CAMBRIDGE CARES

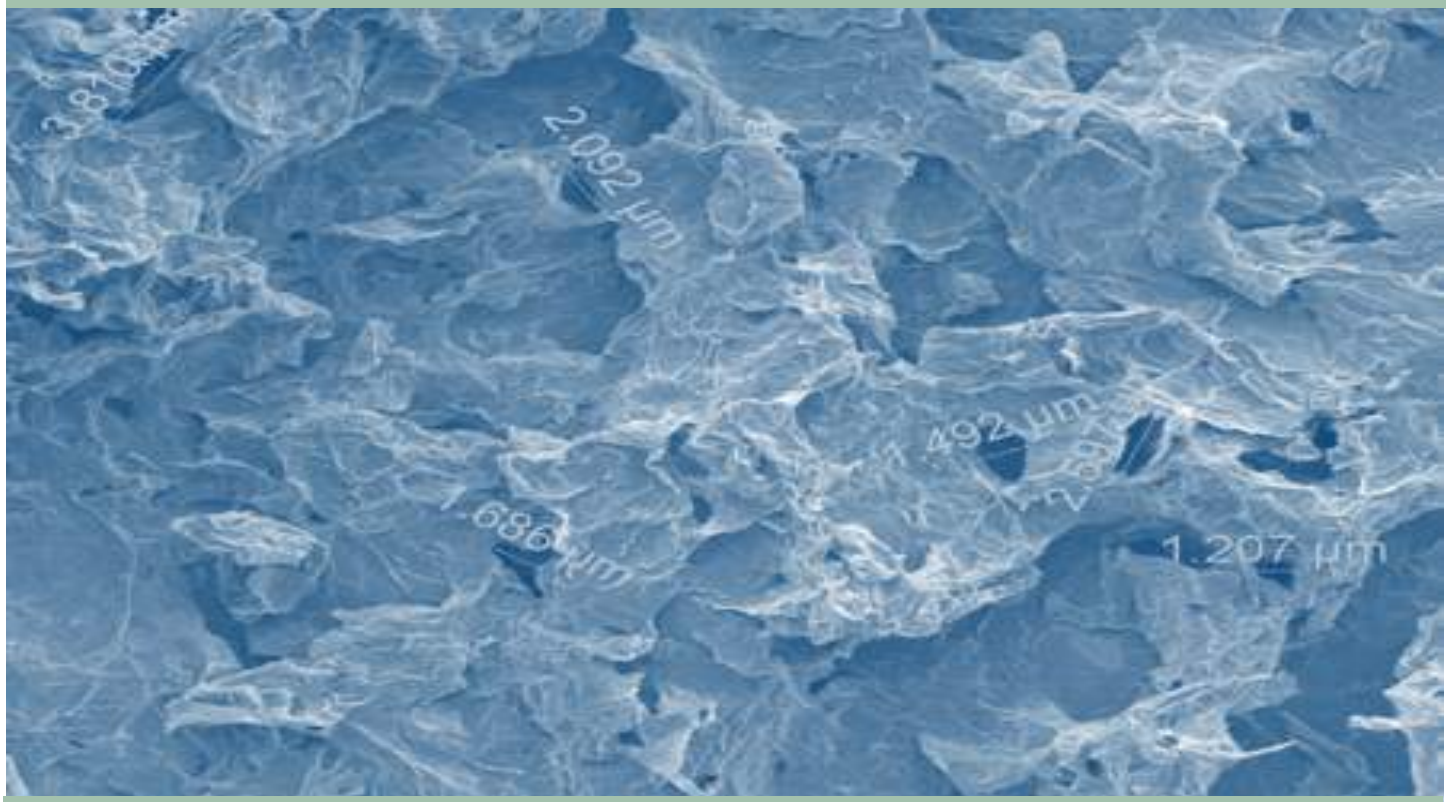
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH IN ENERGY EFFICIENCY IN SINGAPORE LTD.

Biannual Research Report

May—September 2014

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

2 Foreword

Prof. Markus Kraft,

CARES Director.

September 2014

The first half of Programme Year Two has been busy for the Cambridge Centre for Advanced Research in Energy Efficiency in Singapore (CARES) and the first CARES research programme, the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T).

We now have 14 researchers (Senior Research Fellows and Research Fellows) dedicated to the programme in Singapore and Cambridge. Twenty PhD students are working on C4T projects in our collaborating institutions of Nanyang Technological University (NTU) and the National University of Singapore (NUS). The current work of these teams is described in this report and is beginning to produce significant results.

For a flavour of these results, I would like to draw your attention to the Scientific Highlights section of our Research Report. In this section, each of the Interdisciplinary Research Programmes (IRPs) has given a brief overview of their most exciting scientific achievement during the reporting period. The current achievements are not only interesting in their own right, but are laying the groundwork for the future direction of the programme. The work of the IRPs is enhanced and supported by collaborations with industry. The Cambridge-CARES Studentship Scheme has opened up opportunities for industrial collaboration, with several global companies currently interested in providing 50% match funding for the C4T contribution to students on this scheme. We are grateful to all of our industrial and commercial collaborators and actively pursuing further connections with relevant organisations.

This reporting period has also been a productive one for C4T's work with both graduate and undergraduate students. The framework for the Cambridge-CARES Studentship Scheme has been formalised; this scheme will allow University of Cambridge students to spend up to two years based in Singapore with the C4T team. We look forward to the first student starting on the scheme with IRP3 in October 2014. In addition, as part of the C4T outreach programme, Dr Adrian Fisher (Principal Investigator, IRP2) hosted a successful summer school in Singapore and Cambridge for a group of Chinese undergraduates in July 2014. Plans are currently being made to expand this programme and increase the Singapore element in 2015 and beyond.

Of course, as might be expected in a major new research programme such as C4T, there have also been some challenges. One of the most significant pieces of work absorbing both the administrative and scientific teams in 2014 has been inputting to the specification and design of the CARES offices and laboratory in the CREATE buildings. Some unforeseen difficulties have been encountered with the infrastructure of the CREATE Research Wing, which have delayed the outfitting of these spaces. However, the teams are working closely with NRF to resolve these problems and we hope to report positive news in the next update.

Looking forward to the next six months, scientifically there are many interesting prospects on the horizon. All of the IRPs are looking forward to welcoming new members of the research teams who are due to take up their posts within the next few weeks.

