential collaboration in the development of advanced teaching techniques and facilities. The company has shown interest to introduce the Siemens Automation Cooperates with Education (SCE) programme to continuously improve the quality of vocational training for young people in Singapore. This package provides practical training in educational institutions in the area of industrial automation.

- **Participation in the 36th International Symposium on Combustion** Prof. Markus KRAFT (PI, IRP3, Cambridge) was invited as co-chair of the Soot and Nanoparticle topic presentations. IRP3 team had a strong presence in the

conference with two oral presentations, one of them in collaboration with Stanford University and two poster presentations.

- **Mid-Term Review** As part of the Scientific Advisory Committee Mid-Term Review in Singapore in July, the IRP3 team produced and presented 17 posters containing a summary of all the research work conducted over the past 3 years. Furthermore, the J-Park Simulator development team gave a presentation and live demonstration to the Committee members and the Principal Investigators. The experimental team gave three lab demonstrations: 1- Measurements of soot particle size distributions in flames, 2- Flame synthesis and coating of titania nanofilms, 3- Coating of water container with titania film though combustion-assisted synthesis.
- **2016 International Forum of New Materials** Prof Xu RONG (Co-PI, IRP3, NTU) has been invited to give a talk on the 2016 International Forum of New Materials in Nianjing, China. She presented her work on "Cobalt Phosphonate Hybrid Materials and Their Derived Cobalt Phosphates as a New Class of Catalysts for Sustainable Energy Conversion".
- **Jacob MARTIN** (PhD student, IRP3, Cambridge) recently attended three conferences, ChemEngDay at Bath University organised by IChemE and Cambridge Particle Meeting where a poster was presented and the Joint British, Spanish and Portuguese Section Combustion Meeting where a talk was presented both were based on the paper published on gas-soot interactions.

GEP intern SNG Yii Ren (centre) and members of IRP3

- **IRP3 Global Engineering Programme (GEP) internship** From May until August 2016 IRP3 hosted SNG Yi Ren, an intern from the NUS Global Engineering Programme. After an initial orientation phase during which Yi Ren was introduced to the various underlying concepts of our current J-Park Simulator design and hands-on training in the use of software development tools, for instance the Geographic Information Systems ArcGIS, he acquired new technical skills (basic Java, AutoCAD, Protégé, Unity5), new conceptual knowledge (ontology) and practical project management experience both as a student and as a supervisor. His internship continues a successful collaboration with the NUS GEP that started in 2015. CARES is looking forward to welcoming future GEP students to the team.

3.3.3 Scientific output of IRP3

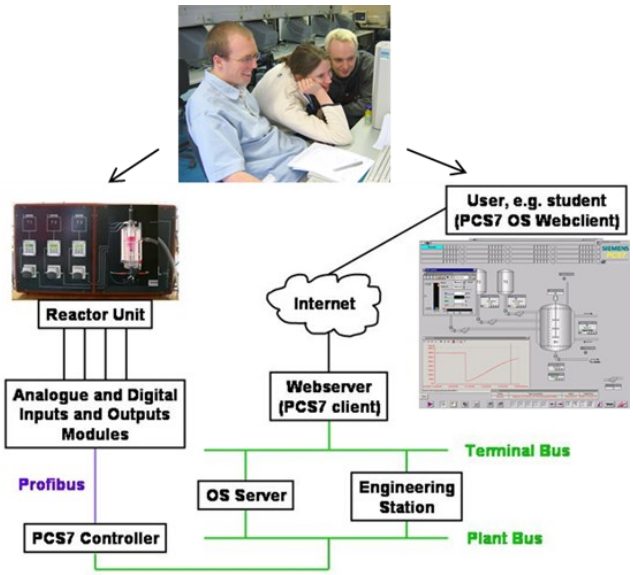
The following are some examples of the CREATE-acknowledgement papers and other outputs generated by IRP3 during the reporting period. A full list of publications during the period may be found in Appendix A.

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

Botero, Maria L.; Selmer, Anders; Watson, Roger; Bansal, Mukta; Kraft, Markus

DOI: 10.1016/j.ece.2016.04.001

Highlights:



• A remotely controlled experiment suitable for reactor engineering and process control teaching.

• With SIEMENS industry standard control software we introduce students to real-world systems.

• We have shared the experiment on the web enabling remote access from anywhere in the world.

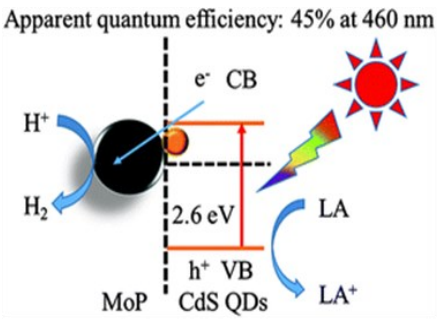
Abstract:

Continually assessed project work forms a core part of the Chemical Engineering curriculum at Cambridge. We have designed and built a remotely controlled chemical reactor that has been used and evaluated in undergraduate chemical engineering education. The purpose was to provide a pedagogical and authentic experience to students with essential training when laboratory usage was impossible or impractical, and be able to run and share the experiments as a fully functioning chemical engineering plant. A state-of-the-art SIMATIC PCS 7 Process Control System from Siemens is used for controlling, monitoring and providing results output. We describe the experimental setup, the hard- and software used, the teaching assignment and finally the results of the student evaluation. We also describe the challenges on the sustainability of the weblabs.

