CAMBRIDGE CARES

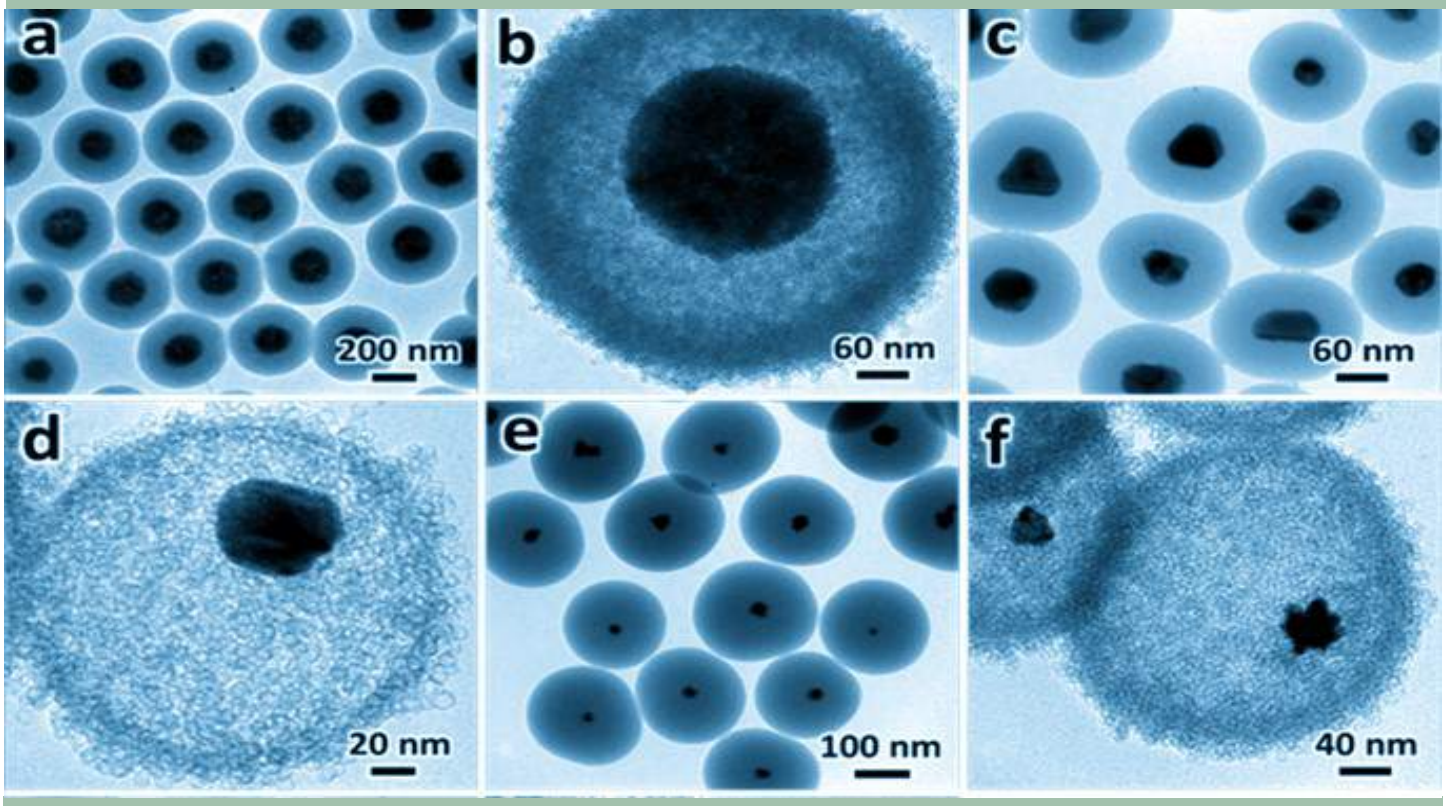
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH IN ENERGY EFFICIENCY IN SINGAPORE LTD.

Biannual Research Report

November 2014 — April 2015

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.

April 2015

I am delighted to present the 2nd 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 in Energy Efficiency in Singapore (CARES).

Since our last report in October 2014, the size of our team has continued to grow as more scientists and support staff join us at our base in Singapore. We have just passed the milestone of one hundred members formally involved in the programme. The contributions of the young scientists involved in the programme will be evident from this report; C4T is currently training 25 PhD students and is expecting further student members in the August 2015 intake. A particular highlight of 2015 will be the arrival in Singapore of the very first student to take part in the Cambridge-CARES Studentship Scheme – Janusz Sikorski, IRP3.

On the scientific front we have been very active, as may be evident from the length of this report!. Across our four Interdisciplinary Research Programmes (IRPs) we have now published fifty-six papers in peer-reviewed journals and conference proceedings, with a further fifteen in press. I am particularly pleased that C4T has been able to make four technology disclosures to NTUitive (the NTU Technology Transfer Office), one of which has already resulted in a patent application. NTUitive, Cambridge Enterprise and the C4T research teams are currently working together to ensure these inventions reach their full commercial potential.

We have also been enjoying working with a number of industrial partners. The Client Innovation Forum Singapore took place on 4th November 2014 in the CREATE Tower and was co-hosted by CARES, Atos and Siemens. This half-day seminar was focussed on ways in which automation systems and IT could support companies in driving innovation. The C4T J-Park Simulator concept was presented and was well received by attendees. In addition, IRP2 has been grateful to receive generous in-kind support from Schlumberger Gould Research (SGR) in the form of access to a world-leading analytical facility in Cambridge. Finally, our Cambridge-CARES Studentship Scheme has attracted interest from industry, with Huntsman Tioxide now in the final stages of discussions to match-fund two students under this scheme.

As those readers who have visited us in Singapore will know, we are currently kindly hosted in temporary offices and laboratories at Nanyang Technological University. Since the last report, we have made excellent progress towards moving into our long-term home at CREATE. At the time of writing, the tender interviews for the C4T construction have just happened and we are looking forward to the contractors starting their work shortly. A great deal of hard work went into preparing for the tender from both C4T and NRF teams; we are grateful for the support shown to us throughout the process by NRF.

I am proud of the science being generated by the C4T teams and of the great potential shown across the programme. As we mature and gain access to the excellent C4T facilities at the CREATE tower, I fully expect our ability to contribute new knowledge to increase even further. I present this report to you, both as a statement of the current high-quality work of C4T and as an invitation to all stakeholders to engage actively with our future work – we look forward to providing new evidence bases and tools to think with in both the national and global discussions on creating sustainable industry.

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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)

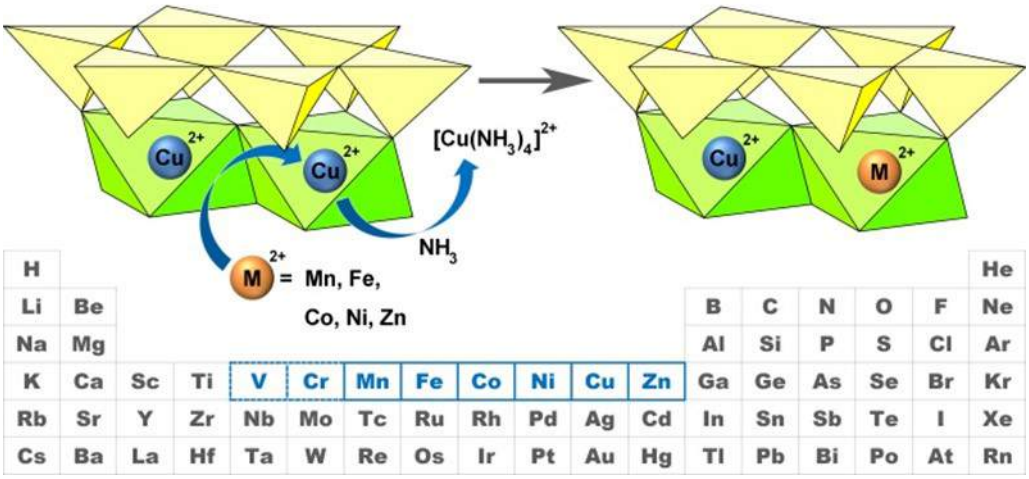
The impact of the dynamic response of the chemical plant on its batch output over varying time scales will be evaluated using a combination of methods developed in IRPs 1, 2, 3 and 4.

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.

2.1 IRP1: Single-Walled 3*d* Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts

*Yuan Sheng and Hua Chun Zeng**

Chem. Mater. 2015, 27, 658−667. DOI: 10.1002/chem.201405697



Highlights:

- A series of new single-walled silicate nanotubes containing 3d transition metal elements (Cu, Mn, Fe, Co, Ni and Zn) has been developed.
- Up to 80% of Cu in pre-synthesized copper silicate can be replaced by other transition metals through complex-assisted ion exchange, while the original tubular structure remains intact.
- The metal silicate nanotubes can serve as solid precursors for designed nanocatalysts.
- Enhanced catalytic performance has been demonstrated using CO_2 hydrogenation as a testing reaction.

Abstract: Copper silicate has so far been the only transition metal silicate to form single-walled nanotubes. Herein, we developed a general method to synthesize a series of new single-walled silicate nanotubes containing other 3d transition metal elements (M = Mn, Fe, Co, Ni and Zn); up to 80% of Cu in pre-synthesized copper silicate can be replaced with these metals (M) through complex-assisted ion exchange, while the original tubular structure remains intact. These metal silicate nanotubes can serve as solid precursors for design-made nanocatalysts; enhanced catalytic performance has been demonstrated using CO_2 hydrogenation as a testing reaction.

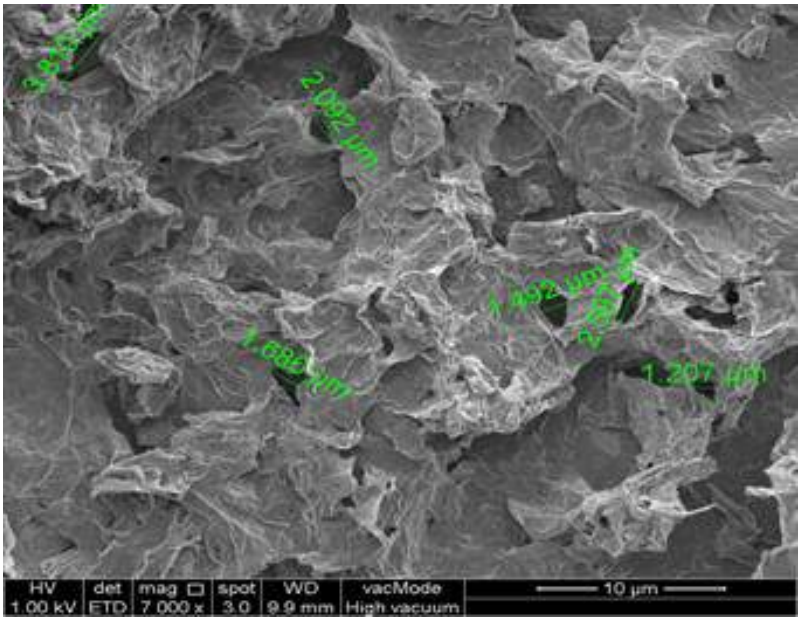
2.2 IRP2: Reduced Graphene Oxide (rGO) Anodes for Potential Application in Algae Biophotovoltaic Platforms

Fong-Lee Ng, Muhammad Musoddiq Jaafar, Siew-Moi Phang, Zhijian Chan, Nurul Anati Salleh, Siti Zulfikriyah Azmi, Kamran Yunus, Adrian C. Fisher & Vengadesh Periasamy

Nature Scientific Reports, 2015, 4, in press

Key points:

- Development of electrode-biological substrate materials for electricity generation
- Electroanalytical investigation of current/voltage characteristics
- Current/Voltage efficiency improvements from novel electrode architectures



Abstract:

The search for renewable energy sources has become challenging in the current era, as conventional fuel sources are of finite origins. Recent research interest has focused on various biophotovoltaic (BPV) platforms utilizing algae, which are then used to harvest solar energy and generate electrical power. The majority of BPV platforms incorporate indium tin oxide (ITO) anodes for the purpose of charge transfer due to its inherent optical and electrical properties. However, other materials such as reduced graphene oxide (RGO) could provide higher efficiency due to their intrinsic electrical properties and biological compatibility. In this work, the performance of algae biofilms grown on RGO and ITO anodes were measured and discussed. Results indicate improved peak power of 0.1481 mWm^{-2} using the RGO electrode and an increase in efficiency of 119%, illustrating the potential of RGO as an anode material for applications in biofilm derived devices and systems.

2.3 IRP3: Applying Industry 4.0 to the Jurong Island Eco-industrial Park

Ming Pan, Janusz Sikorski, Catharine A Kastner, Jethro Akroyd, Sebastian Mosbach, R. Lau, and Markus Kraft

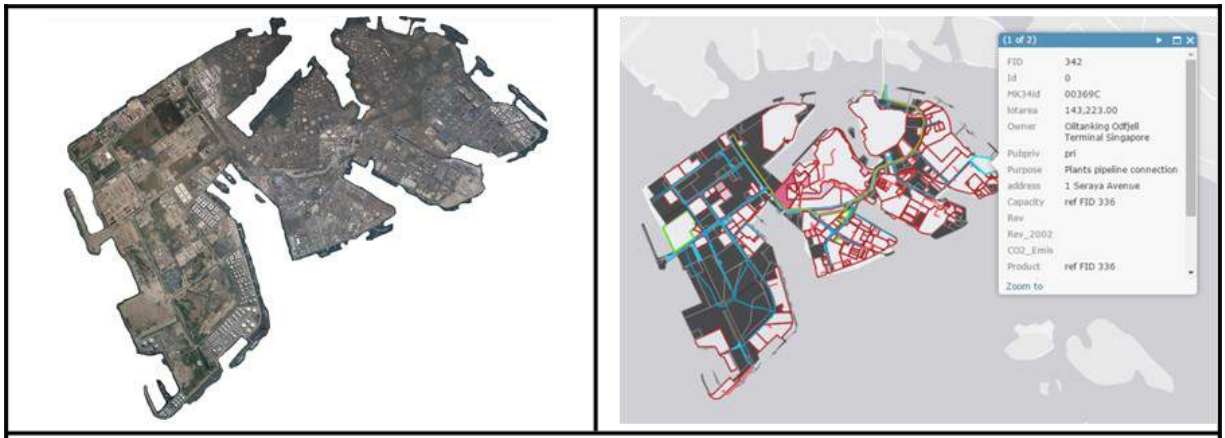


Figure 1: *Jurong Island and the J-park simulator.*

Energy Procedia, in press, (2015).