I commend this report to you, both as indication of the current productivity of C4T and CARES and as a demonstration of the potential of this new organisation to create and foster cutting-edge science in the area of energy efficiency in chemical technologies. I hope it will encourage all stakeholders to take a keen interest in the future output of our researchers – I have every reason to hope that their contribution to science both in Singapore and globally will be highly significant.

1.1 Structure and Organisation

The Cambridge Centre for Energy Efficiency 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)

The impact of the dynamic response of the chemical plant on its batch output over varying time scales will be evaluated using a combination of methods developed in IRPs 1, 2, 3 and 4.

The C4T group is temporarily kindly hosted by ERI@N in the School of Chemical and Biomedical Engineering (SCBE) of Nanyang Technical University. Eventually, the group will move to its permanent home in the CREATE buildings.

1.2 CARES and C4T collaborations

The fruitful and productive collaborations that CARES and C4T enjoy with Nanyang Technological University (NTU) and the National University of Singapore (NUS) are integral to the work of the programmes.

The following brief updates give an flavour of the C4T work currently happening in the collaborating institutions. More detailed updates on the progress of the IRPs can be found in section three.

Nanyang Technological University (NTU)

Corporate: CARES and C4T would like to express gratitude to NTU for kindly hosting the CARES offices whilst the permanent base in the CREATE buildings is prepared.

IRP1: Work on (1) CO_2 methanation and (2) synthesis of novel oxide materials for chemical looping has started at NTU.

IRP2: An SRF and RF have been recruited to WP2.2 targeting the development of novel electrode materials. Current chemical conversion targets include CO_2 electroreduction and hydrogen peroxide generation. A further RF and SRF have accepted offers to work on WP2.3, with expected start dates in late 2014. Two 'in kind' PhD studentships are currently in post, working on WP2.2 and WP2.3. Two CARES and an 'in kind' NTU PhD studentship are currently advertised.

IRP3: One RF is currently in post working on WP3.1 and WP3.5 under the joint supervision of Profs LAU and KRAFT. In addition Prof LAU has identified around 10 undergraduate students at NTU who are now working on WP1. They have already made some important contributions to finding important data on the industries on Jurong Island. We have also identified hardware which we plan to put in the newly designed media room in the CREATE lab. One SRF and RF have been made an offer to work on WP3.2 under the joint supervision of Profs RONG and KRAFT. Another RF has been made an offer to work on WP3.2. We have ordered computers and software for the new Singapore members of C4T.

IRP4:

WP1: Processor-aware computation will be investigated for MPC algorithms. The effects of early termination of optimization in case of real-time constraints will be investigated, as well as early termination in case of 'sufficiently good' approach to the optimum, which could be important in case a processor is shared with other tasks.

WP2: A Research Fellow is currently being recruited to work on WP1 and WP2. Expertise with numerical constrained optimization for convex and/or non-convex problems is required. We are looking for a candidate with experience of at least one of the following: implementation under real-time constraints (for example for MPC); implementation on special-purpose processors such as FPGAs or GPUs; distributed/decentralized optimization.

WP3: Formulations of appropriate MPC problems for power grids with industrial loads will be developed. In particular, 'Economic MPC' formulations will be evaluated.

The work on 'Quadratic dissipativity constraint for decentralized power system control' will be written up for journal publication (Tran, Ling, Maciejowski) by October 2014.

The work on 'MPC with a quadratic dissipativity constraint' (to be presented at IEEE-CDC in December 2014) will be developed and written up as a journal paper (Tran, Ling, Maciejowski, Gooi, Foo) by December 2014.

The newly-developed MHE state estimator, and the GT-based estimator, will be compared against the 'traditional' state estimator used on the Microgrid (Chen Tengpeng, Zhou Dexiang, Eddy Foo). This comparison is expected to be completed by mid-November 2014.

Consideration is being given to the purchase of a real-time power system simulator. The main products under consideration are *RTDS* and *OPAL-RT*. These are expensive products, costing in the region of SGD 300k each. The choice will be determined by which best supports the widest range of IRP4 activities.

WP6: Further consideration will be given to the development of a low-voltage, low-power emulator, and to the modality of such a development if it is pursued. Research Fellow Dr Tran will provide further motivation and justification, and draft an initial project plan, indicating personnel, effort and expenditure required. The potential market for such an emulator will be investigated.

National University of Singapore (NUS)

IRP1: A RF working with Prof. Zeng on novel materials has been appointed.

IRP2: Recruitment to an RF is position for WP1 is currently ongoing, with interviews scheduled for early October. An 'in kind' Cambridge PhD student is working with NUS colleagues in WP2.1 and has recently visited NUS for a research and knowledge transfer. Two CARES funded PhD studentships are currently available for WP2.1.

IRP3: In the Department of Chemical and Biomolecular Engineering two PhD students have been appointed under the joint supervision of Professor I. KARIMI and Professor M. KRAFT. They will work on WP 3.1, 3.2, and contribute to WP3.5. A RF position for the same work packages has been advertised. This RF will be jointly supervised by Profs KARIMI and KRAFT. In the department of mechanical engineering in the section of energy and bio-thermal systems Professor YANG Wenming has identified a PhD student who will commence his studies in January 2015. This student will be working on WP 3.2. An additional RF position for WP3.2 and WP3.3 under the joint supervision of Profs YANG and KRAFT has been advertised. Computers and software for the new members have been ordered.

IRP4: **WP3:** A journal paper on the recursive GT-based MHE estimator will be prepared (Zhou, Ho, Ling, Maciejowski) – note this is joint NTU-NUS work.

University of Cambridge

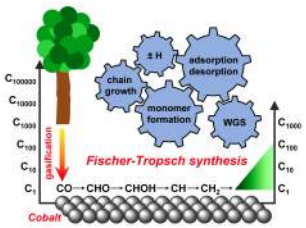
IRP1: The Research Fellow post in Cambridge is being advertised. A rig and a PhD student are committed for testing novel materials for chemical looping in Cambridge.

IRP2: An RF post has been filled and is working on WP2.3 activities. Two 'in kind' PhD students (WP2.1 and WP2.3) are working full time on IRP2 projects. A CREATE/Cambridge academic visitor has been working on WP2.2.

IRP3: A new Laboratory technician post has been filled to work on WP 3.2 and WP3.3. The new extension to the HPC cluster Kraftwerk has been designed and quotes have been arranged which are currently looked at by the Cambridge procurement section. The first PhD student taking part in the CARES scholarship programme will start in MT14. He will mainly work on aspects from WP3.1 and WP3.5.

IRP4: Main centre of activities is Singapore.