A highly efficient noble metal free photocatalytic hydrogen evolution system containing MoP and CdS quantum dots

Yin, Shengming; Han, Jianyu; Zou, Yinjun; Zhou, Tianhua; Xu, Rong

DOI: 10.1039/C6NR00989A

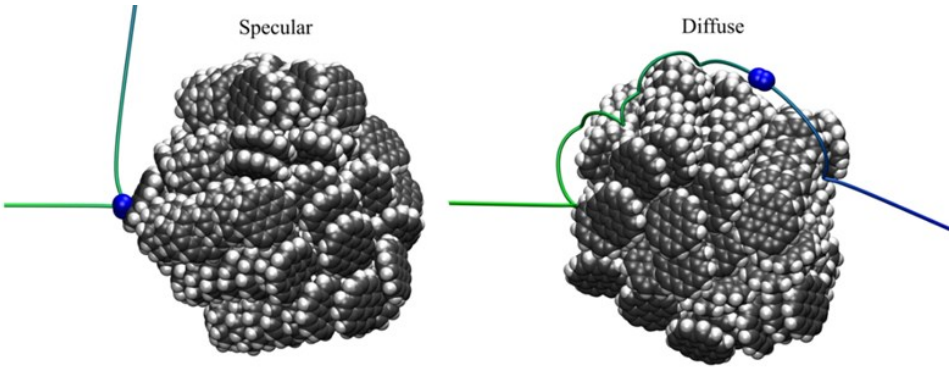


Abstract:

We report the construction of a highly efficient noble metal free photocatalytic hydrogen (H2) evolution system using CdS quantum dots as the light absorber and metallic MoP as the cocatalyst. MoP can be prepared by a facile temperature programmed reduction method and small clusters of MoP nanoparticles sized 10–30 nm were obtained by probe ultrasonication. The effect of synthesis conditions on the electrocatalytic and photocatalytic H2 evolution activity of MoP was investigated. The highest H2 evolution rate of 1100 μmol h−1 can be achieved by the optimized system under

visible light (λ ≥ 420 nm), which is comparable to that when Pt was used as the cocatalyst. A high quantum efficiency of 45% is obtained at 460 nm irradiation.

Can nascent soot particles burn from the inside?



Grancic, Jacob W. Martin, Dongping Chen, Sebastian Mosbach, and Markus Kraft

DOI: 10.1039/C6NR00989A

Highlights:

- Collisions between nitrogen molecule and coronene clusters are investigated via classical molecular dynamics simulation.
- Residence time distributions of the nitrogen probe exhibit bimodality, corresponding to a combination of specular and diffuse molecular scattering regimes.
- Nitrogen trajectories are found to be highly tortuous with the majority of atomic sites visited belonging to the edge of the coronene molecules.
- Coronene clusters are shown to be impenetrable below their thermal dissociation point.

Abstract:

The trajectories of a single nitrogen molecule resulting from a series of collisions with coronene molecular clusters of varying size are determined numerically by means of classical molecular dynamics simulations at two system temperatures, corresponding to the clusters being in solid and liquid state. The observed bimodality of the residence time distributions that corresponds to a combination of specular and diffuse molecular scattering tends to disappear with increasing temperature due to the more rapid rearrangements of the coronene cluster constituent molecules in the liquid state. The mean residence time decreases with increasing system temperature and appears to be independent of the coronene cluster size within the cluster size-range considered here. The recorded trajectories of the nitrogen probe are relatively tortuous, on average one order of magnitude longer than the shortest path connecting the impact and desorption points. The vast majority of the sites visited during the nitrogen molecule residence period correspond to the atoms at the edge of coronene molecules, mainly hydrogens. The intermolecular cohesive forces between the molecules cause that the coronene clusters are impenetrable by the nitrogen probe at temperatures below their thermal dissociation point.

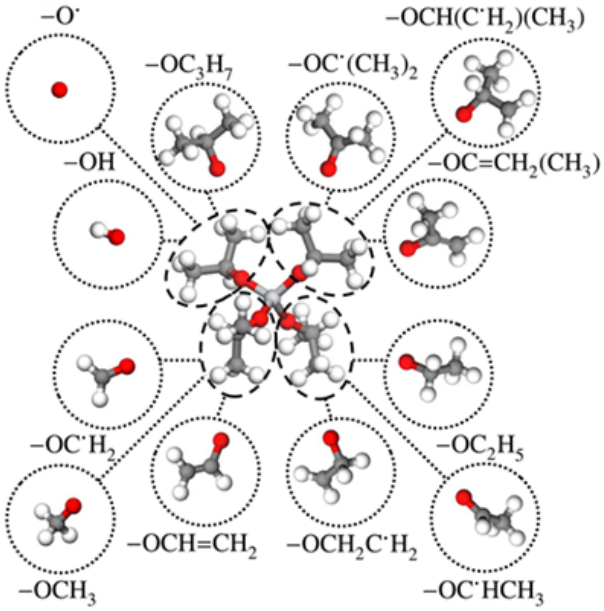
A kinetic mechanism for the thermal decomposition of titanium tetraisopropoxide

Philipp Buerger, Daniel Nurkowski, Jethro Akroyd, Markus Kraft

Highlights:

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

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



Abstract:

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

Skeletal chemical mechanism of high-temperature TEOS oxidation in hydrogen-oxygen environment

Daniel Nurkowski, Philipp Buerger, Jethro Akroyd, Sebastian Mosbach, Markus Kraft

DOI: 10.1016/j.combustflame.2016.01.025

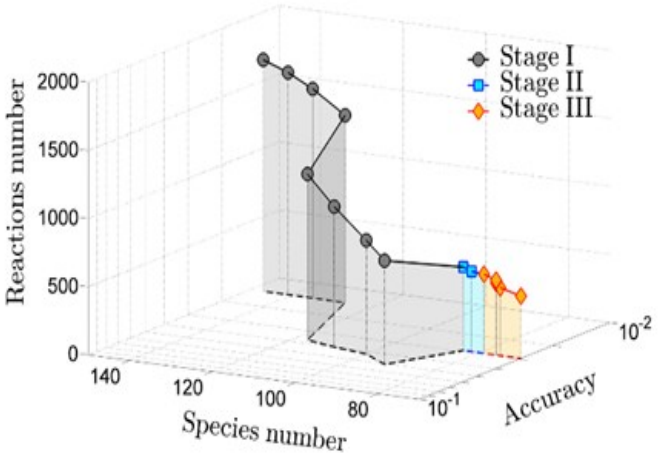
Highlights:

- A skeletal mechanism describing TEOS oxidation in flames is proposed.
- A three-stage reduction is used to eliminate unimportant species and reactions.
- Rate parameters for the main TEOS decomposition pathways are refined using transition state theory.
- Energetics of the key reaction channels is improved using CBS-Q method.