Highlights:

- Industry 4.0 technologies are implemented to eco-industrial park (EIP) of Jurong Island in Singapore.

- A framework is built for modeling Jurong Island EIP.

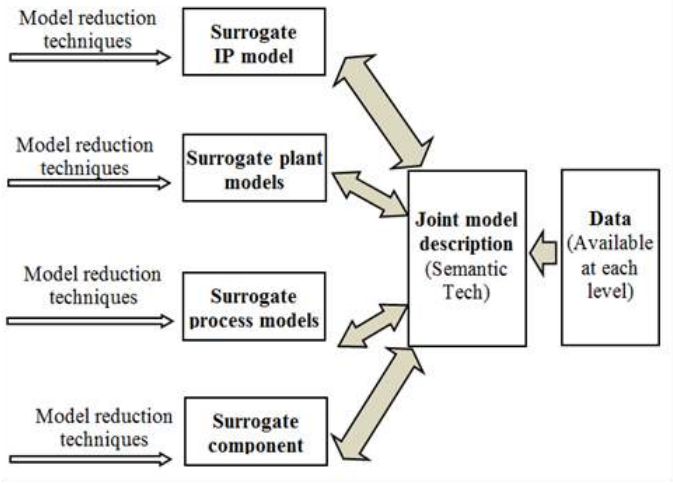


Figure 2: *Framework of EIP modelling based on Industry 4.0.*

- An expert system is proposed to use of the latest advances in high performance computing (HPC), advanced mathematical modelling, and semantic web technologies.

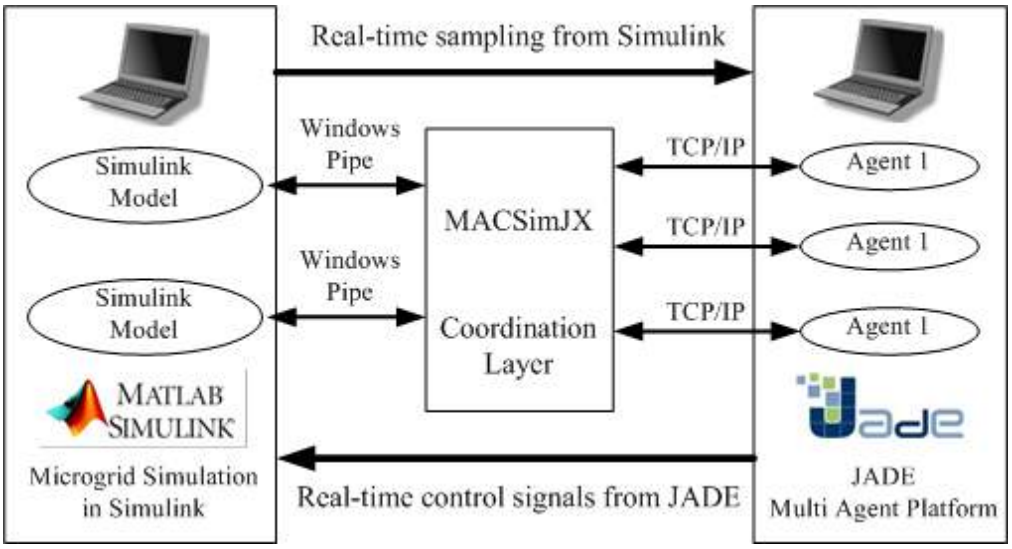
Abstract:

The concept of eco-industrial parks (EIPs) has recently become the subject of a great deal of attention from industry and academic research groups. The interest stems from the structural ability of an EIP to create more sustainable industrial activities through the use of localised symbiotic relationships. An EIP is an industrial park where businesses cooperate with each other and, at times, with the local community to reduce waste and pollution, efficiently share resources (such as information, materials, water, energy, infrastructure, and natural resources), and minimize environmental impact while simultaneously increasing business success. Numerous aspects of EIPs have been widely studied in the expert literature over the past decade. Currently, the primary existing way to design an optimal EIP is to create the exchanges of materials, water and energy through a network between tenants of the EIP, where the benefits are evaluated based on improvements to social, economical and environmental impacts.

The optimal symbiotic relations among industries in an EIP require considering all resources simultaneously within the whole network. More importantly, variability of resource supplies should be addressed in more realistic model due to inherent uncertainties. Complete understanding of the complexity of these issues requires a substantial amount of supporting data relative to each potential member of the EIP. Thus, this paper presents a new insight on implementing Industry 4.0 technologies to overcome the aforementioned barriers, where a cloud-based cyber-infrastructure of a virtual EIP is developed with the use of high performance computing (HPC), advanced mathematical modelling and semantic web technologies. Several aspects of the technical problems that arise in terms of model building, data representation and uncertainty are addressed and will form the important elements of the virtual EIP see Figure 1, above. Industry 4.0 is a term that originated in the area of

manufacturing engineering and represents the fourth industrial revolution: the ability of industrial components to communicate with each other. This communication may be within intranet facilities or external internet and will lead to datasets which are too big to be stored in a conventional database structure. Hence, technologies for the analysis of "Big Data" will have to be employed to adequately control and manipulate these datasets. In order to achieve this, it is proposed to associate each technical component in a plant with its own semantic representation which will also include executable mathematical models. These models are fed data from sensors in each device using techniques developed from machine learning and statistics. A plant forms a network of such models which can, in turn, be represented by a surrogate model after employing model reduction techniques. The process by which these semi-empirical models are formed requires analysis of the vast amounts of data that are constantly being produced by the plant. Fig. 2 describes the framework of EIP modeling based on Industry 4.0.

To achieve the reality of Jurong Island EIP, a set of specific tasks has been considered, including semantic representation of data, models, and algorithms, detailed process models on different scales, parameterisation of high-dimensional models, numerics of networks of parameterised models, geographic representation of industrial park for virtual reality, and evaluation of models with global sensitivity and uncertainty analysis. The ultimate aim of the J-Park Simulator is to enable stakeholders to make informed decisions on how to reach their strategic targets in the optimal way whilst minimising their environmental impact.



2.4 IRP4: Multi-Agent System for Distributed Management of Microgrids

Foo Eddy, Y.S.; Gooi, H.B.; Chen, S.X.
Power Systems, IEEE Transactions on, vol.30, no.1, pp.24-34, Jan. 2015.doi: 10.1109/TPWRS.2014.2322622.

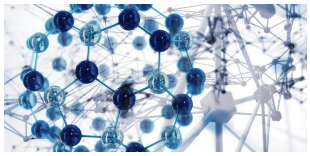
Highlights

- Using agents to represent both distributed generations (DGs) and loads to participate in a local microgrid electricity market.
- Agents are assigned tasks/objectives to perform various functions e.g. scheduling, coordination and market clearing
- The agent objectives can be either biased towards one side i.e. DGs or loads, or unbiased which will affect the outcome of the market clearing.
- Simulated response of the DGs and loads were done to verify the stable operation of the microgrid after market clearing.

- Proposed distributed agent control can be implemented on the petrochemical plants in Jurong Island to reduce carbon emissions as part of the IRP4 requirements.

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

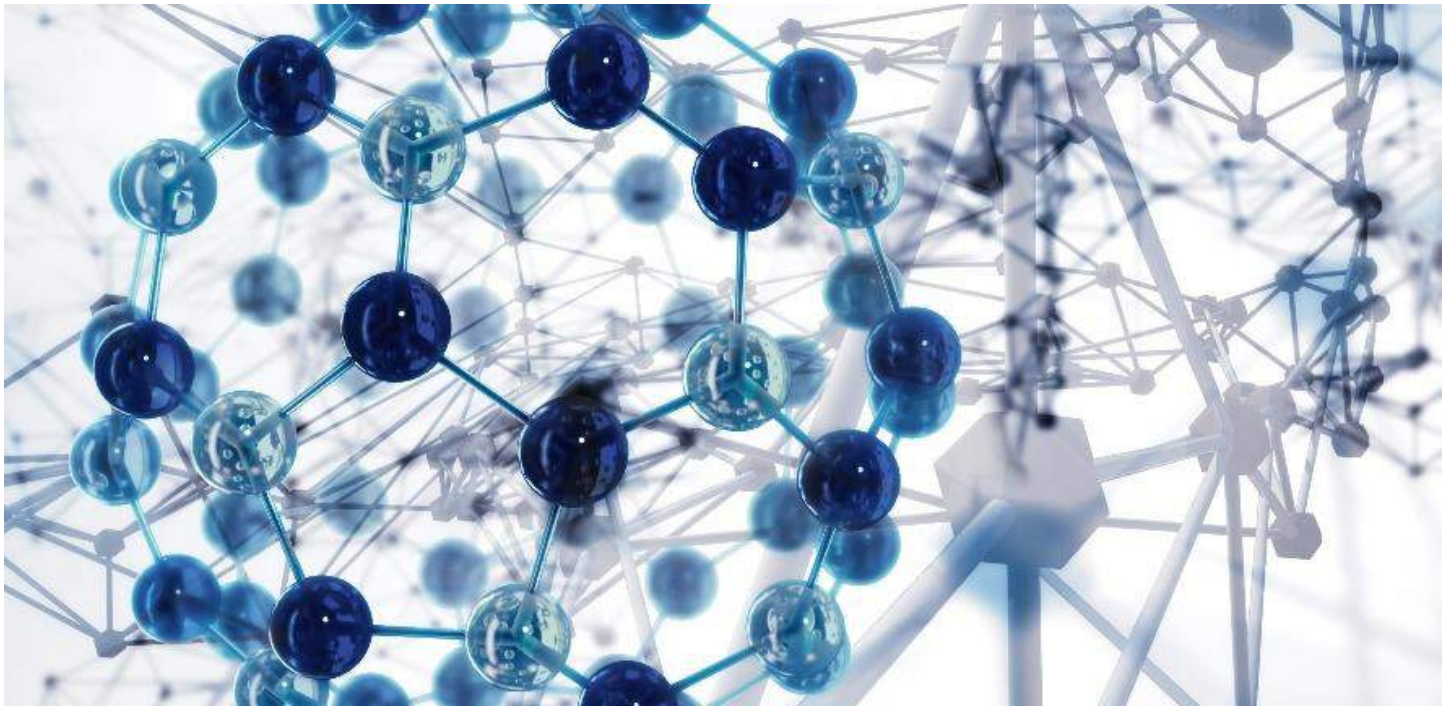
3.3 IRP3 — CAPRICORN

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

3.4 IRP4 — ICESO

Integrated Chemicals and Electrical Systems Operation

3.1 IRP1 — MUSCAT



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 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 John DENNIS (Cam)

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

Prof. John Dennis,

University of Cambridge

PI, IRP2

April 2015

3.1.1 IRP1 Research Overview

The overall objective of this IRP 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 capture and use of greenhouse gas emissions). Major projects currently in progress are as follows:

- Chemical looping with advanced oxide carriers.
- CO_2 methanation and other gas-to-liquid approaches.
- New materials and MOFs for sorption, chemical looping and catalysis.
- Scale-up of adsorption processes, *e.g.* for CO_2 capture in the presence of contaminants.
- Modelling of fluidisation and granular solids.

This reports highlights significant progress in each of these areas, with particular highlights being the linkage between the preparation of new materials in Singapore and process evaluation at Cambridge which has, for example, solved a long-standing problem in improving hydrogen production from crude synthesis gas. Opportunities are also being explored for applying looping materials outside traditional areas in combustion, such as extension to selective oxidation reactions, which would be safer and cheaper than traditional processes. This is an area where we are in active discussion with colleagues from Johnson Matthey.

3.1.2 Update on work packages

Work package 1: Chemical looping with advanced oxide carriers *(Prof. J. S. DENNIS, Prof. Y. YANG, Prof. H. C. ZENG)*

Dr. Wen LIU (CARES SRF, NTU/NUS) is in charge of the activities of this work package. He has been synthesising novel spinel structured chemical looping materials, with the aid of Dr Ping LI (CARES RF, NUS). Some of the synthesised materials are being tested on bench-scale reactors, by a first-year PhD student, Martin CHAN (Cambridge). Preliminary results have been presented and discussed in a group seminar in Cambridge in March 2015. At NTU, Mr Jijiang HUANG, has started his first year of a CARES-funded PhD, supervised by Prof YANG. He has been synthesising and characterising novel nano-structured materials using MOFs as precursors, for intermediate temperature (600 - 800°C) chemical looping applications. Wen LIU and Jijiang HUANG are also setting up experimental apparatus for chemical looping tests in laboratories in NTU.

Mr Chao HE joined IRP1 as a Technician/Project Officer. He has been working on a novel gasification process, which utilises biomass and waste to provide fuels for chemical looping combustion. His work has led to a technology disclosure under the CARES programme and is currently being assessed by NTUitive for patentability.

Work Package 2: CO_2 methanation and biomass conversion *(Prof. J. S. DENNIS, Prof. Y. YANG)*

Dr. Yihu DAI (CARES SRF, NTU) is in charge of the research activities for this work package. The first Ph.D. student (Mr. Jun ZHAO) started in Aug 2013 and the second (Mr. Yong YAN) in Jan. 2014, both NTU in-kind contributions to the project. Jun ZHAO and Yong YAN have been working on catalytic conversion of biomass and CO_2 value added products. CARES-funded NTU PhD student, Ms. Chunmiao JIA, joined in Jan. 2015. She has been reviewing action models in the literature and developing a multi-scale model for the CO_2 conversion reactions. Mr Chao HE, CARES NTU Project Officer/Technician IRP1, will be assisting Dr DAI with work on CO_2 methanation.

Work Package 3: New materials and MOFs *(Prof. J. S. DENNIS, Prof. H. C. ZENG)*

Dr. Ping LI (CARES RF, NUS) joined C4T in Nov. 2014. Materials design for nanostructured solid absorbents has been started. Several systems are currently under investigation: (1) mesoporous silica supported CaO/MgO, (2) mesoporous silica protected hydrotalcite-like compounds, and (3) porous transition metal silicate materials. In the field of carbon dioxide conversion, two nanostructured catalysts have been developed: (1) hollow spheres of manganese silica for encapsulation or support of metal nanoparticles (published as Zhan, Yec, and Zeng*, 2015; see Appendix A), and (2) transition metal silicate nanotubes as precursor for nanocatalysts (published as Sheng and Zeng*, 2015; see Appendix A).