2.1 Collaboration between IRPs 1 and 3: Microkinetic Modelling of Fischer-Tropsch Synthesis over Cobalt Catalysts



Pooya Azadi, George Brownbridge, Immanuel Kemp, Sebastian Mosbach, John Dennis, Markus Kraft

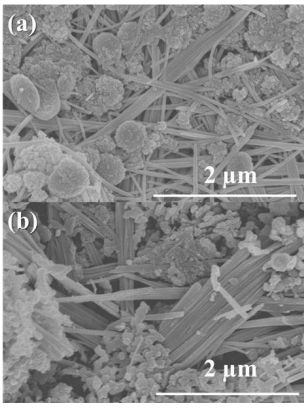
ChemCatChem, 2014. To appear.

Key points:

- A detailed kinetic mechanism for Fischer-Tropsch synthesis is presented.
- Carberry batch reactor experiments are carried out for a range of hydrogen/carbon monoxide ratios and temperatures.
- A two-stage parameter estimation is carried out to determine Arrhenius pre-exponential factors and activation energies.

Abstract:

We present a detailed microkinetic analysis of Fischer-Tropsch synthesis on a Co/gamma-Al2O3 catalyst over the full range of syngas conversions. The experiments were performed in a Carberry batch reactor with initial H2/CO ratios of between 1.8 and 2.9, temperatures of 469 and 484 K, and an initial pressure of 2 MPa. A reaction mechanism based on the hydrogen-assisted CO activation pathway, which comprises of 128 elementary reactions with 85 free parameters, was compiled to model the experimental results. Each of these elementary reactions belongs to one the following reaction groups: adsorption/desorption, monomer formation, chain growth, hydrogenation/hydrogen abstraction, or water-gas shift. A two-stage parameter estimation method, based on a quasi-random global search followed by a gradient-free local optimization, has been utilized to calculate the values of pre-exponential factors and activation energies. The use of data from batch experiments allowed for an effective analysis of dominating reactions at different stages of syngas conversion.



2.2 IRP1: Inhibiting the interaction between FeO and Al_2O_3 during chemical looping production of hydrogen.

Liu, W., Mohammad, I., Dunstan, M.T., Hu, W., Zhang, Z., Fennell, P.S., Scott, S.A., Dennis, J.S.

RCS Advances (Submitted)

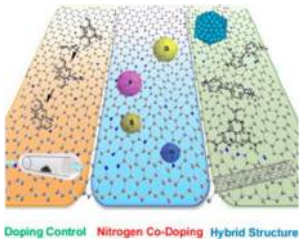
Key points:

- A oxygen carrier with promising performance was synthesized via the co-precipitation of $NaAlCO_3(OH)_2$ (dawsonite) and $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ (quintinite)
- The thermodynamic properties of various spinel phases were utilized to prevent the interaction in the Al-Fe-O system.
- Na_2O was found to be worse “inhibitor” of the Fe-Al-O interaction than MgO because of the formation of solid solution between $NaAlO_2$ and $NaFeO_2$.

Abstract:

Hydrogen of high purity can be produced by chemical looping using iron oxide as an oxygen carrier and making use of the reaction between steam and either iron or FeO. However, this process is viable only if the iron oxide can be cycled between the fully-oxidised and fully-reduced state many times. This can be achieved if the iron oxide is supported on refractory oxides such as alumina. Unfortunately, the interaction between alumina and oxides of iron to form $FeAl_2O_4$ hinders the kinetics of the reactions essential to the production of hydrogen, *viz*. the reduction of Fe(II) to metallic iron by a mixture of CO and CO_2 prior to the oxidation by steam. Here, oxygen carriers containing Fe_2O_3 and Al_2O_3 were doped with Na_2O and or MgO, in order to inhibit the formation of $FeAl_2O_4$ by forming $NaAlO_2$ and $MgAl_2O_4$, respectively. The performance of the modified oxygen carriers for producing hydrogen, *i.e*. cyclic transitions between Fe_2O_3 (or Fe_3O_4) and metallic Fe at 1123 K were investigated. It was found that the interaction between FeO and Al_2O_3 was successfully mitigated in oxygen carrier containing Mg, with an Al : Mg ratio of 2, resulting in consistently stable and high capacity for producing hydrogen by chemical looping, whether or not the material was oxidised fully in air on each cycle. However, the oxygen carrier without Mg only remained active when a step to oxidise the sample in air was included in each cycle. Otherwise it progressively deactivated with cycling, showing substantial interaction between Al_2O_3 and oxides of Fe.

2.3 IRP2: Strategies on the Design of Nitrogen-Doped Graphene



*Haibo Wang, Mingshi Xie, Larissa Thia, Adrian Fisher and Xin Wang**

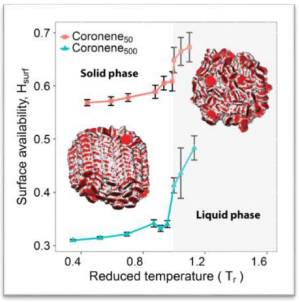
J. Phys. Chem. Lett. 2014, 5, 119−125

Key points:

- This Perspective reviews several recent strategies to control nitrogen doping and improve performance
- To get a better understanding of the doping effect in many applications, the ability to control the doping level and type is a prerequisite
- Co-doping nitrogen with other heteroatoms such as B, S, and P has been proposed as a strategy to further tune the properties of mono-doped N-graphene

Abstract:

Substitutional nitrogen doping in graphene has been a very powerful tool to tailor the pristine property of graphene and furthermore extend its application. While nitrogen-doped graphene (*N*-graphene) has shown many potential applications in catalysis, electronics, sensors and so on, there is still a lack of accurate control of substitutional nitrogen doping, and higher performance toward various applications is always needed. This Perspective summarizes the ongoing developments toward better control of nitrogen doping. Moreover, two recent strategies aiming to promote the activity of *N*-graphene are also discussed.



2.4 IRP3: Surface reactivity of homogenous polycyclic aromatic hydrocarbon nano-clusters

D. Chen, J.W.J. Akroyd, S. Mosbach, and M. Kraft

Proceedings of the Combustion Institute 35, 2014. In press.

Key points:

- A scheme to characterise surface atoms on molecular representations of clusters of polycyclic aromatic hydrocarbons is proposed.
- The availability of active sites on the surface of pyrene and coronene clusters is determined for various gaseous species.
- The surface availability is found to be inversely proportional to the particle size.