Abstract:

This paper improves the tetraethoxysilane (TEOS) oxidation mechanism proposed by Nurkowski et al. (Proc. Comb. Inst., 35:2291-2298, 2015) by refining the rate parameters of the key reaction channels in the mechanism. A skeletal version of the mechanism is proposed for hydrogen-oxygen environment. The rates of ethylene-loss from (tetra-, tri-, di- and dimethyldi-) ethoxysilane are comput-

ed using transition state theory. The energetics of the main pathways are refined by performing detailed ab initio calculations using the CBS-Q technique. An analysis of ethanol formation via silicates is also performed resulting in the addition of 27 new silica species to the model. Thermodynamic properties for these species are calculated via the balanced reactions method. Reasonably good agreement between the improved model and available experimental data is observed. The subsequent elimination of unimportant species and reactions is achieved via a three-stage reduction procedure. The first and second stages involve the Directed Relation Graph with Error Propagation (DRGEP) method, whereas the third stage analyses rate of progress of each reaction. The investigated conditions are taken from the experimental studies of TEOS oxidation in oxygen-hydrogen flames. The final skeletal mechanism comprises 70 species and 457 reactions and retains good reproduction of the key model properties across the chosen operating conditions as compared to the full mechanism.

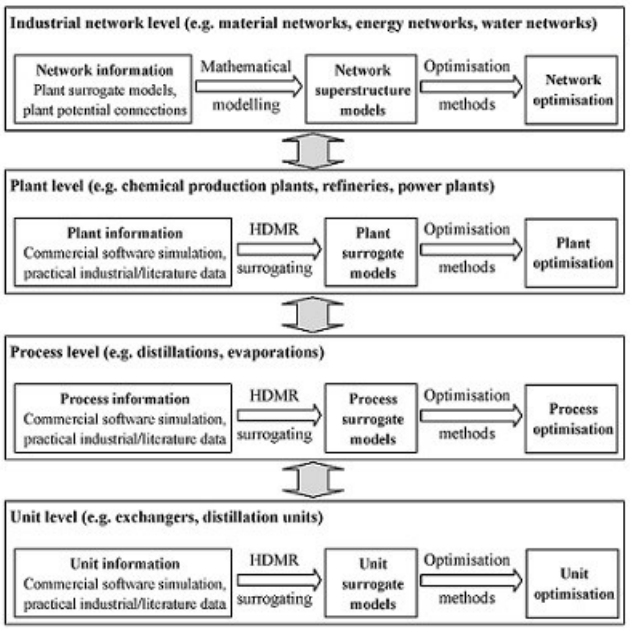


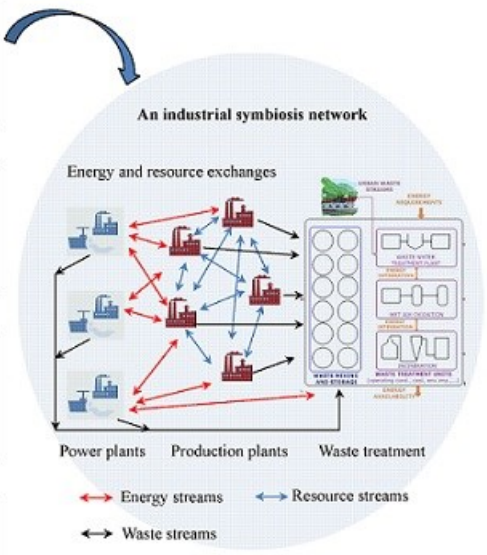
Design technologies for eco-industrial parks: from unit operations to processes, plants and industrial networks

Pan, Ming; Sikorski, Janusz; Akroyd, Jethro; Mosbach, Sebastian; Lau, Raymond; Kraft, Markus

DOI: 10.1016/j.apenergy.2016.05.019

Highlights:





- Highlights: -A four-level modelling framework is built for the EIP research. -
- Advanced mathematical modelling approaches are proposed for each level of problem. -
- Efficient optimisation methodologies are developed for solving EIP problems. -
- Industrial symbiosis is addressed combining material, water and energy networks.

This paper proposes a series of systematic approaches for multi-level modelling and optimisation in EIPs. It is the first work to implement innovative technologies to improve energy and resource efficiency throughout the whole EIP system. The novelties of this work include, (1) building a four-level modelling framework (from unit level to process level, plant level and industrial network level) for EIP research, (2) applying advanced mathematical modelling approaches to describe each level operation, (3) developing efficient methodologies for solving optimisation problems at different EIP levels, (4) considering symbiotic relations among the three networks (material, water and energy networks) at the top EIP level with the boundary conditions of economic, social and legal requirements. For methodology demonstration, two cases at process level and industrial network level respectively are tested and solved with the developed modelling and optimisation strategies. Finally, challenges and applications in future EIP research are also discussed, including data collection, the extension of the current networks to EIPs with the combination of material exchanges, energy systems and wastewater treatment networks, and the feasibility of the proposed methodologies for EIP optimisation when more complex aspects are taken into account. The system presented in the paper is expected to share services, utility, and product resources among industrial plants to add value, reduce costs, improve environment, and consequently achieve sustainable development in a symbiosis community.

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

October 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.