Work Package 4: Multi-scale modelling *(Prof. J. S. Dennis, Dr. S. Scott, Prof. J. Chew)*

Dr Shiliang YANG (CARES RF, NTU) joined IRP1 at the end of February 2015. A Ph.D student, Eddie

Sandjaya PUTRA, funded by CARES, started at NTU in Jan 2015. Review, experimental and simulation efforts on gas-solid fluidization have started.

Work Package 5: Fundamentals of adsorption and PSA *(Prof. S. Farooq, Prof. L. Gladden, Prof. J. S. Dennis)*

Dr Mark PURDUE (CARES RF, NUS) has accepted his job offer and will join IRP1 shortly.

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 during the period may be found in Appendix A.

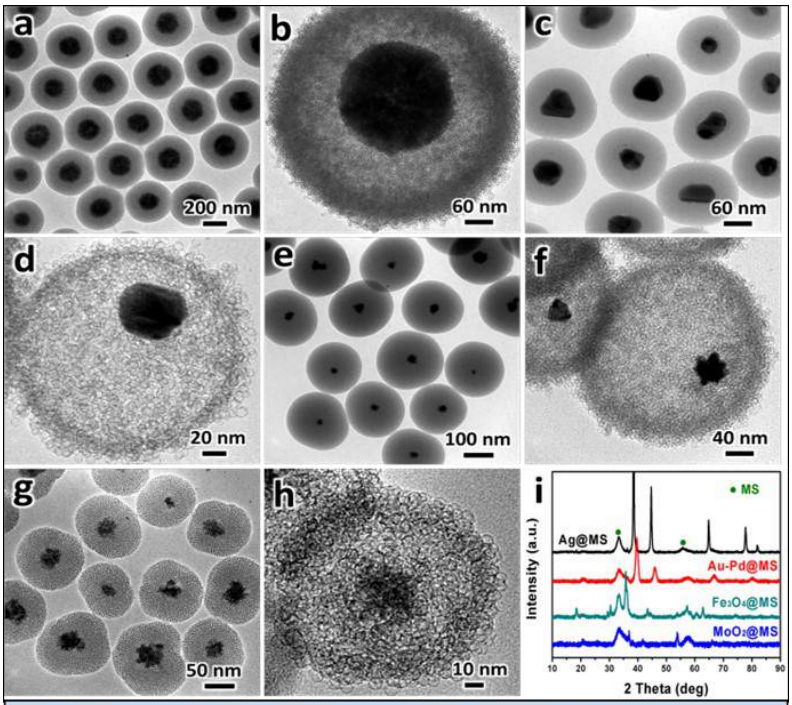


Figure: TEM images of (a) Fe_3O_4@SiO_2 core-shell, (b) Fe_3O_4@MS yolk-shell, (c) Ag@SiO_2 core-shell, (d) Ag@MS yolk-shell, (e) Au-Pd@SiO_2 core-shell, (f) Au-Pd@MS yolk-shell, (g) MoO_2@mSiO_2 core-shell, (h) MoO_2@MS yolk-shell; and (i) XRD patterns of these studied structures. MS denotes "manganese silica nanobubbles".

Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts

Guowu Zhan, Christopher C. Yec, and Hua Chun Zeng Chem. Eur. J. 2015, 21, 1882–1887. DOI: 10.1002/chem.201405697*

Relevance to the work of the IRP: This paper deals with the development of new materials for conversion of carbon dioxide to useful fuels.

Highlights:

- Manganese silica has been prepared into nanobubbles for the first time.
- A new class of yolk-shell nano-hybrids has been developed using manganese silica nanobubbles.
- Inter-bubble space and the bubble structure can be used to hold and support catalytic nanoparticles.
- These catalysts show high activity for conversion of carbon dioxide to fuels.

Abstract: Manganese silica in bubble-like morphology was used as a versatile platform to prepare a new class of yolk-shell hybrids. Mesoporosity of shell was generated from the inter-bubble space and the bubble structure of manganese silica was used to hold and support nanoparticles (e.g., Au, Ag, Pt, Co, Ni, Au-Pd alloy, MoO_2, Fe_3O_4, carbon nanotubes and their combinations). We also used heterogeneous catalysis reactions to demonstrate the workability of these catalysts in both liquid and gas phases.

Single-Walled 3*d* Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts

*Yuan Sheng and Hua Chun Zeng**

Chem. Mater. 2015, 27, 658−667. DOI: 10.1002/chem.201405697

Relevance to the work of the IRP: This paper deals with the materials design for catalytic conversion of carbon dioxide to useful fuels.

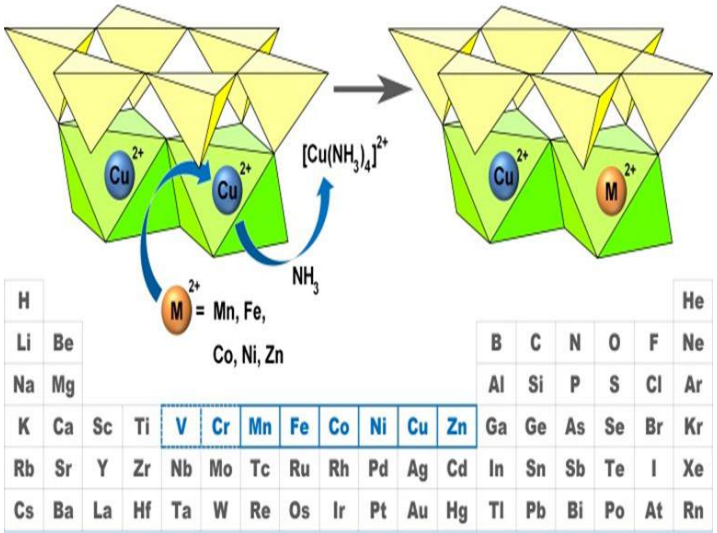


Figure: Ion exchange of Cu^{2+} in CuSiNT with 3*d* transition metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}). Corner-sharing tetrahedron are $[Si_2O_5]^{2-}$ layer (yellow) and edge-sharing octahedrons are transition metal hydroxide layer (green). The exchange process is facilitated with NH_3 complexation.

Highlights:

- A series of new single-walled silicate nanotubes containing 3d transition metal elements (Cu, Mn, Fe, Co, Ni and Zn) has been developed.
- Up to 80% of Cu in pre-synthesized copper silicate can be replaced by other transition metals through complex-assisted ion exchange, while the original tubular structure remains intact.
- The metal silicate nanotubes can serve as solid precursors for designed nanocatalysts.
- Enhanced catalytic performance has been demonstrated using CO_2 hydrogenation as a testing reaction.

Abstract: Copper silicate has so far been the only transition metal silicate to form single-walled nanotubes. Herein, we developed a general method to synthesize a series of new single-walled silicate nanotubes containing other 3d transition metal elements (M = Mn, Fe, Co, Ni and Zn); up to 80% of Cu in pre-synthesized copper silicate can be replaced with these metals (M) through complex-assisted ion exchange, while the original tubular structure remains intact. These metal silicate nanotubes can serve as solid precursors for design-made nanocatalysts; enhanced catalytic performance has been demonstrated using CO_2 hydrogenation as a testing reaction.

3.1.4 Further Achievements

Technology disclosure

IRP1 (Prof YANG Yanhui and HE Chao) filed an invention disclosure in March 2015, which is currently being assessed by NTUitive for patentability.

Co-editorship of special issue of *Catalysis Today*

Prof John DENNIS (PI, Cambridge) and Prof YANG Yanhui (PI, NTU) co-edited a special issue of *Catalysis Today* (issue 233, Elsevier) on the topic of "low-carbon technology". Prof Mark SAEYS (NUS during the editorship, recently moved to Europe) was also a co-editor. The special issue contains 24 research articles and the preface was kindly written by Prof Gary HALLER (Yale University).

Awards

Prof H.C. ZENG (NUS PI, IRP1) received an award of "Highly Cited Researcher" from Thomson Reuters. He also received the same recognition from the Faculty of Engineering NUS.

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)

Dr. Adrian Fisher,

University of Cambridge

PI, IRP2

April 2015

3.2.1 IRP2 Research Overview

The primary goal of EMSET is the creation of a multi-scale electrochemical research partnership with a focus on harnessing and exploiting electrical energy to deliver net carbon emission reductions. EMSET specialises in the discovery, analysis, design and development of methodologies, with a long-term focus on electrical energy recovery during chemical synthesis.

Existing electrochemical technologies operating within the Jurong Island envelope include the electricity intensive chloroalkyl industry as well as electricity generation technologies such as fuel cell and batteries. The IRP2 group is taking a ''bottom up'' look at each of the key elements which control and ultimately define the efficiency of an electrolyser or electrochemical electricity generator. This has led to the recruitment of research staff within the IRP2 group in Singapore with core skills in ***advanced electrocatalysis materials*** synthesis & testing, ***numerical modelling*** of optimal reactor designs, as well as the development of ***high sensitivity & selectivity electroanalytical techniques*** for the multiscale resolution and analysis of electrolysis pathways. In Cambridge existing expertise in ***rapid prototyping electrochemical reactor fabrication, mathematical analysis, electronic hardware controllers*** and ***algal bioelectrochemical energy*** systems complement the expertise of the Singapore team allowing IRP2 researchers to investigate existing, but also potentially new methodologies for the coupling of electricity for chemical production and/or analysis.

The current IRP2 focus is addressing the development of prototype reactors for the generation of a value added chemical product or the electroanalysis of a chemical component using a localised DC power supply. These types of reactors align with the current move towards a more distributed model for electricity production and a longer term vision for a DC rather than AC electricity supply system. By exploiting the IRP2 skill set using multi-scale analysis, exploring numerical modelling in combination with innovative electroanalytical approaches and rapid prototyping techniques for experimental reactor development we are already on the path to deliver, high sensitivity electroanalytical methodologies, fundamental insights into electron transfer coupled chemical reactions, innovative electrode architectures using (bio)electrocatalytic substrates and electrosynthetic/cogeneration reactors applied to chemical synthesis.

Recently synergies between IRP1 PI Prof Zeng Hua-Chun and the IRP2 advanced electrocatalysis materials group have been identified in areas such as CO_2 and integrated hybrid reactor design. We are currently in discussion regarding collaboration opportunities and links between IRP2/1 researchers.

IRP2 has been delighted to accept valuable in-kind contributions in the form of equipment access and consumables from Schlumberger Gould Research. This is anticipated to be an ongoing contribution to the programme with an annual value of SGD440000.

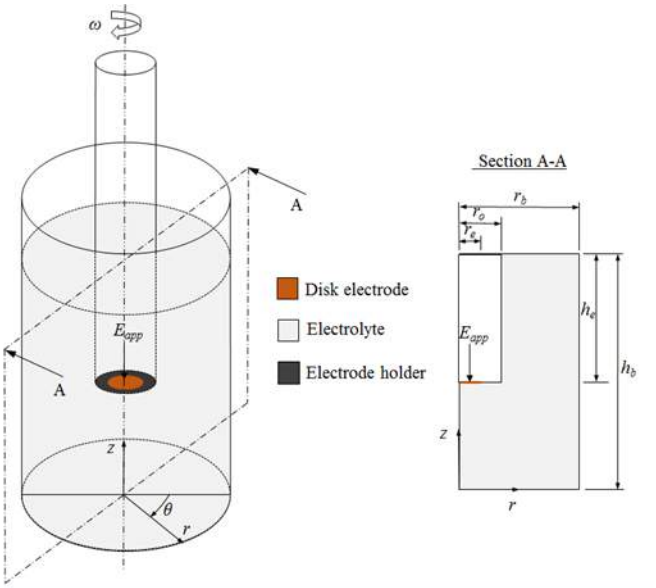


Figure: Schematic of a RDE and section A-A showing the 2D axisymmetric computational domain

3.2.2 Update on work packages

WP 2.1 Numerical Multi-Scale Electrochemical Modelling and Analysis

In this work package, IRP2 are deriving and implementing multi-scale mathematical models for electroanalytical tools (eg. the rotating (RDE) and rocking (RoDE) disk electrodes) to investigate catalytic reactions as well as to understand and quantify their characteristics in a range of applications.

Thus far, an axisymmetric two-dimensional (2D) model has been developed for a standard rotating disk electrode as illustrated in the figure, left. It consists of a disk of the electrode material imbedded in a rod of an insulating material; the rod is attached to a motor and rotated at a specified angular velocity ω.
The reaction considered in this study is the oxidation of ferricyanide to ferrocyanide:

$$Fe(CN)_6^{4-}(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq) + e^-$$

The mathematical model accounts for the conservation of momentum and mass for steady-state and transient conservation of the oxidizing and reducing species. The redox reaction is modelled with Butler-Volmer kinetics coupled with the species conservation. An example of the steady-state velocity field along with the streamlines for a rotational speed of 50 rpm is shown right. Another example is the voltammogram highlighted in the figure, following page, for a given voltage scan rate predicted by the model at different angular speeds. The limiting current identified by the model compares well with the standard Levich equation for rotational speeds around 100 rpm. One aim is to derive modified Levich-type equa-

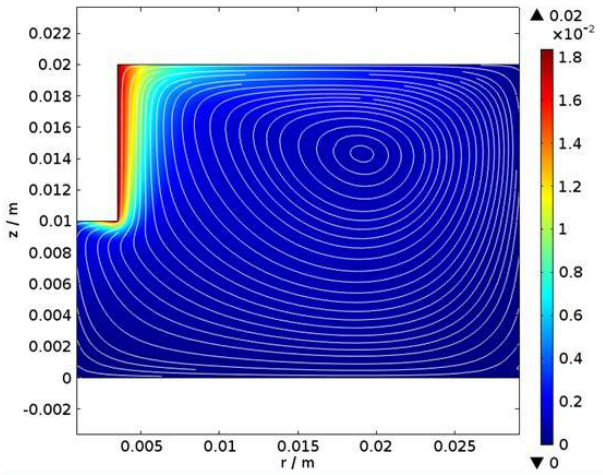


Figure: Steady state velocity profile at 50 rpm

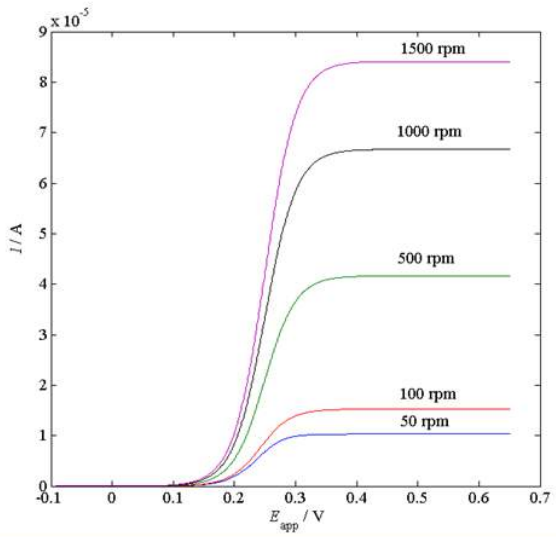


Figure: Rotating disk voltammogram predicted by the model (scan rate 0.1 V/s) for oxidation of ferricyanide to ferrocyanide

tions for the rocking disc electrode as well as modified rotating disc electrodes that will be studied here.