Abstract:

A scheme to characterise surface atoms is proposed to probe molecular representations of homogenous pyrene and coronene clusters. The concept of solvent-excluded surface, which is widely used for proteins, forms the basis of this scheme. The scheme is used to provide insights into the surface reactivity in terms of the surface availability of active atoms and sites for di□erent gaseous species. It was found that the surface availability of active sites varies with gaseous species, system temperature and particle size. The number of active sites available for a small gaseous species is always greater than that for a large species. Surface exposure increases with an increase in temperature and an obvious enhancement exists when transforming to liquid-like configurations. The surface availability decreases with increasing particle size following a linear relation with reciprocal size. The upper bound of parameter α□, which is used in the soot literature to empirically quantify surface reactivity, was further estimated from the surface availability of hydrogen atom in the context of HACA mechanism and was well below 0.1 for reactions between mature soot particles and acetylene. By exploring one particular pocket on the surface of a coronene cluster with 100 molecules, it was noted that it is feasible for both oxygen and acetylene molecules to penetrate inside the cluster. This fact indicates that the surface reactions occurring on particles are not limited to the actual boundary of the configuration but also certain regions beyond the boundary via surface pockets.

2.5 IRP4: Decentralized Constrained-State Feedback Control with Quadratic Dissipativity Constraint

Tri Tran, K-V. Ling, and J. Maciejowski

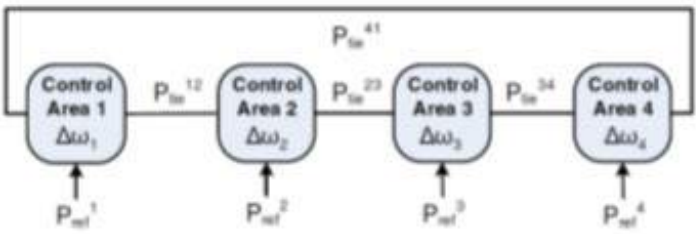
Proceedings of IEEE International Conference on Control, Automation, and Information Science (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014.

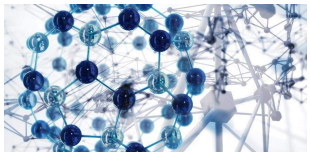
Key points:

- Assumes 'distributed' control structure, suitable for power networks, with local controllers controlling local parts of a network.
- Each controller enforces a quadratic 'dissipativity' constraint to ensure stable operation of the whole network.
- The new concept of 'input-and-power to state stability', based on the established notion of 'input to state stability', is introduced.

Abstract:

In market operations, distributed generators (DGs) and price-sensitive loads participate in a microgrid energy market implemented in JADE. Each DG and each price-sensitive load is represented by the respective agents which perform various functions such as scheduling, coordination and market clearing subject to system, DG and load constraints. Each agent is assigned to one of the several agent objectives which maximizes either DG or load surpluses or both. In simulated operation of a microgrid, hourly power reference signals and load control signals from JADE are passed to DG and load models developed in MATLAB/Simulink using MACSimJX. Simulated operation of DGs and loads are studied by performing simulations under different agent objectives. Results from simulation studies demonstrate the effectiveness of implementing multi-agent system (MAS) in the distributed management of microgrids.





3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

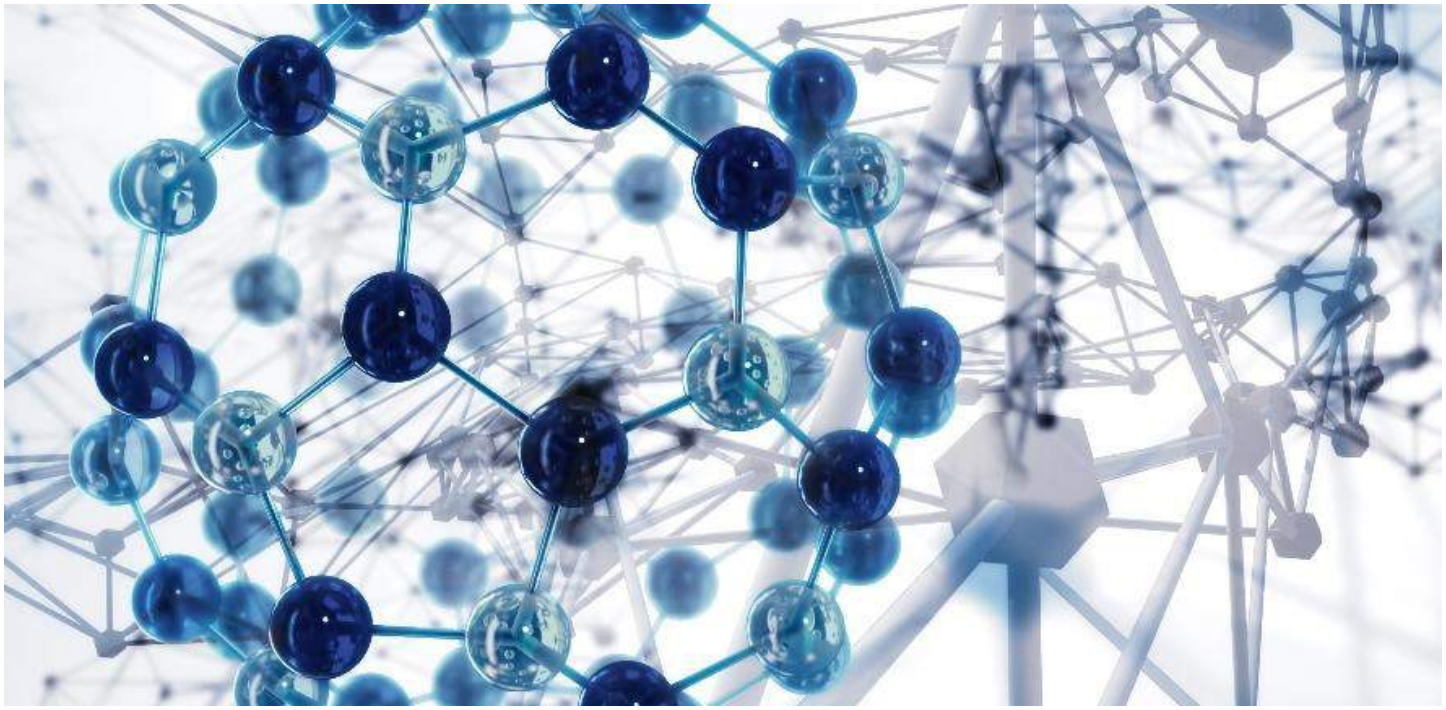
Electrochemical Multi-scale Science, Engineering and Technology

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 and 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 CO2 capture strategies into existing processes. The aim is at tackling a range of problems relevant to industry in Singapore with the potential to have short- and long-term deliverables that improve the economic and environmental performance of both existing and new processes

MUSCAT was originally comprised of six work packages. The precise content of these has now been revised to better reflect the current management of the IRP on the ground.