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

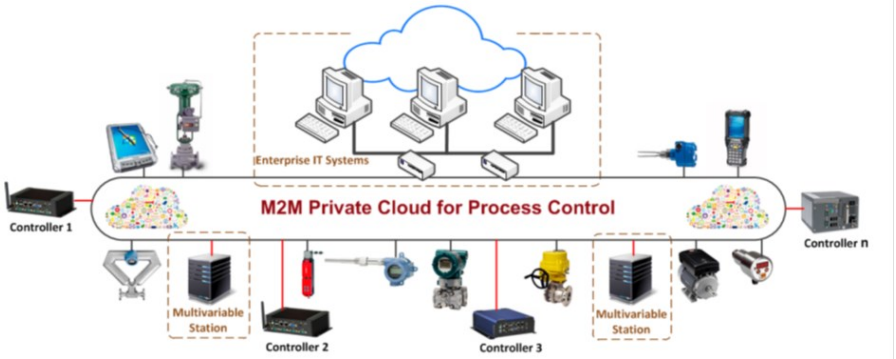
IRP4 PIs discussing their work at the Mid-Term Review, July 2016, Singapore

3.4.2 Update on work packages

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

Dr Anthony TRAN (SRF, NTU, IRP4) has been working on a number of projects:

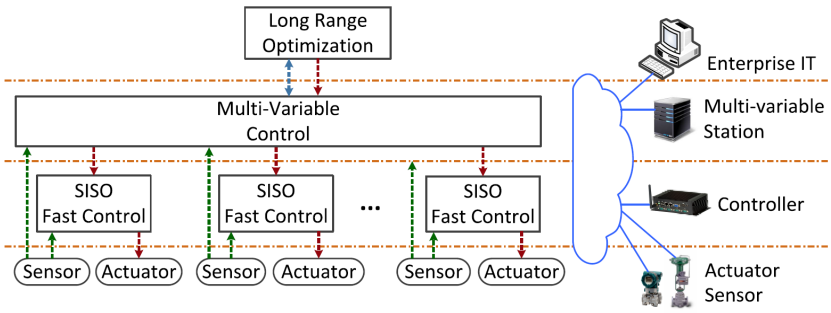
- A new framework for feedback control design and synthesis for nonlinear systems with 'General Dissipativity Constraint' (extending previous work on linear systems).
- A novel approach to solving the intermittent data loss problem for the 'distributed moving horizon state estimation' of power systems using the 'incremental dissipativity constraint'.
- A Lagrange stability and boundedness approach to the stability guarantee problem of 'periodic economic model predictive control' that has high potential for future dynamic operation of power systems.
- A novel 'private machine-cloud architecture' for Operational Technology Systems.



Above – Private Machine-Cloud Architecture for Operational Technology (OT) Systems.

Ashok KRISHNAN (PhD student, NTU, IRP4) is collaborating with other researchers in IRP4 on the Optimal Power Flow and Excitation Control problems. He compares global optimization approaches developed for the Optimal Power Flow problem with existing approaches in literature. The possibility of using a Nonlinear Model Predictive Control scheme for the excitation control problem is being explored. Initial results obtained have been encouraging. Further testing for various fault scenarios and comparison with state of the art methods are in progress.

DANG V Thuy (PhD Student, NTU, IRP4) has been working on a journal paper entitled "Event-triggered anytime control as an event-triggered Markov jump system" which is an upgrade of my CDC2015 paper. In this work, we propose a new approach based on Markov jump system for stability analysis of event-triggered anytime control schemes. Using the proposed approach, we not only recover existing results in the literature, but also be able to systematically extend to a more sophisticated E-SAC scheme for which, until now, no analytical expression had been obtained.



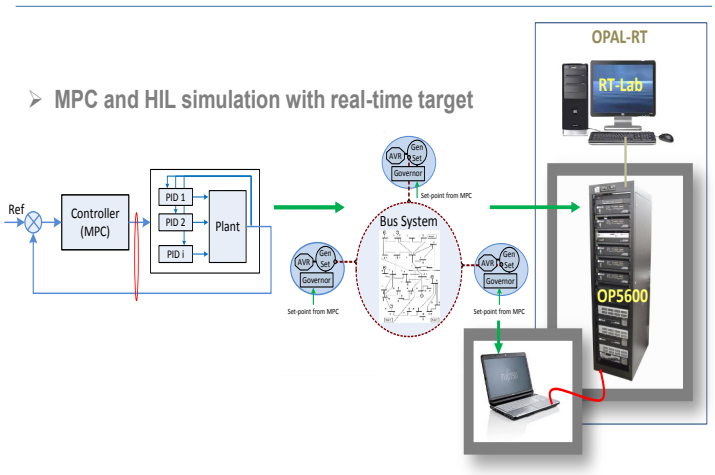
Right – Software-Defined Architecture for Private Machine Cloud

In addition DANG V Thuy (PhD Student, NTU, IRP4) has completed a draft paper for upcoming IFAC 2017 World Congress. The topic of this paper is to use null space and ADMM for solving QP problem arising from sparse MPC. The null space method is used to reduce the size of QP problem. To preserve the structure of matrices in sparse MPC formulation, we construct a banded null basis. Then an ADMM-based algorithm with structure exploiting technique is used to solve the new smaller size QP problem. Preliminary results obtained from C implementation in a PC, for a particular and random MPC problems, show an improvement in term of timing to solve QP problem comparing with

other ADMM variants, and a comparable performance with a state-of-the-art QP solver CVXGEN. Embedded implementation on ARM-Cortex A9 processor is being carried out.

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

The previously-developed 'Multiplexed model predictive control' scheme for interconnected systems, using a 'quadratic dissipativity constraint' and invariant sets, designed for application to the 'automatic generation control' problem in power systems, has been validated using the OPAL-RT real-time power system simulator.



Above – Hardware-In-the-Loop setup for verifying MPC algorithms for multi-variable feedback control and real-time optimization of power systems with Opal -RT linking to external PCs via Modbus/TCP.

PATIL Bhagyesh Vijay (RF, NTU, IRP4) has been working on development of the global optimization algorithms with specific applications in the nonlinear exciation control and optimal power flow problems. Self scheduling problem for a combined cycle gas turbine was solved with one such algorithm (preliminary results on which were presented in American Control Conference held 6th-8th July, Boston, USA). Currently, the work is focusing on the experimenting of efficient algorithms for solving the aforementioned problems for small to medium size power networks.

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

Dr Anthony TRAN (SRF, NTU, IRP4) has been working on realistic models of electrical power transmission systems, with traditional generators implemented and tested in the OPAL-RT real-time simulator. A communication channel based on the MODBUS protocol has been implemented to allow emulation of one or more control algorithms running on external processors (pCs), controlling a power network simulated on OPAL-RT.