Furthermore, the 2D model has been extended to account for a sinusoidal motion of the electrode rather than the steady rotating motion of a traditional RDE; this will provide a stepping stone towards the rocking motion. In particular, the behaviour of the boundary layers and their transient response to the varying/rocking motion will be of interest.

Finally, for the case of a rocking disk electrode, a 4-bar mechanism has been analysed based on rigid-body dynamics to obtain the rocking motion, which we have coupled with the conservation equations.

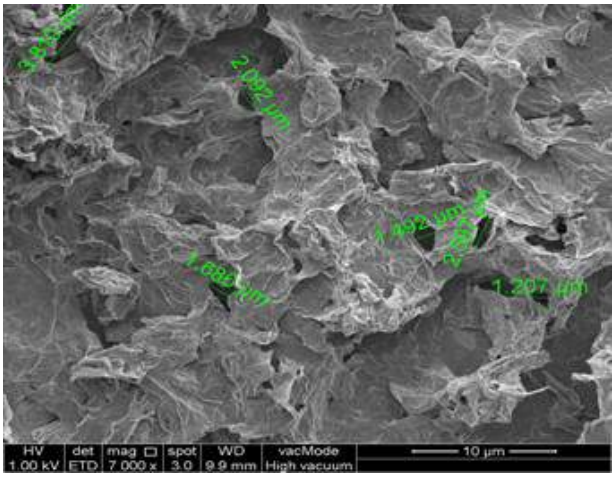
WP 2.2 Electrode Development and Testing

In the current reporting period, the IRP2 Advanced Materials and Eletrocatalysis Groups (led by Prof Xin Wang and colleagues Prof Bin LIU, Prof Zhichuan Xu and Prof Jong-Min LEE and Co-Is, NTU) have developed a variety of novel materials for electrocatalytic applications, including three-dimensional nanostructured oxygen evolution reaction (OER) electrocatalyst with large anodic current and low onset overpotential.

WP2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

IRP2 has appointed Peng SONG (CARES RF, Cambridge) to the Department of Chemical Engineering and Biotechnology, Cambridge in April 2015. Dr SONG will work closely with collaborators at NTU and NUS to design, develop and test novel electrochemical reactors, for applications in sensing, analysis and synthesis. Early stage work has already started in collaboration with an academic colleague from University of Malaya who was seconded to Cambridge to work with Dr Adrian FISHER (PI IRP2, Cambridge) and Dr Kamran YUNUS (proposed Co-I IRP2, Cambridge) on IRP2 topics. The work focused on the analysis of integrated biological and electrochemical systems.

The IRP2 Electroanalytical Group (led by Prof Martin PUMERA and Prof Richard WEBSTER, Co-Is, NTU) has appointed Dr Bahareh Khezri (CARES RF, NTU) to the School of Physical and Mathematical Sciences, NTU. Dr KHEZRI will work on the development, testing and application of novel high sensitivity and selectivily electroanalytical techniques. She will work closely with Peng SONG (CARES RF, Cambridge) who will be working from The Department of Chemical Engineering and Biotechnology, Cambridge.



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.

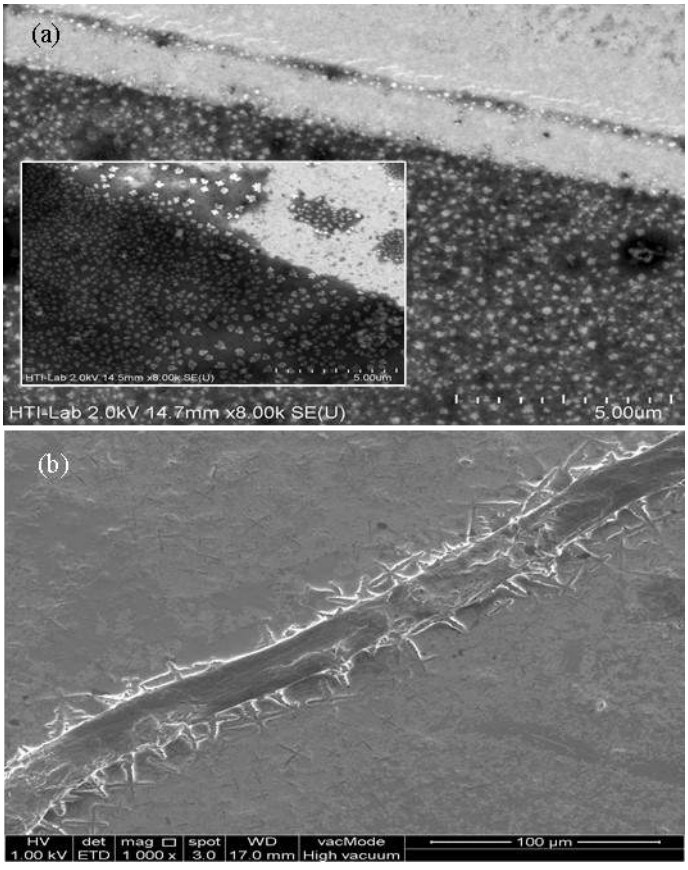
Reduced Graphene Oxide (rGO) Anodes for Potential Application in Algae Biophotovoltaic Platforms

Fong-Lee Ng, Muhammad Musoddiq Jaafar, Siew-Moi Phang, Zhijian Chan, Nurul Anati Salleh, Siti Zulfikriyah Azmi, Kamran Yunus, Adrian C. Fisher & Vengadesh Periasamy
Nature Scientific Reports, 2015, 4, in press

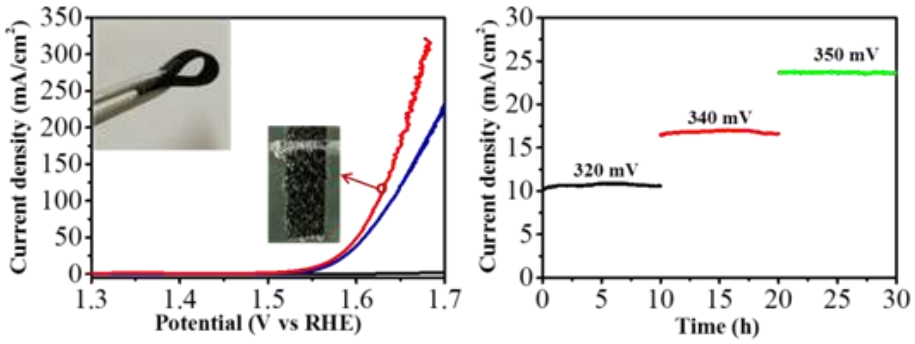
The search for renewable energy sources has become challenging in the current era, as conventional fuel sources are of finite origins. Recent research interest has focused on various biophotovoltaic (BPV) platforms utilizing algae, which are then used to harvest solar energy and generate electrical power. The majority of BPV platforms incorporate indium tin oxide (ITO) anodes for the purpose of charge transfer due to its inherent optical and electrical properties. However, other materials such as reduced graphene oxide (RGO) could provide higher efficiency due to their intrinsic electrical properties and biological compatibility. In this work, the performance of algae biofilms grown on RGO and ITO anodes were measured and discussed. Results indicate improved peak power of 0.1481 mWm^{-2} using the RGO electrode and an increase in efficiency of 119%, illustrating the potential of RGO as an anode material for applications in biofilm derived devices and systems.

Capillary Force Assisted Fabrication of DNA Templated Silver Wires

P. Vengadesh, G. P. M. K. Ciniciato, C. Zhijian, M. Musoddiq, A. C. Fisher and K. Yunus
*RSC Advances, 2015, **5**, 8163*



We demonstrate for the first time the formation of micron scale conductive silver (Ag) wires induced by capillary forces through scribed micro-cuts on a deoxyribonucleic acid–silver nanoparticle (DNA–AgNPs) film. The writing flexibility based on the physical rearrangement of the particles may prove to be prominent towards the fabrication of conductive wires. Fabrication of the proposed silver microwires involves three major stages; self-assembly of DNA-AgNPs suspension, scribing process and material rearrangement. A silicon (Si) wafer (single side polished, <100>, n-type, undoped) with a dimension of 2.0 inch x 0.5 mm bought from Sigma, UK was used as a substrate for the microwire formation.

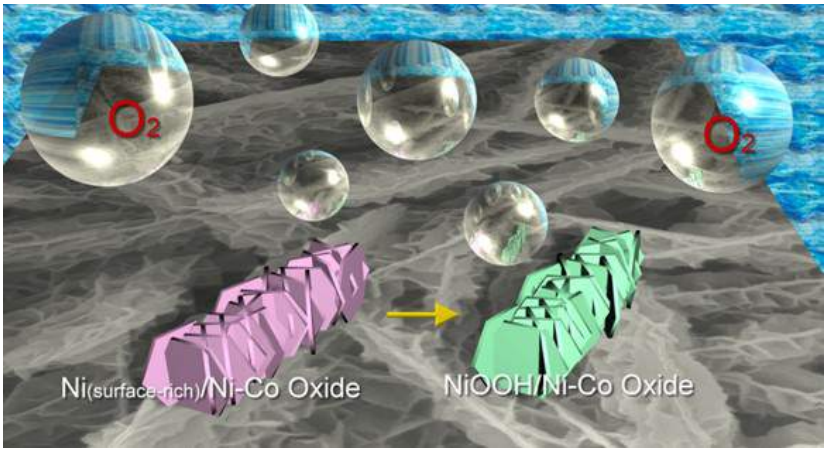


A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional $NiCo_2O_4$ Core-Shell Nanowires

Rong Chen, Hsin-Yi Wang, Jianwei Miao, Hongbin Yang and Bin Liu
Nano Energy, 2015, 11, 333-340

Three-dimensional $NiCo_2O_4$ core-shell nanowires made up of $NiCo_2O_4$ nanowire core and $NiCo_2O_4$ nanoflake shell have been fabricated by a simple two-step wet chemical method on flexible conductive carbon cloth substrate for oxygen evolution reaction (OER). The combination of high surface area, enhanced mass and charge transport as well as three-dimensional conducting pathway enables superior oxygen evolution reaction. Notably, the $NiCo_2O_4$ core-shell nanowire electrode exhibits large anodic current and low onset overpotential for OER with an overpotential of~320 mV at a current density of 10 mA/cm^2. Furthermore, the $NiCo_2O_4$ core-shell nanowire electrode possesses excellent electrocatalytic stability with long hour electrolysis showing no visible degradation, which is highly desirable for a promising OER electrocatalyst.

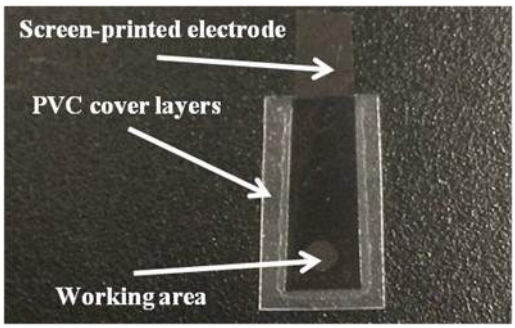
Surface Ni^{3+} Induced Formation of Active NiOOH on Spinel Ni-Co Oxide for Efficient Oxygen Evolution Reaction



Hsin-Yi Wang, Ying-Ya Hsu, Rong Chen, Ting-Shan Chan, Hao Ming Chen and Bin Liu
Advanced Energy Materials, in press

Efficient and earth abundant electrocatalyst for high-performance oxygen evolution reaction (OER) is essential for the development of sustainable energy conversion technology. In the present work, a new hierarchical Ni-Co oxide nanostructure, composed of small secondary nanosheets grown on primary nanosheet arrays, was synthesized via a topotactic transformation of Ni-Co layered double hydroxide (LDH). The Ni^{3+} rich surface benefited the formation of NiOOH, which is the main redox site as revealed via *in-situ* X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The Ni-Co oxide hierarchical nanosheets (NCO-HNSs) deliver a stable current density of 10 mA/cm^2 at an overpotential of ~0.34 V for OER with a Tafel slope of as low as 51 mV/decade in alkaline media. The improvement in the OER activity could be ascribed to the synergy of large surface area offered by the 3D hierarchical nanostructure and the facile formation of NiOOH as the main active sites on the surface of NCO-HNSs to decrease the overpotential and facilitate the catalytic reaction.

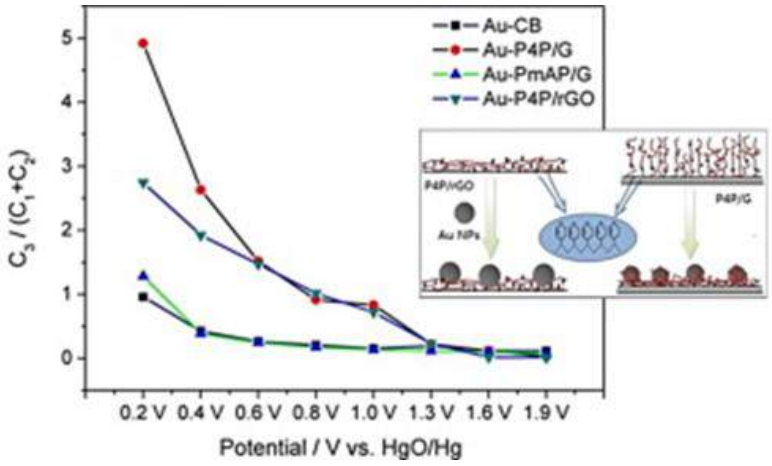
Screen Printed Alizarin-based Carbon Electrodes: Monitoring pH in Unbuffered Media



Chencheng Dai, Peng Song, Jay D. Wadhawan, Adrian C. Fisher, Nathan S. Lawrence
Electroanalysis, 2015, in press

An alizarin based voltammetric pH sensor is introduced. This device is fabricated by screen printing the alizarin, which is a pH-sensitive redox compound, mixed with carbon ink onto the carbon aluminum (aluminum foil coated with carbon paste). This electrode shows a Nernst response to both the buffered and unbuffered media, with a potential shift by 55.8 mV/pH unit and a working range up to pH 10. This approach suggests a disposable, reproducible, low-cost method for pH sensing with the possibility of miniaturization. A further study of this type of sensor coated with nafion reveals possible method to expand the working range and improve the stability.