New work package	**Contains original work packages**
WP 1	WP2.2 and 4
WP 2	WP1.1, 1.2, 2.1 and 2.2
WP 3	WP4
WP 4	WP3
WP 5	WP2.2 and WP4
WP 6	WP1, 2, and 4

MUSCAT is led by PIs:

Prof John DENNIS (Cam)

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

3.1.1 Update on work packages

Following the C4T PI workshop in February 2014, IRP1 revised its original six work packages. The new classifications better reflect the current management of the IRP and so will therefore be used for future reporting. Updates using both classifications are given below.

For reference, a table relating the original work packages to the new ones is given on page 12.

Update on current work package classifications

Work package 1. The Senior Research Fellow (Dr Paul Wen LIU) started September, 2014. Due to the delay on suitable laboratory facilities, SRF 1 will work in Singapore generating new oxygen carriers of interest and process-scale evaluation will be undertaken in Cambridge with the new materials, using a dedicated PhD student (non-CARES funded). The principal activity will be to identify mixed oxide carriers for the steam-iron reaction, reducing coking in chemical looping combustion of methane and the use of oxygen carriers for oxidative dehydrogenation. SRF1 has spent a lot of time on laboratory design for the CARES programme: the time will have to be reduced in the next quarter to ensure he keeps his scientific momentum.

Work package 2. Remit widened to include, also, some GTL reactions (*e.g.* CO_2 to methanol) and investigating interesting new catalysts, *e.g.* Ru nanoparticles. Senior Research Fellow (Dr Yihu DAI) appointed and in post at NTU. As above, process-scale evaluation will be undertaken at high temperature and pressure in Cambridge.

Work package 3. Research to be coordinated largely by NUS and NTU. Research Fellow (Dr Ping LI) appointed and in post, working with Professor Zeng (NUS).

Work package 4. Post of research fellow was advertised and a good candidate identified, but he then decided not to take up the offer. Post will be re-advertised in late September.

Work package 5. Advertised for research fellow in Singapore, but post not yet advertised in UK. Latter to be done as soon as possible. Currently, no suitable candidates identified.

Work package 6. This is funded through the Cambridge contribution to CARES and will concentrate on 3D electron microscopy of catalysts and sorbents and the interpretation of the results. It will interact strongly with all of the above projects. Currently seeking suitable RF candidates.

Update on original work package milestones

WP1: Multi-phase, Fixed-bed Reactors

WP1.1: Gas-liquid-solid processes
WP1.2: Advances in liquid-solid catalytic processing
D1.1 Appointment of PDRAs for WP1.
Update: *Dr Yihu Dai is appointed as SRF2, who will be mainly working on WP1.*

D1.2 Establishment of detailed work-plan for years 1-3 through detailed discussions involving the University of Cambridge, NUS, NTU and A*STAR.

Update: *A detailed work plan between Cambridge and NTU is in place. A work plan between Cambridge and NUS is being discussed.*

D1.3 Development of experimental protocols for test reactions in WP1.1 and WP1.2, see M1.1
Update: *Two high pressure micro reactors are being installed in Prof. Yanhui Yang's laboratory. There is a potential to set up more rigs for testing catalysts.*

D1.4 Preparation of annual report for internal dissemination.
Update: *An annual report will be prepared at the end of year 1.*

M1.1 Selection of initial reactions of study in WP1.1 and WP1.2 based on available materials and expertise of recruited staff. Methanol synthesis is anticipated to be a key target reaction. Future reactions will be introduced as the project develops.
Update: *The PDRAs has started working on WP1. The work in NTU has produced some preliminary results.*

WP2: Separation and Use of CO2

WP2.1: CO2 capture using novel materials(SRF1)
WP2.2: CO2 conversion(SRF2)
WP2.3: Oxides in energy processes(SRF1, RF4)
D2.1 Appointment of PDRAs for WP2.
Update: *Dr Wen Liu is appointed SRF1, who will be working on WP2.1 and WP2.3. Dr Dai, SRF2, will be working on WP2.2. Dr. Ping Li is appointed as RF4, who will be working on novel oxide materials with Prof. Hua Chun Zeng from NUS.*

D2.2 Establishment of detailed work-plan for years 1-3 through detailed discussions involving the University of Cambridge, NUS, NTU and A*STAR.
Update: *Work plan for Programme Year 2 is in place. Work plan of year 3 and 4 will be dependent on the preliminary results in the first year.*

D2.3 Selection of benchmark materials against which to evaluate synthesised novel materials (see D4.1).
Update: *There has been some initial results on three systems for CO2-methanation.*

D2.4 Preparation of annual report for internal dissemination.
Update: *An annual report will be prepared in 2015.*

M2.1 Selection novel oxides and catalysts for CO_2 capture and utilisation. These initial selections will be based on available materials and expertise of recruited staff.
Update: *the selection of initial reaction are being discussed between the PIs and RFs within IRP1. Achieving M2.1 by the end of Programme Year 2 is highly likely.*

WP3: Gas-Solid Reactors

WP3.1: Development of feasible design tools(RF3)
WP3.2: Catalytic gas-solid technologies for chemicals and fuels(RF3)
D3.1 Appointment of PDRAs for WP3.
Update: *An initially successful candidate withdrew. The post for RF3 will be re-advertised.*

D3.2 Establishment of detailed work-plan for years 1-3 involving detailed discussions between the University of Cambridge, NUS, NTU and A*STAR.
Update: *A detailed work plan between Cambridge (Prof. John Dennis, Dr Stuart Scott) and NTU (Prof. Jia Wei Chew) is being discussed.*

D3.3 Establish needs and protocols for working at the interface between DEM and approaches developed in IRP3 (WP4). Preparation of annual report for internal dissemination.
Update: *This work will begin as soon as RF3 starts.*

M3.1 Selection of initial systems, both reacting and non-reacting, to investigate in WP3.1 and WP3.2. In WP3.2 the catalytic steam reforming of methane is anticipated to be of particular interest.
Update: *The initial system will be selected based on the expertise of the recruited RF and the PIs in Cambridge and NTU. Therefore the work required to achieve this milestone will begin as soon as RF3 starts.*