Dr Anthony TRAN (SRF, NTU, IRP4) completed a Real-time simulation study for Hydro Quebec 23-bus, Adelaide 42-bus and Illinois 44-bus systems with the governor and excitation local controls and 'automatic generation control' using MPC in Matlab and RT-Lab environment.

Tengpeng CHEN (PhD student, NTU, IRP4) has been working on building the mathematical model of a larger power system, for example, IEEE 118-bus system. He is planning to do more simulations and revise a paper "Influence Function Analysis of Robust Power System State Estimation". In this paper, to be submitted to Transactions on Instrumentation and Measurements, analytical equations are derived using influence function approximation to calculate the variance of the state estimate approximately for common robust state estimators such as the Quadratic-Constant, Quadratic-Linear, Square-Root and Multiple-Segment estimator. In addition he is in the process of finishing a paper draft named "Robust Power System State Estimation Using t-Distribution Noise Model". In this paper we propose a t estimator based on the maximum likelihood criterion for robust power system state estimation, where the t-distribution probability density function is used to fit the noise so as to get a noise model with higher accuracy. Instead of solving the maximization problem numerically, the Influence Function (IF) is employed to given an approximate solution to the problem and it can be solved iteratively, as the weighted least squares did. It is more suitable to be implemented in real time. Due to the better noise model approximation, the t estimator can get the better estimated results compared with the ones obtained from the common estimators such as the Quadratic-Linear, *Square-Root and Multiple-Segment estimator.*

Ashok KRISHNAN (PhD student, NTU, IRP4) has been working on modelling the generation network on Jurong Island. He is focussing on preparing a detailed model for the combined cycle gas turbine. This technology is the major contributor to electricity generation on Jurong Island. The model in-

cludes a detailed consideration of the electrical and thermodynamic aspects of the combined cycle gas turbine. The modelling includes a detailed consideration of the start-up and shut-down trajectories and is built using a hybrid systems approach. He is also working on incorporating this model in a system of generators including renewable energy sources and controllable loads.

A hybrid optimal placement method is proposed to solve OPP for distribution network using exhaustive search and bisecting research method. Comparing with OPP algorithms designed for transmission networks, this method is customized to take full advantage of radial topology of distribution networks. Besides exhaustive search method, another algorithm called simulated annealing is also customized. Simulated annealing algorithm is a generic heuristic optimization method which is faster than exhaustive search method because it does not check all combinations exhaustively. However, it will also consume long time when size of network increases. The customization step is executed to accelerate the solving process. The customized simulated annealing algorithm and exhaustive search method are tested on IEEE test feeders. Simulation results show that the customized algorithms are much more effective. In addition, she attended the IEEE ISGT and the tutorial "synchrophasors technology applications in distribution systems".

Dr Yuhao SUN (RF, NTU, IRP4) presenting to Prof Claire ADJIMAN (SAC member) at the C4T Mid-Term Review Poster Session

Pratim BISWAS (PhD Student, NTU, IRP4) reported on the topic of his PhD thesis is "Power System Optimization using Evolutionary Algorithm". The primary objective is to improve efficiency, increase output at a reduced cost, reduce losses of electrical power system. Currently, my research is mainly focused on finding suitability of variants of Differential Evolution algorithms to specific optimization problems. He has been reviewing basic Differential Evolution (DE) algorithm and its variants in the form of JADE, SHADE and L-SHADE. Some more variants and related algorithms are also being reviewed for its relevance of application in Power System problems.

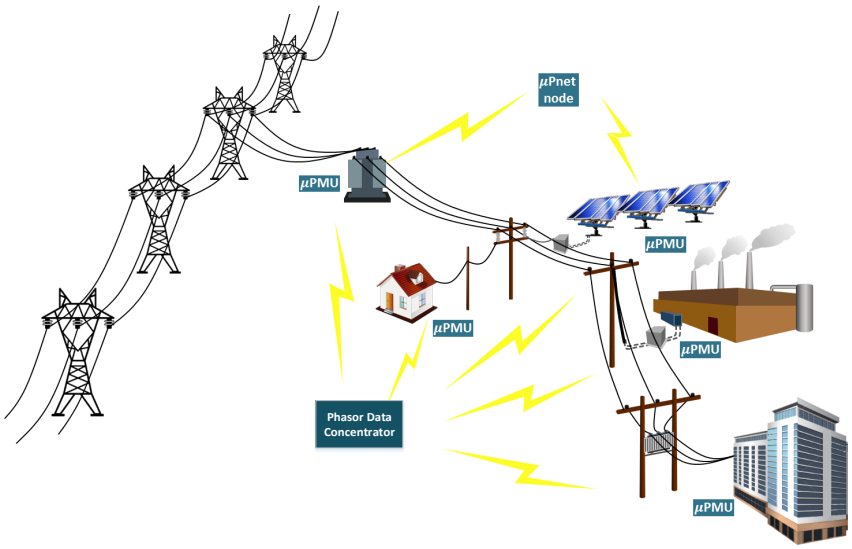
Pratim BISWAS (PhD Student, NTU, IRP4) has applied basic DE algorithm and some of its variants in renewable energy problems as well as in Power Electronics. Currently, focus is on improving the results from previous studies and high-lighting advantages of application of evolutionary algorithms. In future, multi-objective optimization methods shall be studied and will be applied in more complex power system optimization problems. Efforts will be given in forming new optimization problems also.

Differential Evolution (DE) algorithm and specifically its improved variants are state of the art heuristic algorithms which in most cases outperform any other available algorithms for multimodal optimization problems: i. DE can be applied to single or multi-objective problems, ii. DE and its improved variants converge faster to the global optimal solution, iii. DE has been applied to a complex windfarm problems involving numerous decision variables. The windfarm efficiency is improved with optimization of wind turbine rotor diameters and hub heights.