Selective Electro-oxidation of Glycerol over Au Supported on Extended Poly(4-vinylpyridine) Functionalized Graphene



Haibo Wang, Larissa Thia, NanLi, Xiaoming Ge, Zhaolin Liu, Xin Wang .
Applied Catalysis B Environmental, 11/2014; 166-167.
DOI: 10.1016/j.apcatb.2014.11.009

Relevance to the work of the IRP: One specific target of IRP2 will be the electro-oxidation of glycerol, which is the key by-product of biodiesel production, representing 10 wt% of total product. Hence conversion of glycerol to high value-added products is one of the key factors for ensuring that biodiesel production remains economically viable and environmentally sustainable.

Highlights:

•Highly extended polymer on graphene as support causes lower d-band center of Au.
•Lower d-band center induces higher glyceric acid selectivity.
•Au supported on P4P-graphene is promising for direct glycerol fuel cell.

Abstract:

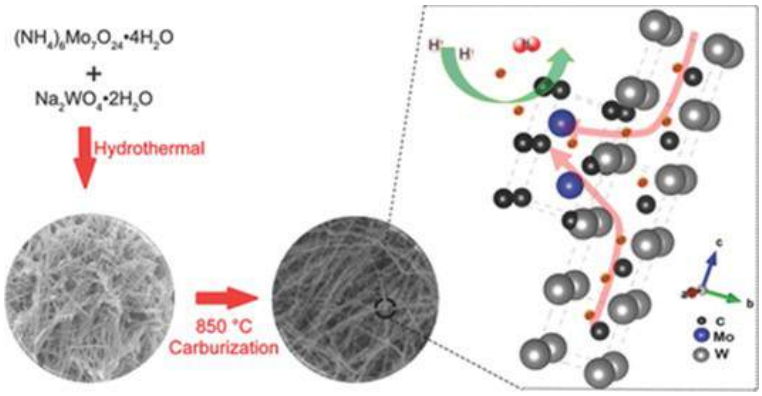
Au nanoparticles (NPs) supported on various supports with different metal support interaction are synthesized and tested for glycerol electro-oxidation. Through off-line HPLC analysis, it is found that Au NPs supported on extended poly(4-vinylpyridine) functionalized graphene (Au-P4P/G) shows a much higher activity and much better selectivity for three carbon products than those on carbon black, P4P functionalized reduced graphene oxide (Au-P4P/rGO) and poly(*m*-aminophenol) (PmAP)

wrapped graphene (Au-PmAP/G), e.g., the glyceric acid production reaches 68.6% at 0.2 V (vs. HgO/Hg), and the ratio between three carbon products and other products is 4.92 for Au-P4P/G compared with 0.96 of Au-CB. XPS results indicate that lower d-band center in Au nanoparticles induces higher three carbon selectivity and the changed adsorption ability for oxygen-containing groups might be the main reason.

Novel Molybdenum Carbide–Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution

Peng Xiao , Xiaoming Ge , Haibo Wang , Zhaolin Liu , Adrian Fisher , and Xin Wang.
Advanced Functional Materials, 25:10, 1520-1526. DOI: 10.1002/adfm.201403633

Relevance to the work of the IRP: IRP2 will support leading-edge research in the fields of electrocatalysis and electrochemical characterization. The project will focus on the development of new catalysts for fuel cell related applications.

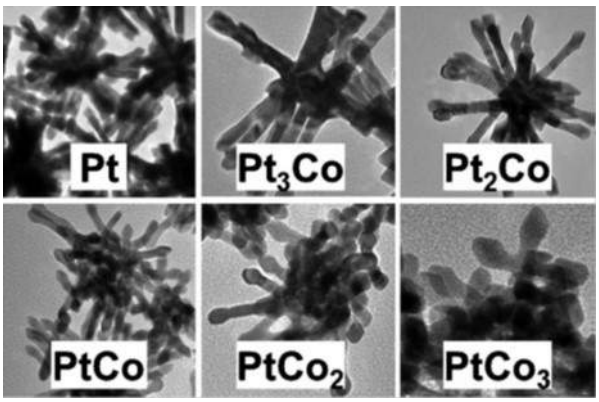


Highlights:

•The well-defined nanowire structure of complex molybdenum carbide–tungsten carbide is realized by a pseudomorphic transformation.
•The catalyst exhibits high activity towards hydrogen evolution reaction after electrochemical activation.

Abstract:

Development of non-noble metal catalysts for hydrogen evolution reaction (HER) is critical to enable an efficient production of hydrogen at low cost and large scale. In this work, a novel bimetallic carbide nanostructure consisting of Mo_2C and WC is synthesized. Based on a highly conductive WC backbone, nanosized Mo_2C particles are integrated onto WC, forming a well-defined and highly robust nanowire structure. More importantly, it is found that electrochemical activation can partially remove surface carbon and activate the catalyst by changing its surface hydrophilicity. As a result, the residual carbon contributes positively to the activity, besides its role of protecting carbide from oxidation. Benefiting from the structure, the catalyst achieves high activity, stable electrolysis towards HER.



One-Pot Synthesis of Pt–Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties

Bao Yu Xia, Hao Bin Wu, Nan Li, Ya Yan, Xiong Wen (David) Lou, and Xin Wang .

Angewandte Chemie International Edition. 54:12, 3797-3801. DOI: 10.1002/anie.201411544

Relevance to the work of the IRP: IRP2 will support leading-edge research in the fields of electrocatalysis and electrochemical characterization. The project will focus on the development of new catalysts for fuel cell related applications.

Highlights:

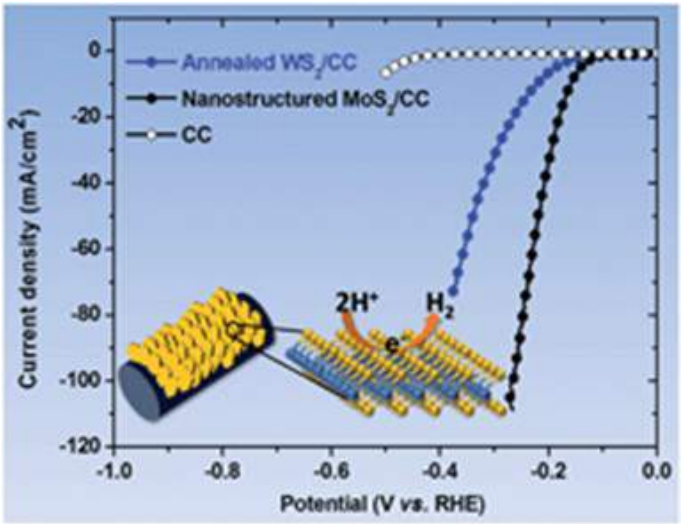
•Three-dimensional (3D) Pt–Co alloy nanostructures with tunable composition are synthesized by an effective solvothermal method.

•The interconnected 3D Pt3Co nanowire assembly exhibits significantly enhanced electrocatalytic activity and durability compared with commercial Pt based catalysts and a 3D Pt nanowire assembly.

•This is mainly attributed to the synergetic effects from composition and structural advantages.

Abstract:

Three-dimensional (3D) Pt-based alloy nanostructures composed of one-dimensional (1D) nanowires/nanorods have recently attracted significant interest as electrocatalysts. In this work, we report an effective solvothermal method for the direct preparation of 3D Pt–Co nanowire assemblies (NWAs) with tunable composition. The composition- and structure dependent electrocatalytic performance is thoroughly investigated. Because of the bimetallic synergetic effect and unique structural advantage, the as-prepared 3D Pt_3Co NWA outperforms commercial Pt/carbon and Pt black catalysts and even 3D Pt NWA. The electrochemical results demonstrate that the 3D Pt_3Co NWA is indeed a promising electrocatalyst with enhanced catalytic activity and improved durability for practical electrocatalytic applications.



Vertically Oriented MoS_2 and WS_2 Nanosheets Directly Grown on Carbon Cloth as Efficient and Stable 3-Dimensional Hydrogen-Evolving Cathodes

Ya Yan, BaoYu Xia, Nan Li, Zhichuan Xu, Adrian Fisher and Xin Wang .

J. Mater. Chem. A, 2015,3, 131-135. DOI: 10.1039/c4ta04858j

Relevance to the work of the IRP: IRP2 will support leading-edge research in the fields of electrocatalysis and electrochemical characterization. The project will focus on the development of new catalysts for fuel cell related applications.

Highlights:

•A simple solvothermal method is developed to directly grow MoS_2 and WS_2 on carbon cloth with vertically oriented nanosheet layers.

•The prepared 3-dimensional electrodes exhibit high activity towards the HER and prominent electrochemical durability.

Abstract:

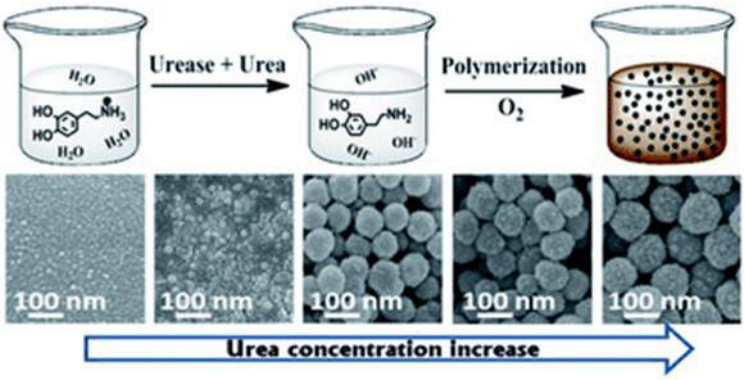
The development of non-noble-metal based hydrogen-evolving catalysts is essential to the practical application of water-splitting devices. Improvement of both the activity and stability of such catalysts remains a key challenge. In this work, a simple solvothermal method is developed to directly grow MoS_2 and WS_2 on carbon cloth with vertically oriented nanosheet layers. With the unique layer orientation that maximally exposes active edge sites as well as a rapid release of small gas bubbles to maintain a large working area, such prepared 3-dimensional electrodes exhibit high activity towards the HER. In addition, they also exhibit prominent electrochemical durability, thanks to the strong bonding between the nanosheet layers and the substrate along with the self-removal of the as-formed H2 bubbles from the nano-porous electrode surface.

Enzymatic-Reaction Induced Production of Polydopamine Nanoparticles for Sensitive and Visual Sensing of Urea

Nan Li, Hai-Bo Wang, Larissa Thia, Jing-Yuan Wang and Xin Wang .

Analyst, 2015,140, 449-455. DOI: 10.1039/C4AN01900H

Relevance to the work of the IRP: IRP2 will support leading-edge research in the fields of electrocatalysis and electrochemical characterization. The project will focus on the development of new catalysts for fuel cell related applications.



Highlights:

•A facile assay for urea detection based on spectroscopic or particle size analysis of DA polymerization to PDA NPs was developed.

•Compared with other urea detection methods, our assay possesses several advantages, such as simplicity, easy visualization, good sensitivity, wide detection range and low interference.

•The proof-of-concept that nanostructured material-assisted colorimetric sensing of urea proposed herein provides a potential way to detect urea

Abstract:

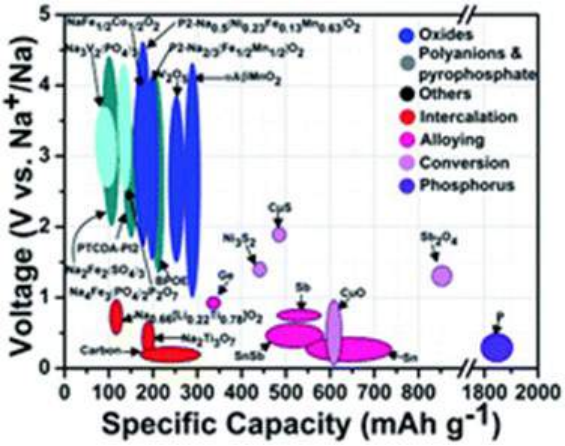
Dopamine (DA) has attracted extensive interest due to not only its important roles in physiological and pathological processes, but also its prospective applications in chemistry and materials science. In this work, we demonstrate that the urease catalytic reaction is an effective new approach for a better control of DA polymerization to polydopamine nanoparticles (PDA NPs). And we further develop an original and novel method for sensitive and visual sensing of urea through spectroscopic or particle size analysis. The detection is based on DA polymerization to PDA NPs that can be controlled by the reaction rate of urease-catalyzed urea hydrolysis, correspondingly, correlated with the varied urea concentration. The composition, morphologies and sizes of the resulting PDA NPs are

characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and dynamic light scattering (DLS) spectroscopy, respectively. Under optimal reaction conditions, the UV absorbance of DA polymerization at 400 nm shows a good response towards urea detection over a range of 1×10^{-7} to 1 × 10−3 M with a limit of detection (LOD) of 100 nM (S/N = 3). Moreover, the sizes of the resulting PDA NPs increase linearly with urea concentration from 5×10^{-6} to 1×10^{-4} M. The newly developed assay allows the enzymatic-reaction driven PDA NPs to be used for quantitative detection of urea with many advantages, e.g. simple preparation, easy visualization, good sensitivity, wide detection range and low interference, in particular, no complex sensor-fabrication required.

Recent developments in electrode materials for sodium-ion batteries

Luyuan Paul Wang, Linghui Yu, Xin Wang, Madhavi Srinivasan, and Zhichuan J. Xu

J. Mater. Chem. A, 2015, Advance Article. DOI: 10.1039/C4TA06467D



Relevance to the work of the IRP: IRP2 will support leading-edge research in electrochemical fields. This review article focuses on the electrochemical application in the field of sodium-ion batteries.