M3.2 Establishment of appropriate 3D two-fluid models adapted for use with homogeneous and heterogeneous reactions.
Update: *The work required to achieve this milestone will begin as soon as RF3 starts.*

WP4: New Catalysts and Materials (RF4&5)

D4.1 Appointment of PDRAs for WP4.
Update: *RF4 (Dr Ping LI) is appointed. RF5 is being advertised*

D4.2 Establishment of detailed work-plan for years 1-3 through detailed discussions involving the University of Cambridge, NUS, NTU and A*STAR.
Update: *A work plan is being discussed between Cambridge, NUS and NTU.*

D4.3 Report on preliminary PFG and MR relaxometry measurements on novel materials.
Update: *This work will take place in Cambridge after the identification of an initial set of materials.*

D4.3 Preparation of annual report for internal dissemination.
Update: *An annual report will be prepared at the end of Programme Year 2.*

M4.1 Decision on initial focus of materials synthesis programme targeted at most promising materials for use in the reactions selected in M2.1.
Update: *The work required to achieve this milestone is dependent on the progress of WP2. It looks promising that there will be sufficient results in 2015.*

WP5: Environmental Footprint of an Interacting Chemical Plant Complex - Jurong Island
M5.1 Agree strategy with operating companies as to how best to obtain the necessary results and have necessary agreements in place. Identify areas where flow sheeting is needed.
Update: *None.*

3.2 IRP2 — EMSET

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)

3.2.1 Update on work packages

WP 2.1 Numerical Multi-Scale Electrochemical Modelling and Analysis

Update: An in kind Cambridge PhD student has begun targeting the quantitative analysis of electrochemical substrates and devices. The focus is 'over-parameterised' electrochemical systems and work has begun to explore a subset of the parameters (or their combinations), which can be identified. A key interest is the distinction between differing mechanistic routes for homogeneously coupled chemical reactions. Manuscripts focused on optimized electrochemical waveforms and novel approaches to assessing the uniqueness of output are currently submitted for publication.

Cambridge researcher Nguyen Viet has been funded by Cambridge CARES to visit the laboratories of Professor Erik Birgersson in September 2014. They will be working together on new electroanalytical techniques for IRP2 activities in WP2.1 and WP2.3.

WP 2.2 Electrode development and testing

Update: NTU researchers working in partnership with CARES have been focused on the development of new materials for selective electrochemical transformations. SRF and RF positions have now been appointed for three projects targeting metallic and semiconductor substrates as electrocatalysts. An electrocatalysis review and a joint publication looking at design strategies for nitrogen doped graphene substrates has been published.

The biological electrodes element of WP2 has been redirected as a result of NTU staff changes since the IRP2 programme was written. Currently we are identifying new collaboration partners at NTU and NUS to tackle biological aspects and working with Cambridge based collaborators who we are seeking to have join the IRP2 project. Two 'in kind' students in Cambridge are working on algae based systems for applications in microbial fuel cell applications. Two manuscripts are currently submitted detailing research outputs.

WP2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

Update: An RF in Cambridge is working on an application for electrical energy recovery in oil well applications. This project seeks to to unlock barriers to exploitation using rapid prototyping reactor fabrication techniques in combination with numerical characterisation and computer aided design methods identified in WP2.1. The work has been presented at a conference this summer and a manuscript has been prepared for submission.

3.2.2 Other Activities and Achievements

2014 Global Chemical Technologies Programme

IRP2 colleagues arranged and hosted the 2014 Global Chemical Technologies Programme.

The Cambridge - BUCT Summer School (CBSS), was hosted by the Cambridge Centre for Carbon Reduction in Chemical Technology (C4T), situated on the Campus for Research Excellence and Technological Enterprise (CREATE) in Singapore and the Department of Chemical Engineering & Biotechnology, Cambridge. The broad aim of the course was to expose the undergraduate delegates to living and studying overseas as a research student and offered the opportunity to visit leading University research laboratories at National University of Singapore, Nanyang Technological University and Cambridge. Specialist lectures from academics gave the technological background and future challenges for the global economy with a focus on Chemical Technology. The formal academic course was complemented by visits to industrial laboratories, CREATE partner Universities: University of Berkeley & Technische Universität München and the A*STAR Institute of Chemical and Engineering Sciences.

A full report of the 2014 programme is available at: http://www.cares.cam.ac.uk/news/c4t-hosts-global-chemical-technologies-programme

ISE 10th ECHEMS 2014 "Electrochemistry in Molecular Understanding"

IRP2 RF Peng Song and IRP2 collaborators Prof Martin Pumera and Prof Richard Webster presented their research at the ISE 10th ECHEMS 2014 "Electrochemistry in Molecular Understanding" in June 2014. Peng presented CREATE ongoing work "A Galvanic Cell for Energy Harvesting" in a session chaired by Prof Pumera. Richard gave a presentation on his research "The effects of trace water on voltammetry in non-aqueous media" and Martin presented his work in the field of "Electrochemically deposited nano- and micromachines".

Visit of Prof Vengadesh Periasamy

CREATE collaborator Prof Vengadesh Periasamy (University of Malaya) is currently based in Cambridge as an academic visitor working on IRP2 related activities with Dr Kamran Yunus. Their work has targeted biological electrode systems and the development of biologically compatible materials.

3.3 IRP3 — CAPRICORN

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

CAPRICORN is split into five interacting work packages:

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

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

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

WP 3.4: Modelling and optimisation of unit operations

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

The CAPRICORN group is led by PIs:

Prof Markus KRAFT (Cam)

Prof Raymond Wai Man LAU (NTU)

Prof Iftekhar KARIMI (NUS)

3.3.1 Update on work packages

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

Update: Six School of Chemical and Biomedical Engineering (SCBE, NTU) students along with an RF are currently working under the supervision of Raymond LAU and Markus KRAFT to gather publically available data on Jurong Island. They have identified corporate entities which operate on Jurong Island and the kind of industrial processes they perform. They have also started to create models of the processes with respect to materials in and out of the individual plant, with particular emphasis on CO2 emissions.

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

Update: In collaboration with Prof Brezinsky from the University of Illinois at Chicago IRP3 has been using the MoDS software to build an improved surrogate model for n-propyl benzene which plays an important role in many fuels.