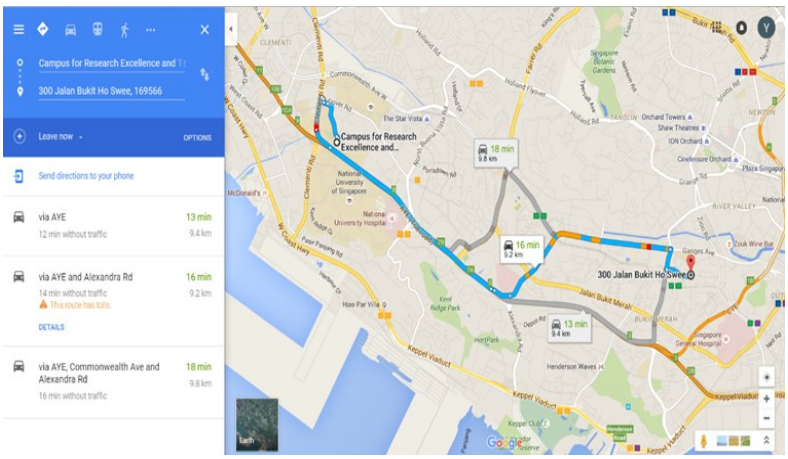
Lu SUN (Phd Student, NUS, IRP4) has, together with CHEN Tengpeng and CHEN Xuebing, been work-

ing on several projects such as Influence Function and Analysis of Robust Estimators in Dynamic Power Systems, Robust State Estimation Using t-Distribution Noise MLE and State Estimate Variance as a Criteria in Optimal PMUs Placement.

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



Dr Yuhao SUN (SRF, NTU, IRP4) *et al.* have been using the Phasor measurement Unit (PMU) to monitor distribution lines extensively. The micro version of PMUs is a newly developed device at a much cheaper cost per unit but with highly accurate measurement ability. The novel technology involving the implementation of micro PMU network is capable of continuously measuring the voltage and current phase angle in a real-time mode and in an ultra-precise manner, 0.001 resolution on phase angles and 2PPM resolution on the magnitudes. As a result, accurate and ultra-fast grid state estimation is reliably provided. Moreover, the new characteristics of grid with increased dispersed generation on the distribution grid also can be closely monitored, such as bi-directional power flows, unstable power supply, unintentional islanding and voltage profile issues.



Two locations identified using Google map

Dr Yuhao SUN (SRF, NTU, IRP4) *et al.* have purchased five of such devices. Once all legally required paper work were ready, three sets of mPMU local signal processing module, voltage sensors, current transducers and the GPS antennas to measure the low voltage grid network, were installed. in the CARES office and in our collaborators' office building which is indicated in Figure 4. Our aim is to measure the atomic-clock synchronised tiny difference of voltages between two geographic locations in Singapore.

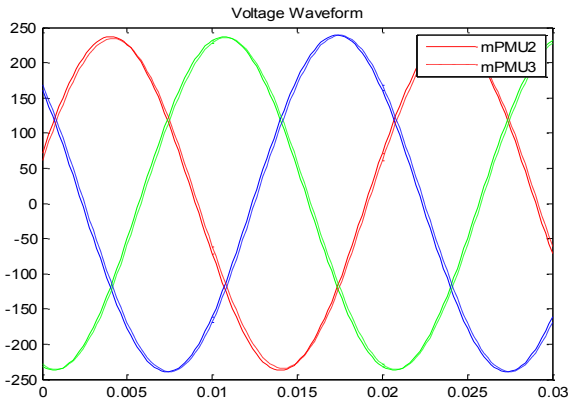
Furthermore, a data management system for mPMU project to achieve data acquisition and centralization has been developed. A transparent remote communication system for the communication for distribution networks has been implemented. This is essential for the project to achieve real-time data process. At current stage, the research showed there is significant amount of data stream coming in at every moment. One simple node generates 600 Megabytes binary data daily. As a result, the concept of Big Data will be explored and data mining technology will be implemented.

Due to different delays from different communication routes among different mPMU modules at various locations and central controller, the data coming in to the data centre from each mPMU module has certain amount of delays. This is known as delay jitter. Dr Yuhao SUN (SRF, NTU, IRP4)

developed an algorithm to pre-process and to align all the GPS timestamp enabled data generated by micro synchrophasor in order to allow phasor information to be processed for real-time state estimation.

Once the micro PMUs network installed in the two distant locations, the phasor difference measured between the two locations is identified as shown in Figure 7 and Figure 8. Further experiments are required to show more differential patterns over longer time span.

Furthermore, Ashok KRISHNAN (PhD student, NTU, IRP4) has been investigating how local generations and renewable energy resources in the biodiesel plant can be managed to support the utility grid in times of emergency and to meet local load demand during normal operation.

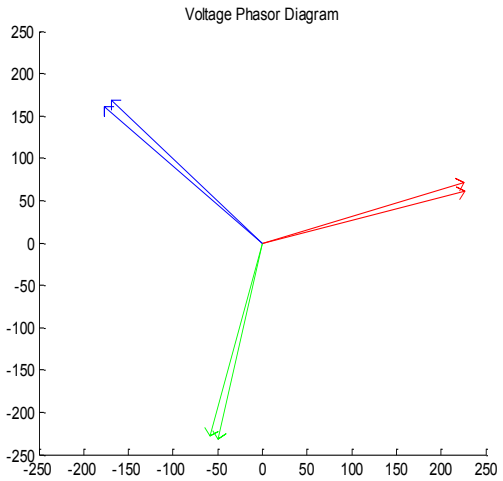


Above - Phase differences between two locations

Joymala MOIRANGTEHM (RF, NUS, IRP4) reported that experiments have been carried out to validate the feasibility of the inverter operation using the Selective Harmonic Optimization (SHO). This involves construction of H-bridge, integration with the driver circuit, and testing the hardware initially using Hysteresis Band Current Control. As a next step 3-level operation and discrete optimization will be tested.

Srinivasa Rao KAMALA (PhD Student, NUS, IRP4) reported that in a typical petroleum processing industry, variable speed drives (VSDs) are used in vapour recovery systems, pumping operations and approximately 80% of the electrical load in the petroleum process industry are induction motors driven by these VSDs. The VSDs cause distortions to the voltage/current waveforms and it would affect the operation of the power system.