Highlights:

•A wide group of materials, including layered oxides, polyanionic phosphates, pyrophosphates, has be extensively reviewed.

•Some perspectives on possible solutions and suggestions that could be of significant interest for progress in sodium-ion battery have been concluded with.

Abstract:

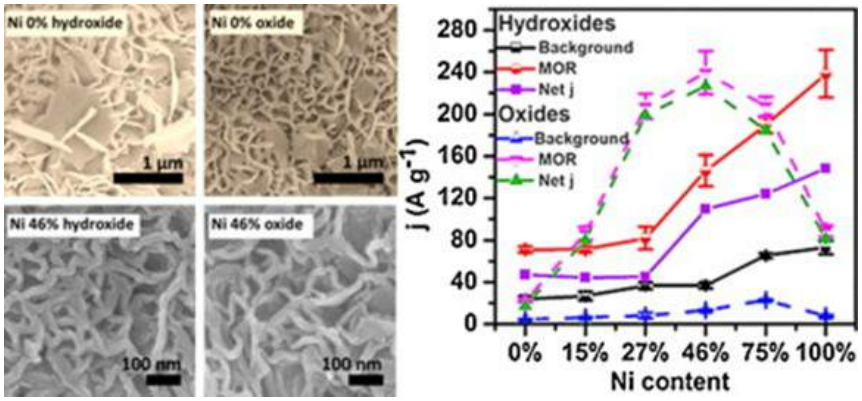
The rapid consumption of non-renewable resources has resulted in an ever-increasing problem of CO2 emissions that has motivated people for investigating the harvesting of energy from renewable alternatives (e.g. solar and wind). Efficient electrochemical energy storage devices play a crucial role in storing harvested energies in our daily lives. For example, rechargeable batteries can store energy generated by solar cells during the daytime and release it during night-time. In particular, lithium-ion batteries (LIBs) have received considerable attention ever since their early commercialization in 1990s. However, with initiatives by several governments to build large-scale energy grids to store energy for cities, problems such as the high cost and limited availability of lithium starts to become major issues. Sodium, which also belongs to Group 1 of the periodic table, has comparable electrochemical properties to Lithium, and more importantly it is considerably more accessible than lithium. Nonetheless, research into sodium-ion batteries (NIBs) is currently still in its infancy compared to LIBs, although great leaps and bounds have been made recently in terms of research and development into this technology. Here in this review, we summarize the recent advancements made, also covering the prospective materials for both the battery cathode and anode. Additionally, opinions on possible solutions through correlating trends in recent papers will be suggested.

Composition dependence of methanol oxidation activity in nickel–cobalt hydroxides and oxides: an optimization toward highly active electrodes

Shengnan Sun and Zhichuan J. Xu

Electrochimica Acta, Volume 165, 20 May 2015, Pages 56–66

Relevance to the work of the IRP: IRP2 will support leading-edge research in electrochemical fields. This project focuses on investigating the methanol oxidation reaction performance of Ni–Co oxides in accordance with the requirement of IRP2.



Highlights:

- A first and complete study on composition dependence of Ni–Co hydroxides and oxides for methanol electro-oxidation has been presented.
- The MOR performance on Ni–Co oxides presented an inverted volcano shape. Oxides show better performance than hydroxides.

Abstract:

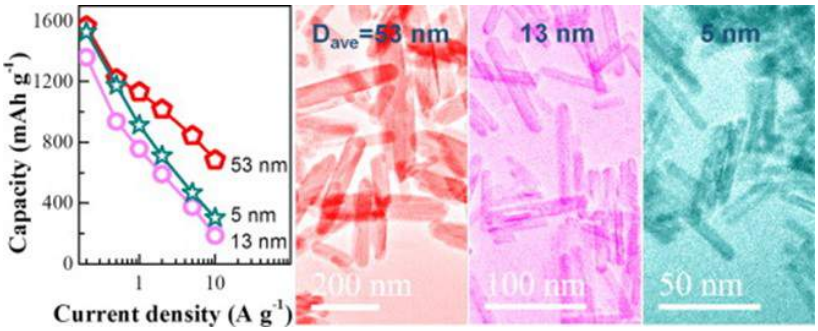
Non-precious metal electrodes, Ni and Co hydroxides and oxides, have been recently found active towards electro-oxidation of methanol in alkaline. In this article, we present a first and complete study on composition dependence of Ni–Co hydroxides and oxides for methanol electro-oxidation. Ni–Co hydroxide electrodes were prepared by co-electrodeposition on stainless steel mesh (SSM). The atomic ratio of Ni/Ni + Co in Ni–Co hydroxides was controlled by adjusting the ratio of precursor concentration. Ni–Co oxide electrodes were further obtained by annealing the Ni–Co hydroxides. The morphology factors of Ni–Co hydroxides and oxides were revealed by measuring double layer capacitance using cyclic voltammetry (CV). Methanol oxidation reaction (MOR) performance of these Ni–Co hydroxides and oxide electrodes was investigated by CV, and electrochemical impedance spectroscopy (EIS) techniques at room temperature (RT, ~25 °C). It is found that the MOR performance of Ni–Co hydroxides increased with the increase of Ni content, while the performance of Ni–Co oxide electrodes presented a volcano plot. The highest MOR performance, the smallest charge transfer resistance and Tafel slope were found at the atomic composition of 46% Ni. Such an enhancement probably was due to the synergistic effect of co-existing Ni and Co in the spinel structure. In contrast, the electrode with the mixture of Ni oxide and Co oxide was una-

ble to reach such a high activity. The function of Ni in Ni–Co hydroxides and oxides was attributed to facilitating the methanol oxidation, and in low potential it presented high absorption of intermediate products.

Controlled synthesis of high-performance β-FeOOH anodes for lithium-ion batteries and their size effects

Linghui Yu, Chao Wei, Qingyu Yan, and Zhichuan J. Xu

Nano Energy, Volume 13, April 2015, Pages 397–404



Relevance to the work of the IRP: IRP2 will support leading-edge research in electrochemical fields. This project focuses on the electrochemical applications in the energy field. Alignment with IRP2 is related to integrated electrical and chemical platforms for chemical conversion.

Highlights:

•A study on the effects of particle size on their lithium storage performance and the kinetics associated with the redox reactions has been presented.

•The kinetic study reveals the initial size of the material influences the formation of the SEI layers on the material and has significant effects on the kinetics of the redox reactions that lead to different rate behaviour.

Abstract:

β-FeOOH has recently been reported to have a very high lithium storage capacity of ~1400 mAh g−1, 20–40% higher than those widely reported for iron-based anodes, such as Fe2O3 and Fe3O4. However, many properties of this material that are important for their use in lithium-ion batteries remain unknown. Here, we present a study on the effects of particle size on their lithium storage performance and the kinetics associated with the redox reactions. The study is based on β-FeOOH nanorods prepared by a simple hydrolysis method which is able to control the size of the rods in a wide range, diameter from tens of nanometers down to ~5 nm. Three materials with different sizes, mean diameter 5, 13 and 53 nm, are investigated for lithium storage. They show a very high and comparative capacity at a low current density, but different initial coulombic efficiencies and rate capabilities. The kinetic study reveals the initial size of the material influences the formation of the SEI layers on the material and has significant effects on the kinetics of the redox reactions that lead to different rate behaviors. This study provides fundamental information and understanding of β-FeOOH anodes for their further development.

Surface segregation in bimetallic nanoparticles: a critical issue in electrocatalyst engineering

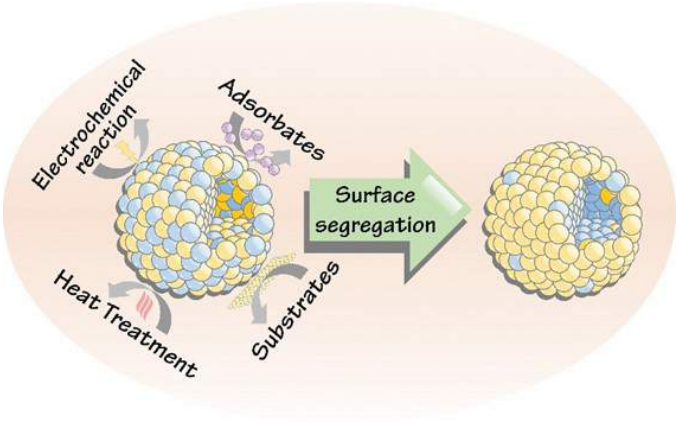
Hanbin Liao, Adrian Fisher, and Zhichuan J. Xu
Small, in press. DOI: 10.1002/smll.201403380

Relevance to the work of the IRP: This review article centres on the effect of surface properties towards electrocatalysis, which can be supported by IRP2 in the fields of electrocatalysis and electrochemical characterization.

Highlights:

•A study on the effects of particle size on their lithium storage performance and the kinetics associated with the redox reactions has been presented.

•The kinetic study reveals the initial size of the material influences the formation of the SEI layers on the material and has significant effects on the kinetics of the redox reactions that lead to different rate behaviour.



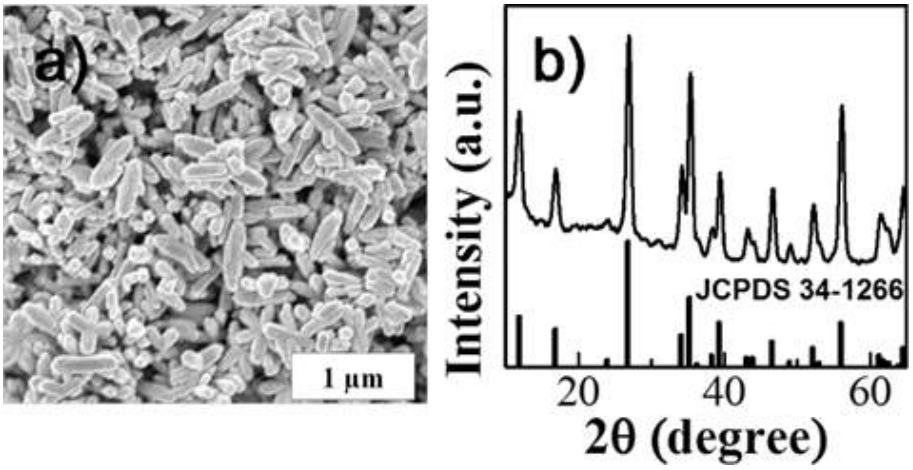
Abstract:

Bimetallic nanoparticles are one class of most important electrocatalysts. They usually exhibit a synergistic effect that signifies the whole greater than the sum of its parts. Such a synergistic effect critically depends on the surface composition, which determines the surface properties and the adsorption/desorption behaviors of reactants and intermediates during the catalysis. The surface composition can be varied as nanoparticles are exposed to certain environments through the surface segregation. Thermodynamically, the surface segregation is due to the difference of surface energy between two metals. It may lead to the enrichment of one metal on the surface and the other in the core. The external conditions those can influence the surface energy may lead to the variation of the thermodynamic steady state of the particle surface and thus offer chances for varying the surface composition. In this review article, we introduce the most recent and important progress of the surface segregation in bimetallic nanoparticles and the impacts in electrocatalysis. Typical segregation inducements and surface characterization techniques are discussed in details. We conclude that the surface segregation is a critical issue when designing bimetallic catalysts. It is necessary to explore methods to control it and utilize it as a way towards the robust bimetallic electrocatalysts.

Superior Lithium Storage Properties of β-FeOOH

Linghui Yu, Shibo Xi, Chao Wei, Wenyu Zhang, Yonghua Du, Qingyu Yan, and Zhichuan Xu
Advanced Energy Materials, Volume 5, Issue 6, March 18, 2015

Relevance to the work of the IRP: This project focuses on the development of anode materials for hybrid electrochemical reactors.



Highlights:

•β-FeOOH has a very high reversible capacity of ≈1400 mAh g^{-1} in the potential range of 0.005–3 V versus Li^+/Li, which is 20%–40% higher than Fe_2O_3 and Fe_3O_4.

•Very long cycling performance, which has never been achieved for any conversion materials, was obtained by a simple electrode design.

Abstract:

Several crystal forms of FeOOH are recently reported to be highly promising for lithium storage due to their high capacity, low cost, and environmental friendliness. In particular, β-FeOOH has shown a capacity of ≈1000 mAh g−1, which is comparable to other promising iron-based anodes, such as Fe2O3 and Fe3O4. However, its storage mechanisms are unclear and the potential for further improvement remains unexplored. Here, it is shown that this material can have a very high reversible capacity of ≈1400 mAh g−1, which is 20%–40% higher than Fe2O3 and Fe3O4. Such a high capacity is delivered from a series of reactions including intercalation and conversion reactions, formation/deformation of solid-state electrolyte interface layers and interfacial storage. The mechanisms are studied by a combination of electrochemical and X-ray absorption near edge spectroscopic approaches. Moreover, very long cycling performance, that is, after even more than 3000 cycles the material still has a significant capacity of more than 800 mAh g−1, is obtained by a simple electrode design involving introducing a rigid support into porous electrodes. Such long cycling performance is for the first time achieved for high-capacity materials based on conversion reactions.

3.2.4 Other Activities and Achievements

Research Exchange Workshop

A joint C4T-Peking (SPURc-CREATE) information exchange workshop was held on 23rd April at CREATE. The programme involved

the IRP2 Advanced Materials Group. Presentations by Dr FISHER (IRP2 PI, Cambridge), Dr. YAN Ya (CARES RF, NTU): "Development of highly efficient and stable non-noble metal electrocatalysts for production of hydrogen", Ms. CHEN Rong, (IRP2 Collaborator) "A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional NiCo2O4 Core-Shell Nanowires", Mr. XIE Ming Shi (CARES PhD NTU), "Amino Acid Functionalized Cu Electrodes for the Enhanced Selective Electroreduction of CO2 towards Hydrocarbons", and Dr. LIAO Hanbin, (CARES RF, NTU), "Electrochemical Characterization of Metal@Phosphide Core/Shell Nanoparticles and Their High Electrocatalytic Activity for Hy for Hydrogen Evolution Reaction"

Research Collaboration Visit to University of Bath

The IRP2 Numerical Modelling Group and IRP2 Electroanalytical Group visited the University of Bath, UK for research exchange discussions. At the University of Bath, IRP2 researchers, Dr Bahareh KHREZI, (CARES RF, working with Prof Martin Pumera and Prof Richard Webster at NTU) and Karthik SOMASUNDARUM, (CARES RF, working with Prof Jim Yang Lee and Prof Erik Birgersson at NUS), presented talks and discussed research opportunities with the C4T IRP2 group. As a result of these discussions Professor Frank MARKEN (University of Bath) has donated novel electroanlytical instruments to the IRP2 programme which will be housed in Cambridge and at NTU with Profs PUMERA and WEBSTER. It is planned that IRP2 researchers will explore numerical modelling and novel experimental applications and assess potential developments of the techniques for multiscale high sensitivity and selectivity electroanalysis.