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

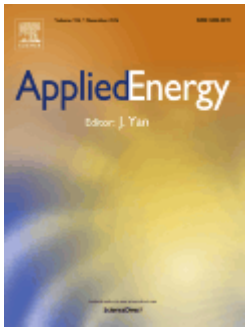
Update: IRP3 has developed a detailed understanding of the gasphase composition in the synthesis of silica nanoparticles which act as carrier material for other catalytically active particles. The MoDS software has been used to understand the sensitivity of the detailed silica population balance model. The melting behaviour and particle properties of carbon clusters formed from PAHs by employing molecular dynamics simulations is being investigated.

WP 3.4: Modelling and optimisation of unit operations

Update: This work package has not started in its entirety as an appropriate PhD student is still to be recruited. However, there has been a study on fluidised bed gasifiers and the associated life cycle analysis in the context of algae gasification. This connects directly to WP3.1 in which we have to develop models for the chemical plants on Jurong Island.

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

Update: Work is ongoing to further develop our ability to assess the influence of data on models. This is important to decide which data point to focus on and to design new experiments. Two strategies for constructing influence diagnostics have been developed and applied to a problem which is relevant to the development of surrogate fuels in WP3.2. In cooperation with Professor John Dennis and co-workers from IRP 1, the MoDS software has been used to create a kinetic model of Fischer-Tropsch synthesis over cobalt catalyst.



3.3.2 Other achievements

- Professor Kraft has taken on the role of Subject Editor of the Journal Applied Energy (Impact Factor 5.261) http://www.journals.elsevier.com/applied-energy/editorial-board/
- Professor Kraft has been invited to deliver plenary lectures at the:

  - Tenth IMACS Seminar on Monte Carlo Methods (MCM 2015) at the Johannes Kepler University (JKU) and the Radon Institute for Computational and Applied Mathematics (RICAM), Linz, in July 2015. http://www.mcm2015.jku.at/index.php?id=2

  - ICCK9, 9th International Conference on Chemical Kinetics 2015, JUNE 28-JULY 2, 2015, GHENT BELGIUM

The Integrated Chemicals and Electrical Systems Operation , or ICESO (pronounced I-say-so), group focuses on the Jurong Island electrical sub-network to address the dynamic response of the chemical plants therein when adverse electrical system conditions prevail. ICSCO seeks to discover how a more tight 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

Organisation of the work according to the six originally-defined work packages may benefit from being reconsidered in the next few months. There is no urgent need to do this immediately. A possible re-definition would be: Merge and generalize WP1 and WP2 to become ‘WP1: Generic MPC/MHE algorithm development’. Separate out algorithms for power systems from hardware development and experiments: ‘WP2: Algorithms for control of power systems with industrial loads’, ‘WP3: Development and experiments on the NTU microgrid’. WP4,5,6 can probably remain as they are.

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)

3.4.1 Update on work packages

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

Update: Work has continued on 'Economic MPC' in which the cost function is as close as possible to the real objective being optimized, as distinct from an artificial cost function which delivers good dynamic behaviour under feedback. In particular, work has continued on the concepts of 'quadratic dissipativity' and 'asymptotic quadratic constraints', which help to ensure stability for 'Economic MPC'. This work can be considered to be a contribution to WP3 as well as to WP1.

Work has also been continued on Moving Horizon Estimation (MHE) with the assumption that noise has a Generalised-T distribution rather than Gaussian. This class of distributions does not appear to have been considered before for estimation in dynamic systems; it has previously been considered only in the 'robust statistics' literature. The resulting estimator has the form of a Kalman filter, but acting on a modified error term. Also, a distributed version of the MHE estimator has been proposed and developed.

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

Update: Work on this WP has not started yet, but we are currently in the process of recruiting a Research Fellow.

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

Update: The 1kW synchronous generator set has been decommissioned from the NTU microgrid and a 13.5 kVA set has been commissioned in its place. A fixed state estimation problem has been formulated for the Micro Grid Energy Management System and a corresponding algorithm has been implemented and validated. The microgrid line impedance data have been verified through experimental measurements.

Carbon emission studies for generation/co-generation technologies have been performed.

A multi-agent system for distributed management of microgrids has been proposed.

WP4: Modelling of chemical process load and local generator-based electrical network akin to Jurong Island and WP5: Model building, integration and maintenance

Update: Not started yet.

WP6: Demonstration of proposed algorithms on pilot scale

Update: An initial proposal for a low-voltage, low-power, hardware emulator was developed.

A.1 Publications

A.1.1 IRP1— MUSCAT

- Dunstan, M.T.; Liu, W., Pavan, A.F., Kimpton, J.A., Ling, C.D., Scott, S.A., Dennis, J.S.; Grey, C.P. (Grey, Clare P.)(March 2014). Reversible CO2 Absorption by the 6H Perovskite Ba4Sb2O9. *Chemistry of Materials*, **25**, 4881-4891.
- Boyce, C.M., Holland, D.J., Scott, S.A.and Dennis, J.S. (May 2014). Novel fluid grid and voidage calculation techniques for a discrete element model of a 3D cylindrical fluidized bed. *Computers and Chemical Engineering*, **65**, 18-27.
- Saucedo, M.A., Lim J.Y., Scott, S.A. and Dennis, J.S. (July 2014). CO_2-gasification of a lignite coal in the presence of an iron-based oxygen carrier for chemical-looping combustion. *Fuel*, **127**, 186-201.
- Boyce, C.M., Holland, D.J., Scott, S.A.and Dennis, J.S. (September 2014). The origin of pressure oscillations in slugging fluidized beds: Comparison of experimental results from magnetic resonance imaging with a discrete element model. *Chemical Engineering Science*, **116**, 611-622.