The impact of non-linear loads on the electrical power system and harmonic mitigation technique using shunt active filter (SAF) of a system with linear load and non-linear load (motor drive) has been simulated through MATLAB/Simulink. Srinivasa Rao KAMALA (PhD Student, NUS, IRP4) observed from the test results that, the total harmonic distortion (THD) reduced from 45.27% to 0.45% with the SAF.



Right - Phase differences between two locations

In addition, Srinivasa Rao KAMALA (PhD Student, NUS, IRP4) reported that renewable energy based distributed generation (DG) systems are being connected to the distribution network, these could contribute ancillary services such as reactive power and harmonic compensations. A MATLAB/Simulink based simulation is being carried out to mitigate the harmonics using solar photovoltaic (PV) system with motor drive load.

CHEN Xuebing (PhD Student, NTU, IRP4) has been working on a distribution system monitoring with micro-PMU. Motivated by pressure to reduce CO_2 emissions, today's power systems increasingly focus on the integration of renewable energy sources. These renewable energy sources bring power distribution system new characteristics such as: bi-directional power flows, unstable power supply and unintentional islanding. These new characteristics necessitate close monitoring for distribution systems. Her work consists of two parts: determine an optimal placement of micro-PMU and formulate a linear state estimator for distribution network.

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

with the help of accurate fault prediction methods. His research field has been mainly focused on deep learning methods and ensemble algorithms.

In his study, various kinds of time series forecasting algorithms have been reviewed, including Artificial Neural Network (ANN), Support Vector Regression (SVR), Deep Belief Network (DBN) and ensemble methods. Moreover, two ensemble deep learning approaches have been proposed for load demand forecasting. The first one is an ensemble methods composed of DBN and SVR. We train a group of DBNs using different number of Back-Propagation (BP) epochs, and use an SVR to aggregate the outputs from DBNs. Another method is an Empirical Mode Decomposition based deep learning approach. In this work, the load demand series are first decomposed into several intrinsic mode functions (IMFs). Then a DBN with two Restricted Boltzmann Machines (RBMs) is used to model each of the extracted IMFs, so that the tendencies of these IMFs can be accurately predicted. Finally, the prediction results of all IMFs can be combined by either unbiased or weighted summation to formulate an aggregated output for load demand.

In addition, Xueheng QIU (PhD student, NTU, IRP4) also investigated a randomized version of neural network, which is called Random Vector Functional Link Network (RVFL), and proposed a both effective and efficient learning model for short term electricity load demand forecasting by combining EMD and RVFL.

For future research directions, multivariate time series forecasting models shall be constructed making using of the potential learning ability of deep learning methods. Moreover, the concept of deep learning can also be applied with RVFL to develop deep RVFL structure to make use of RVFL's advantages in computation time

Dr Joymala MOIRANGTEHM (RF, NUS, IRP4) presenting her work to Prof Claire ADJIMAN

Xueheng QIU (PhD student, NTU, IRP4) has also been working on the development of an ensemble method composed of Empirical Mode Decomposition algorithm and random vector functional link neural network is developed for load demand time series forecasting.: i. EMD based hybrids methods normally outperform the corresponding single structure models for load demand in time series forecasting, ii. The computation of the RVFL network is the shortest among all of the machine learning models, iii. The proposed EMD based RVFL network achieves the best performance for short-term load demand forecasting, and also has the advantages of efficiency.

Dr Joymala MOIRANGTEHM (RF, NUS, IRP4) reported that the future of high renewable energy penetration and the consequent power variability produces the need for fast power-flow computations for the useful management of power. Such management must have least requirements for human intervention, achievable through fast and reliable automations. A Geographic Information System (GIS) integrated automation of a non-iterative power-flow method known as Holomorphic Embedded Power Flow (HEPF) so as to produce a power-flow service over a communication network is proposed. Since HEPF reliably guarantees the solution and reaches it very fast through constructing the solution, it is an ideal candidate for near real-time updates of the electrical states of a power system.

A few test cases (12 bus system, IEEE 9 bus system and 209 Bus system) have been considered to

illustrate the HEPF method and the solutions obtained by the HEPF method are compared with the solutions obtained by the PowerWorld Simulator to validate the idea of the HEPF algorithm. This is under study at present.

Joymala MOIRANGTEHM (RF, NUS, IRP4) reported that the test results obtained with the proposed HEPF method clearly and closely matched with those obtained with standard PowerWorld simulators.

WP5: Model building, integration and maintenance

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

IRP4 members discussing their work at the Mid-Term Review, July 2016, Singapore

- IRP4 members integrated OPAL-RT with the JParkSimulator via the Cloud communication system. The JPS can remotely trigger a real-time simulation request on the OPAL-RT and retrieves the simulation results through the Cloud communication system.
- IRP4 members have been looking into trying to interface OPAL-RT to the power converters from TriPhase to conduct power hardware in the loop (PHIL). Research discussions have been established with Newcastle University to explore the PHIL Implementation.
- IRP4 members collaborated with IRP3 colleagues to develop the Semakau microgrid simulator and the process of parameterizing the electrical model whish is similar to the JPS has started.

WP6: Demonstration of proposed algorithms on pilot scale

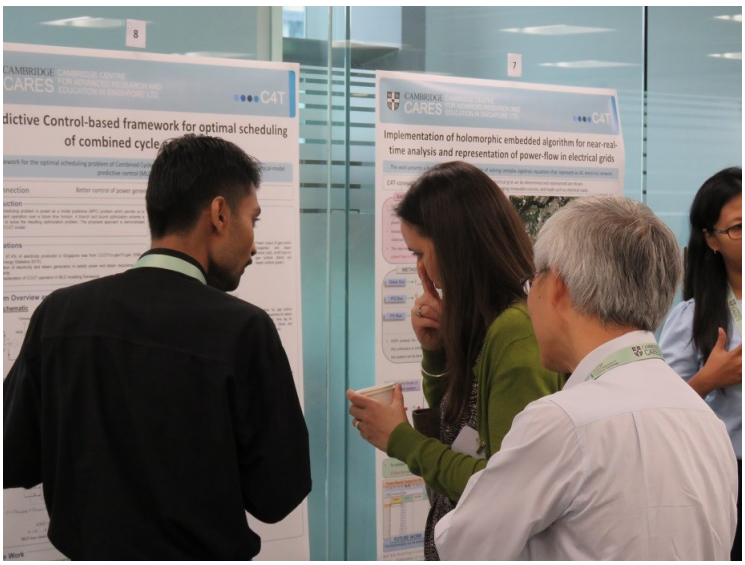
In lieu of pilot-scale implementations, this WP is being pursued using the OPAL-RT simulator and the hardware micro-grids.