33 3.3 IRP3 — CAPRICORN

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

CAPRICORN is split into five interacting work packages:

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

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

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

WP 3.4: Modelling and optimisation of unit operations

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

The CAPRICORN group is led by PIs:

Prof Markus KRAFT (Cam)

Prof Raymond Wai Man LAU (NTU)

Prof Iftekhar KARIMI (NUS)

Prof. Markus Kraft,

University of Cambridge

PI, IRP3

April 2015

3.3.1 IRP3 Research Overview

IRP3 covers a number of energy-related topics and links to all other IRPs. Firstly, in WP1 and WP5 we develop a comprehensive simulation environment, the "J-Park simulator", which will be used to study how the current processes in an industrial park of similar size and type to Jurong Island can be optimised and controlled. This research activity links closely to IRP 4 in which the electrical network aspects are investigated. The simulator also offers the opportunity to assess new technology at different TRL levels with respect to its CO_2 reduction ability. This activity is closely linked to IRP1.

Secondly, we examine the refinery operation with respect to modern developments in internal combustion engines. We would like to answer the questions: What is the best fuel for the internal combustion engine of the future and how does fuel composition influences refinery operations? This very challenging question is being addressed in a number of ways. This reporting period has shown some good progress in the area of characterisation of the sooting propensity of different fuel mixtures. For example, it was found that aromatic fuels substituted with larger aliphatic chains produce particles with smaller mean diameters. Another very interesting result from the more fundamental studies of the internal structure of soot shows that the transition from solid to liquid particles plays an important role at the onset of fractal growth.

Finally, we are working on new materials and catalysts that are based on flame synthesis to enhance catalytic performance and to scale up synthesis routes which so far have only existed at lab scale. This aspect links to IRP1 and 2. Some aspects of this work will be supported by Tioxide starting in the next reporting period. In the last six months we have made significant progress at modelling the precursor chemistry of titania and silica particles. We also managed to file an invention disclosure and an associated patent application entitled *Combustion-assisted coating of TiO2 and other metal oxides on water container surface for water treatment application.* Overall, IRP3 has made good progress and we are optimistic we will continue to do so in the next reporting period.

3.3.2 Update on work packages

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

IRP3 now has two personnel (Dr Catharine KASTNER, CARES RF, NTU and Dr Martin KLEINE-LANGHORST, CARES SRF, NTU) in place who are working on WP1.1: System level modelling of operations on Jurong Island and WP1.2: Parameterisation of system level models – using the Model Development Suite (MoDS). A paper has been published on optimising the Jurong Island Eco-Industrial Park. Software is now in the process of being put in place to carry this out. The network optimisation tool GAMS is being acquired, and first results regarding the coupling between Aspen and MoDS have been achieved.

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

IRP3 have published a paper in which the MoDS software is used to analyse n-propylbenzene experimental data and how it impacts kinetic combustion models derived from it. Furthermore, progress has been made with WP2.3: Sooting propensity as a function of molecular structure. Another paper considering mixtures of certain fuels, and how the mixture composition influences sooting propensity and soot particle characteristics, is due to be submitted in the very near future.

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

Flame synthesis equipment for metal oxide nanoparticles has been purchased from Stanford University. It will support the experimental aspect of IRP3 and be housed in C4T's NTU lab facility. The equipment will be essential in investigating the kinetics of nanoparticle flame synthesis. IRP3 intends to purchase another soot synthesis equipment to carry out soot formation studies. The experimental work on nanoparticles synthesis through a simple combustion process continues. Technology disclosure is being pursued in this area of investigation. Two papers have been published in the area of chemical kinetics of some precursors in the formation of silica nanoparticles in flames. An additional one studying the thermo-chemistry of a titania particle precursor has just been submitted for publication.

WP 3.4: Modelling and optimisation of unit operations

A paper has been published on simulation and life cycle assessment of algae gasification in fluidised bed gasifiers . This connects directly to WP1 in which we develop models of operations on Jurong Island.

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

One of the papers published as part of WP2 in this period contains a generic technique which considers the influence of individual experimental measurements on the values of model parameters determined through fitting of the model to the data. This is essentially an experimental design technique as it supports the experimenter in their decisions when planning future experiments. This technique has been implemented into the MoDS software.

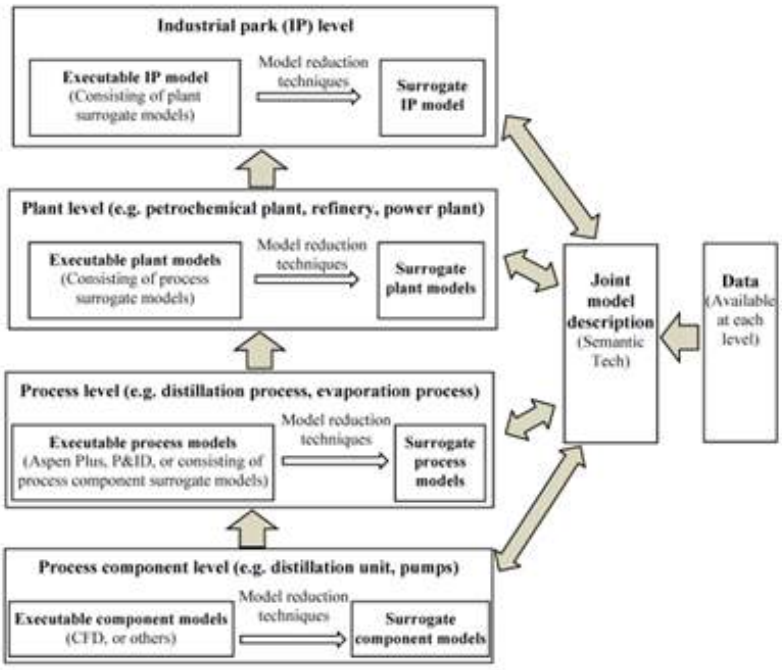
3.3.3 Scientific output of IRP3

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.

Applying Industry 4.0 to the Jurong Island Eco-industrial Park

Ming Pan, Janusz Sikorski, Catharine A Kastner, Jethro Akroyd, Sebastian Mosbach, R. Lau, and Markus Kraft

Energy Procedia, submitted, (2015).



Highlights:

- Industry 4.0 technologies are implemented to eco-industrial park (EIP) of Jurong Island in Singapore.
- A framework is built for modeling Jurong Island EIP.
- An expert system is proposed to use of the latest advances in high performance computing (HPC), advanced mathematical modelling, and semantic web technologies.

Abstract:

This paper presents new insights into the implementation of Industry 4.0 technologies (novel mathematical and computer-based methods) for designing and optimising the eco-industrial park (EIP) of Jurong Island in Singapore. The concept of Industry 4.0 translation to an EIP is introduced, which delivers an expert system allowing users to monitor, control, and optimise the social, economic and environmental repercussions of the industrial activities on Jurong Island. This expert system is a cyber-infrastructure making use of the latest advances in high performance computing (HPC), advanced mathematical modelling, and semantic web technologies. The proposed work addresses end-user driven demands by harnessing HPC resources and advanced data analytics to enable intelligent design, operation, and management of all entities on Jurong Island. The outcome of the work can serve stakeholders from both the private and public sectors.

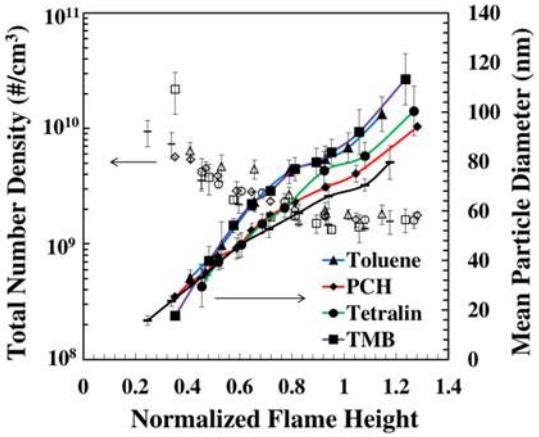
Sooting tendency of surrogates for the aromatic fractions of diesel and gasoline in a wick-fed diffusion flame.

Maria Botero, Sebastian Mosbach, Jethro Akroyd, and Markus Kraft.

Fuel, accepted for publication, (2015).

Highlights:

- Particle size distributions of several aromatic hydrocarbons in a diffusion flame were measured.
- At the smoke point all fuels exhibited similar mean soot particle diameter.
- Aromatic fuels substituted with larger aliphatic chains produce particles with smaller mean diameters.



Abstract:

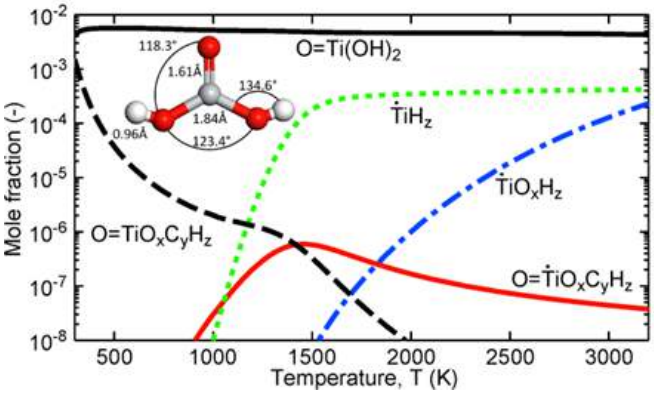
The sooting characteristics of pure aromatic fuels representative of those present in commercial fuels were studied. The experiment involves the non-premixed combustion of the fuel in wick-fed burner. The particle size distributions (PSD) of soot particles were measured at the tip of flames of different heights, using a differential mobility spectrometer (DMS). Substituted aromatics were studied in order to capture the influence of their structure in the final PSD. At the smallest flame height the PSD is bimodal without a strong prevalence of neither the nucleation or coagulation mode, except for trimethylbenze (TMB) that exhibits a large nucleation mode. For larger flame heights the PSD is multimodal, and the coagulation mode enlarges and shifts to larger particle diameters. After the smoke point the PSD presents a single mode of particles with sizes of about 100nm. Around the smoke point, all fuels show a slight slow down in particle growth probably due to stronger oxidation while the tip is changing from a close defined one to an opened soot trail. Toluene, TMB produced the largest soot particles, tetralin, butylbenzene (BB) and phenylcyclohexane (PCH) the lowest. This evidence indicates that aromatics substituted with larger aliphatics tend to produce smaller soot particles.

First-principles thermochemistry for the thermal decomposition of titanium tetra-isopropoxide.

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

Highlights:

- First-principles calculations used to propose set of TTIP decomposition products.
- Internal rotations are important. Free rotor approximation is good compromise.
- Equilibrium composition analysis performed under typical combustion conditions.
- O=Ti double bond species are important, in particular O=Ti(OH)2.
- Carbon-containing Ti-species observed at low temperatures.



Abstract:

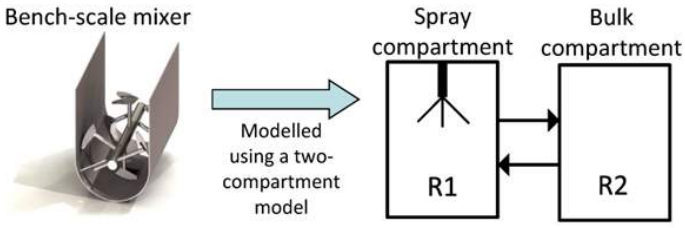
The thermal decomposition of titanium tetra-isopropoxide (TTIP) is investigated using quantum chemistry, statistical thermodynamics and equilibrium composition analysis. A set of 954 Ti-containing candidate species are proposed systematically based on the thermal breakage of bonds within a TTIP molecule. The ground state geometry, vibrational frequencies and hindrance potentials are calculated for each species at the B97-1/6-311+G(d,p) level of theory. Thermochemical data are computed by applying statistical thermodynamics and, if unknown, the standard enthalpy of formation is estimated using balanced reactions. Equilibrium composition calculations are performed under typical combustion conditions for premixed flames. The thermodynamically stable decomposition products for different fuel mixtures are identified. A strong positive correlation is found between the mole fractions of Ti-species containing carbon and the TTIP precursor concentration.

A multi-compartment population balance model for high shear granulation.

Kok Foong Lee, Sebastian Mosbach, Markus Kraft, and Wolfgang Wagner.
Computers and Chemical Engineering 75, 1-13, (2015).

Highlights:

- A batch granulation process is modelled using a compartmental model.
- A population balance model for granulation is extended to have multiple compartments.
- A stochastic weighted algorithm is adapted to the population balance model.
- The compartmental model is optimised using experimentally measured size distribution.
- The fit to experimental data is improved with the compartmental model.

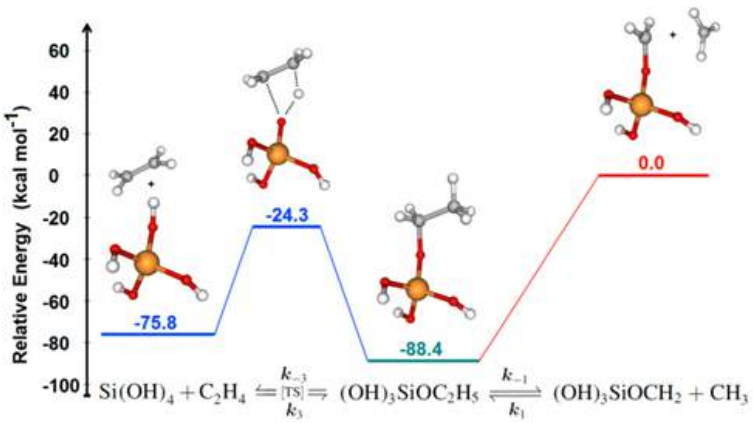


Abstract:

This work extends the granulation model published by Braumann et al. (2007) to include multiple compartments in order to account for mixture heterogeneity encountered in powder mixing processes. A stochastic weighted algorithm is adapted to solve the granulation model which includes simultaneous coalescence and breakage. Then, a new numerical method to solve stochastic reactor networks is devised. The numerical behaviour of the adapted stochastic weighted algorithm is compared against the existing direct simulation algorithm. Lastly, the performance of the new compartmental model is then investigated by comparing the predicted particle size distribution against an experimentally measured size distribution. It is found that the adapted stochastic weighted algorithm exhibits superior performance compared to the direct simulation algorithm and the multi-compartment model produces results with better agreement with the experimental results compared to the original single-compartment model.