A.1.2 IRP2— EMSET

- Haibo Wang, Mingshi Xie, Larissa Thia, Adrian Fisher and Xin Wang (2014) Strategies on the Design of Nitrogen-Doped Graphene. *J. Phys. Chem.* Lett. 2014, 5, 119−125.
- Rern Jern Lim, Mingshi Xie, Mahasin Alam Sk, Jong-Min Lee, Adrian Fisher, Xin Wang, Kok Hwa Lim (2014) A review on the electrochemical reduction of CO_2 in fuel cells, metalelectrodes and molecular catalysts. *Catalysis Today* 233 (2014) 169–180 125.
- Ya Yan, BaoYu Xia, Xiaoming Ge, Zhaolin Liu, Jing-Yuan Wang, and Xin Wang (2013) Ultrathin MoS2 Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution. *ACS Appl. Mater. Interfaces* 2013, 5, 12794−12798 .
- Nan Li, Ya Yan, Bao-Yu Xia, Jing-Yuan Wang, Xin Wang (2014) Novel tungsten carbide nanorods: An intrinsic peroxidase mimetic with high activity and stability in aqueous and organic solvents. *Biosensors and Bioelectronics* 54 (2014) 521–527.
- Peng Xiao, Mahasin Alam Sk, Larissa Thia, Xiaoming Ge, Rern Jern Lim, Jing-Yuan Wang, Kok Hwa Lim and Xin Wang (2014) Molybdenum phosphide as an efficient electrocatalyst for the hydrogen evolution reaction. *Energy Environ. Sci*., 2014, 7, 2624.
- Nan Li, Larissa Thia and Xin Wang (2014) A CO_2-responsive surface with an amidine-terminated self-assembled monolayer for stimuli-induced selective adsorption. *Chem. Commun.*, 2014,50, 4003.
- Ya Yan, BaoYu Xia, Zhichuan Xu and Xin Wang (2014) Recent Development of Molybdenum Sulfides as Advanced Electrocatalysts for Hydrogen Evolution Reaction. *ACS Catal*. 2014, 4,

1693−1705.

- Yi Zhao , Wangliang Wu , Jiaxin Li , Zhichuan Xu, and Lunhui Guan (2014) Encapsulating MWNTs into Hollow Porous Carbon Nanotubes: A Tube-in-Tube Carbon Nanostructure for High-Performance Lithium-Sulfur Batteries. *Adv. Mater*. 2014, 26, 5113–5118.
- Chao Wei, Pooi See Lee, and Zhichuan Xu (2014) A comparison of carbon supports in MnO_2/C supercapacitors. *RSC Advances*, 2014, 4, 31416.
- Luyuan Paul Wang, Linghui Yu, Rohit Satish, Jixin Zhu, Qingyu Yan, Madhavi Srinivasan, and Zhichuan Xu (2014) High-Performance Hybrid Electrochemical Capacitor with Binder-Free Nb_2O_5@Graphene. RSC Adv., 2014, 4, 37389.
- S.M.Phang, P.Vengadesh, K.Yunus and A.C.Fisher (2014) Evaluation of Algal Biofilms on Indium Tin Oxide (ITO) for Use in Biophotovoltaic Platforms Based on Photosynthetic Performance. *PLoS ONE.* 9, e97643, 2014.

A.1.3 IRP3 — CAPRICORN

- Sebastian Mosbach and Markus Kraft. Influence of experimental observations on n-propylbenzene kinetic parameter estimates. *Proceedings of the Combustion Institute* 35, 2014. In press. http://dx.doi.org/10.1016/j.proci.2014.05.061 (WPs 2 & 5)
- Dongping Chen, Jethro W.J. Akroyd, Sebastian Mosbach, Markus Kraft. Surface reactivity of homogenous polycyclic aromatic hydrocarbon nano-clusters. *Proceedings of the Combustion Institute* 35, 2014. In press. http://dx.doi.org/10.1016/j.proci.2014.06.140 (WPs 2 & 3)
- Daniel L. Nurkowski, Philipp Buerger, Jethro W.J. Akroyd, and Markus Kraft. A detailed kinetic study of the thermal decomposition of tetraethoxysilane. *Proceedings of the Combustion Institute* 35, 2014. In press. http://dx.doi.org/10.1016/j.proci.2014.06.093 (WP 3)
- William J. Menz, George Brownbridge, and Markus Kraft. Global sensitivity analysis of a model for silicon nanoparticle synthesis. *Journal of Aerosol Science* 76, 188-199, 2014. http://dx.doi.org/10.1016/j.jaerosci.2014.06.011 (WP 3)
- Dongping Chen, Tim S. Totton, Jethro W.J. Akroyd, Sebastian Mosbach, and Markus Kraft. Phase change of polycyclic aromatic hydrocarbon clusters by mass addition. *Carbon* 77, 25-35, 2014. http://dx.doi.org/10.1016/j.carbon.2014.04.089 (WPs 2 & 3)
- Pooya Azadi, George P.E. Brownbridge, Immanuel Kemp, Sebastian Mosbach, John S. Dennis, and Markus Kraft. Microkinetic Modeling of Fischer-Tropsch Synthesis over Cobalt Catalysts. *ChemCatChem*, 2014. To appear. http://dx.doi.org/10.1002/cctc.201402662 (WPs 1 & 2)

A.1.4 IRP4— ICESO

- Tran, Tri, Ling, K-V and Maciejowski, J (July 2014) Economic Model Predictive Control – A Review. *Proceedings of International Symposium on Automation and Robotics in Construction*

(ISARC'14) – Sydney, Australia, 9-11 July 2014, pages 35-42. http://www.isarc2014.org/

- Tran, Tri, Ling, K-V and Maciejowski, J (2014) Decentralized Constrained-State Feedback Control with Quadratic Dissipativity Constraint. *Proceedings of IEEE International Conference on Control, Automation, and Information Science* (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014.
- Tran, Tri, Ling, K-V and Maciejowski, J (2014) Model Predictive Control via Quadratic Dissipativity Constraint. *Proceedings of IEEE Conference on Decision and Control* (CDC'14) – Los Angeles, 15-17 December 2014.
- Tran, Tri, Foo, Y.S. Eddy, Ling, K-V and Maciejowski, J. (2014) Application of Quadratically-Constrained Model Predictive Control in Power Systems. *Proceedings of IEEE International Conference on Automation, Robotics, Control and Vision* (ICARCV'14) – Singapore, 9-11 December 2014.
- Tran, Tri, Ling, K-V and Maciejowski, J (2014) Model Predictive Control of Nonlinear Input-Affine Systems with Feasibility and Stability Constraints. *Proceedings of IEEE International Conference on Automation, Robotics, Control and Vision* (ICARCV'14) – Singapore, 9-11 December 2014.
- Y. S. Foo. Eddy, H. B. Gooi, and S. X. Chen (2014) Multi-Agent System for Distributed Management of Microgrid. *IEEE Transactions on Power Systems* (early access available now). http://dx.doi.org/10.1109/TPWRS.2014.2322622
- Tri Tran, Q. P. Ha, and J. Maciejowski (2014) Dependable Control Systems with Self-Recovery Constraint. *Proceedings of IEEE International Conference on Control, Automation, and Information Science* (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014.
- Tri Tran (2014) Distributed State Feedback Control of Explicitly-Bounded Nonlinearly-Coupled Systems. *Proceedings of IEEE International Conference on Control, Automation, and Information Science* (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014.