Other Activities and Achievements

- A research paper, entitled " A Combined Methodological Approach Incorporating Chemical and Electrical Models for Analyzing Petrochemical Plant Operation" , as a result of the collaboration between IRP3 and IRP4 members is in preparation.
- Ashok KRISHNAN (PhD Student, NTU, IRP4) presented a conference paper, entitled "How real is real? Comparative Studies on NTU Microgrid Testbed" at the RT16 OPAL-RT User Conference, Munich, Germany, June 2016. The paper discusses the model validation between the NTU smart grid and the electrical model in OPAL-RT Hypersim. The power flow results from OPAL-RT Hypersim are comparable to the experimental measurements from the NTU microgrid.
- Training on OPAL-RT 's new Windows version of Hypersim was provided in NTU microgrid lab.
- Eddy FOO (RF, NTU, IRP4) attended LabVIEW Developer Days in Chevrons Singapore on 20th

May 2016.

- Eddy FOO (RF, NTU, IRP4) has conducted a lab tour of the NTU microgrid and OPAL-RT during the C4T mid-term review to the SAC members
- Eddy FOO (RF, NTU, IRP4) has joined NTU School of EEE as a lecturer
- Prof. GOOI and Dr. Eddy FOO (RF, NTU, IRP4) visited Newcastle University, UK and Grenoble Institute of Technology, France in June 2016 as part of the research visit to discuss research collaborations using OPAL-RT



Dr Bhagyesh PATIL (RF, NTU, IRP4) presenting his work to Prof Claire ADJIMAN (SAC member)

- Ashok KRISHNAN (PhD Student, NTU, IRP4) presented his paper titled 'Predictive Control based Framework for Optimal Scheduling of Combined Cycle Gas Turbines' at 2016 American Control Conference held between 6-8 July, 2016 in Boston, USA.
- Ashok KRISHNAN (PhD Student, NTU, IRP4) co-authored a paper titled 'Examining the Bernstein global optimization approach to optimal power flow problem' which has been accepted for publication in the AIP Conference Proceedings.
- Prof. GOOI and Prof. MACIEJOWSKI co-authored a paper titled 'A Hierarchical EMS for Aggregated BESSs in Energy and Performance-based Regulation Markets' which has been accepted for publication in IEEE Transactions on Power Systems.
- The poster titled "An Integrated Modeling Approach Incorporating Chemical and Electrical Models for Analyzing Biodiesel Plant Operation" was selected as the best IRP4 poster during the C4T poster competition.
- A paper, entitled " Nonlinear model predictive control based Bernstein global optimisation with application to nonlinear CSTR", was presented by Prof Jan MACIEJOWSKI (PI, Cambridge,IRP4) at 15th European Control Conference in Aalborg, Denmark, June 2016.
- Dr Yuhao SUN (SRF, NTU, IRP4) had several meetings with Singapore power systems to discuss the potential collaborations. They were very interested in our initial experimental results and are waiting for further measurement over a longer time span to verify the phasor difference between the two locations. Once it has been demonstrated, very likely we will start the collaboration to help Singapore power systems to continuously monitor two points on 22 kV distribution network.
- Dr Yuhao SUN (SRF, NTU, IRP4) had an initial meeting with Singapore National Metrology Centre, A*STAR. They were very keen to collaborate with us. They were particularly interested in establishing certification to our measurement methodology and data accuracy. Support from the institute will be essential if we finally commercialise our micro PMU technology.
- PATIL Bhagyesh Vijay (RF, NTU, IRP4) presented a research paper entitled "Examining the Bernstein global optimization approach to optimal power flow problem" at the International Conference and Summer School on Numerical Computations: Theory and Algorithms (NUMTA2016), Italy.
- Xueheng QIU (PhD student, NTU, IRP4) is planning to attend IEEE International Conference on Systems, Man and Cybernetics (SMC2016) hosted by IEEE Systems, Man and Cybernetics Society in October 2016, Budapest, Hungary.

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.

Numerical Algorithms for Quadratic Programming in Model Predictive Control - An Overview

Dang, T-V, Tri Tran; K-V. Ling

DOI: 10.13140/ RG.2.1.1885.4885

Abstract:

Dr Bhagyesh PATIL (RF, NTU, IRP4) and IRP4 colleagues present at the C4T Poster Competition

Dynamic modeling of complex systems is an essential part of multi-variable control schemes. Among these schemes, model predictive control (MPC) is the most successful optimization-based strategy for multi-variable constrained systems in industry. And in MPC problem formulations, quadratic objective function and linear inequality constraints are pervasively used. This paper provides an overview of the numerical algorithms that are found widespread used to solve the quadratic programming problem in MPC. Specifically, the algorithms of interior point methods (IPMs), first-order methods, and Alternating Direction Methods of Multipliers (ADMMs) are addressed herein. Discussions on which conditions a particular algorithm should be chosen and its advantages are also given.

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, 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.
- 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, 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

- 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.
- Chan, Martin SC, Wen Liu, Mohammad Ismail, Yanhui Yang, Stuart Scott, and John Dennis. 'Improving Hydrogen Yields, and Hydrogen: Steam Ratio in the Chemical Looping Production of Hydrogen Using Ca 2 Fe 2 O 5'. *Chemical Engineering Journal* 296 (15 July 2016): 406–11. doi:10.1016/j.cej.2016.03.132.
- 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.
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