Ab initio Variational Transition State Theory and Master Equation Study of the Reaction (OH)3SiOCH2 + CH3 <-> (OH)3SiOC2H5.

Daniel Nurkowski, Stephen J. Klippenstein, Yuri Georgievskii, Marco Verdicchio, Ahren W. Jasper,



Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. Zeitschrift fuer Physikalische Chemie, in press, (2015).

Highlights:

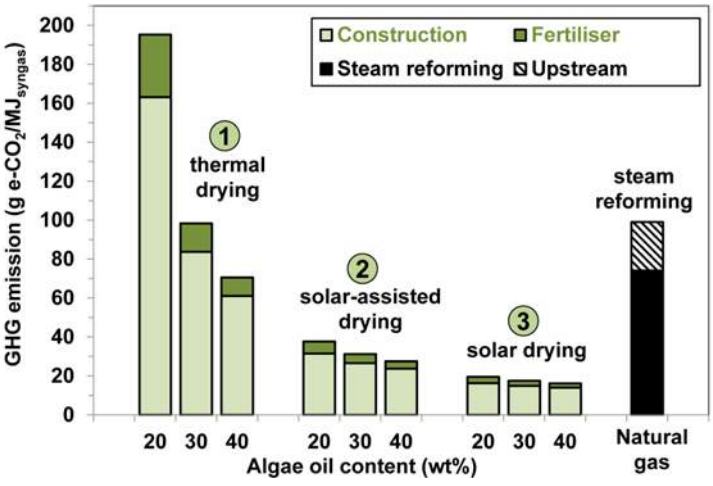
- A detailed study of the kinetics of the title reaction is presented.
- Variable reaction coordinate transition state theory and master equation calculations are used to obtain rate constant coefficients at various pressures and temperatures.
- A comparison is made with an equivalent ethanol reaction computed at the same level of theory.

Abstract:

In this paper we use variable reaction coordinate variational transition state theory (VRC-TST) to calculate the reaction rate constants for the two reactions, R1: (OH)3SiOCH2 + CH3 <-> (OH)3SiOC2H5, and R2: CH2OH + CH3 <-> C2H5OH. The first reaction is an important channel during the thermal decomposition of tetraethoxysilane (TEOS), and its rate coefficient is the main focus of this work. The second reaction is analogous to the first and is used as a basis for comparison. The interaction energies are obtained on-the-fly at the CASPT2(2e,2o)/cc-pVDZ level of theory. A one-dimensional correction to the sampled energies was introduced to account for the energetic effects of geometry relaxation along the reaction path. The computed, high-pressure rate coefficients were calculated to be, R1: k1 = 2.406 * 10 -10 T-0.301 exp(-271.4/T)cm3/molecule/s and R2: k2 = 1.316 * 10^(-10)T^(-0.189)exp(-256.5/T)cm3/molecule/s. These rates differ from each other by only 10% − 30% over the temperature range 300 − 2000K. A comparison of the computed rates with experimental data shows good agreement and an improvement over previous results. The pressure dependency of the reaction R1 is explored by solving a master equation using helium as a bath gas. The results obtained show that the reaction is only weakly pressure dependent over the temperature range 300 − 1700K, with the predicted rate constant being within 50% of its high-pressure limit at atmospheric pressure.

Simulation and life cycle assessment of algae gasification process in dual fluidized bed gasifiers.

Pooya Azadi, George Brownbridge, Sebastian Mosbach, Oliver R. Inderwildi, and Markus Kraft.
Green Chemistry, in press, (2015).



Highlights:

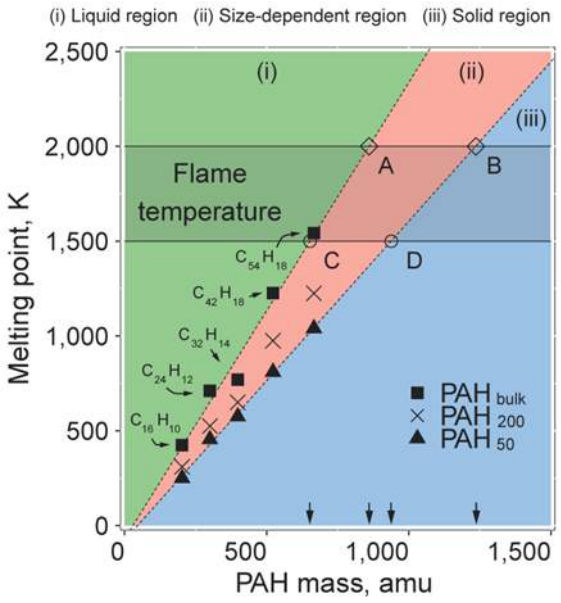
- Algae-derived syngas production using dual fluid-

ised bed gasifiers is simulated.

- A global sensitivity analysis is performed to determine the impact of key input parameters on product yields.
- Decarbonisation via solar energy reduces the carbon footprint to a value competitive with that of steam reforming of natural gas.

Abstract:

We present simulation results for the production of algae-derived syngas using dual fluidized bed (DFB) gasifiers. A global sensitivity analysis was performed to determine the impact of key input parameters (i.e. algae composition, gasification temperature, feed water content, steam-to-biomass ratio, and fuel-air equivalence ratio) on the product yields. The algae oil content was varied from 0 to 40 wt% to account for different algae strains and varying extents of oil extraction prior to the gasification process. It was found that the lower heating value (LHV) of syngas, typically ranging from 15 to 22 MJ/kg algae, is heavily dependent on the algae oil content. The cold gas efficiency (CGE) of the process varies over a range of 75 to 90%, depending primarily on the feedstock water content and steam-to-biomass ratio. A cradle-to-grave life cycle assessment indicated that the carbon footprint of syngas produced from algae feedstocks with 20 to 40 wt% oil fraction that is dried by a gas-fired dryer lies within a range of 70 to 195 g CO2/MJ. However, decarbonization of the drying stage via utilization of solar energy reduce the carbon footprint to values below 40 g CO2/MJ, which would compare favorably with the carbon footprint of syngas produced via steam reforming of natural gas (i.e. ~100 g CO2/MJ).



Solid-liquid transitions in homogenous ovalene, hexabenzocoronene and circumcoronene clusters: A molecular dynamics study.

Dongping Chen, Jethro Akroyd, Sebastian Mosbach, Daniel Opalka, and Markus Kraft.

Combustion and Flame 162, (2), 486-495, (2015).

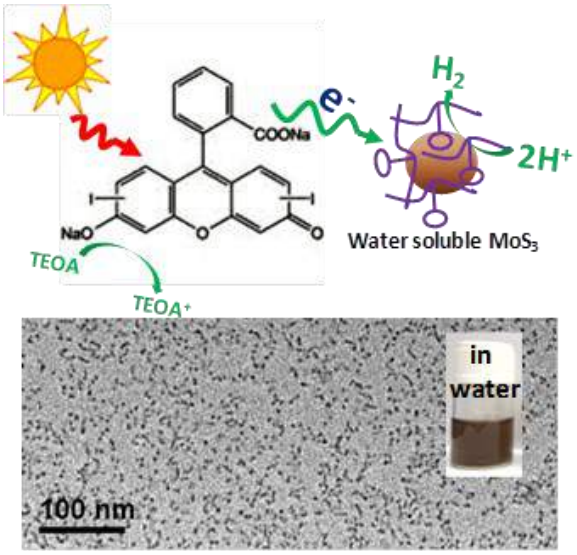
Highlights:

- Molecular Dynamics (MD) simulations of clusters of ovalene, hexabenzocoronene, and circumcoronene molecules are conducted.
- The bulk melting point of peri-condensed Polycyclic Aromatic Hydrocarbons (PAHs) is found to be linearly related to their size.
- A phase diagram is constructed which classifies the phase of a cluster into three regions: liquid, size-dependent, and solid.
- The critical PAH size in nascent and mature soot particles in the solid state is found as C78H22 and C54H18 at 1500 K respectively.

Abstract:

The melting behaviour of ovalene (C32H14), hexabenzocoronene (C42H18) and circumcoronene (C54H18) clusters is analysed using molecular dynamics simulations. The evolution of the intermolecular energy and the Lindemann Index is used to determine the cluster melting points. The bulk

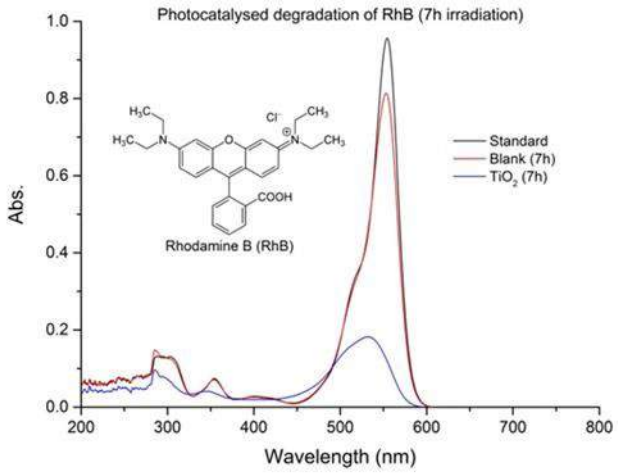
melting point of each material is estimated by linear extrapolation of the cluster simulation data. The value obtained for ovalene is in good agreement with the phase-transition temperature determined by experiment. We find that the bulk melting point of peri-condensed PAHs is linearly related to their size. The extrapolated hexabenzocoronene and circumcoronene bulk melting points agree with this linear relationship very well. A phase diagram is constructed which classifies the phase of a cluster into three regions: a liquid region, a size-dependent region and a solid region according to the size of the PAHs which build up the cluster. The size-dependent region highlights the range where the phase of a cluster also depends on the cluster size. Due to the similar size and density, a cluster with 50 molecules is considered an analogue for nascent soot particles whilst the bulk system of PAH molecules is seen as an approximation to mature soot particles. A detailed investigation of the phase diagram reveals that the critical size for nascent and mature soot particles in the solid state is C78H22 and C54H18 at 1500K respectively.



Water-Soluble PVP-Modified MoS_x Nanoparticles as Highly Efficient Catalyst for Photocatalytic H_2 Evolution from Aqueous Solution

Wei Zhang, Tianhua Zhou, Jindui Hong, Yunxiang Pan, Rong Xu

ChemSusChem (in revision)



Preliminary result of photocatalysed dye degradation reaction (UV/Vis spectrometry) using combustion-assisted coating of TiO_2

Highlights:

- Green light H_2 evolution MoS_x nanoparticles with unusual water solubility up to 1.0 mg/mL were synthesized.
- Its quantum efficiency for H_2 evolution under green light irradiation is up to 36.2%.

Abstract:

PVP-modified MoS_3 nanoparticles with unusual water solubility up to 1.0 mg/mL were synthesized through a facile hydrothermal method in the presence of thioacetic acid. The as-synthesized amorphous nanoparticles wrapped by PVP have sizes of around 2-5 nm, which represent the smallest MoS_3 or MoS_x clusters reported. The photocatalytic performance of the MoS_3 nanoparticles was evaluated under visible light for H_2 evolution using xanthene dyes as photosensitizers. The quantum efficien-

cy of the optimized system for H_2 evolution under green light irradiation (520 nm) is up to 36.2%, which is comparable with those of other excellent photocatalytic systems involving earth-abundant catalysts. The excellent photocatalytic activity can be attributed to its good dispersion in water, amorphous nature and limited layers with abundant surface active sites, and possibly higher CBM potential for proton reduction and larger indirect band gap for a longer lifetime of the excited electrons.

3.3.4 Other achievements and news

Technology disclosure

An invention disclosure titled *Combustion-assisted coating of TiO_2 and other metal oxides on water container surface for water treatment application* was filed in January 2015. An associated patent application was made by NTUitive in March 2015. Albeit in a very early stage of development, the technology has the potential to have great environmental impact. The invention will comprise device design that is able to deposit nanoparticles for various applications, for example water treatment, through a combustion process. The key aspect of the technology is the simple design that allows transfer of nanotechnology from a laboratory facility to everyday use for household water treatment.

IRP3 to host Global Engineering Programme (GEP) intern

In May—July 2015 IRP3 will host an intern from the NUS Global Engineering Programme. Daryl YONG will work with the IRP3 research team on Work Package 1 (the development of the industrial network model of Jurong Island). CARES is looking forward to welcoming Daryl to the team.

7th Summit on the Global Agenda by the World Economic Forum

Professor Markus KRAFT has been invited to participate in the 7th Summit on the Global Agenda by the World Economic Forum in collaboration with the Government of the United Arab Emirates and Government of Dubai. This meeting brought together more than 1,000 experts from 80 countries, all members of the Forum's Network of Global Agenda Councils, the 86 panels of experts and thought leaders working on the most pressing global challenges.

The Global Agenda Councils are a network of invitation-only groups that study the most pressing issues facing the world. Each council is made up of 15-20 experts, who come together to provide interdisciplinary thinking, stimulate dialogue, shape agendas and drive initiatives. Council Members meet annually at the Summit on the Global Agenda, the world's largest brainstorming event, which is hosted in partnership with the government of the United Arab Emirates

Professor Kraft is a member of the Global Agenda Council on Nanotechnology (GACoN). Other members include Chun Ai Lin (Senior Editor of Nature Nanotechnology), Professor Peter P. Edwards (University of Oxford), Professor Robert Langer (MIT) and Professor Markus Antonietti (Max Planck

Institute of Colloids and Interfaces), who is coordinating the activities of the council.

Client Innovation Forum Singapore 2014

***Full report**: http://www.cares.cam.ac.uk/news/cares-siemens-and-atos-co-host-client-innovation-forum*

The Client Innovation Forum Singapore 2014 took place on 4th November in the CREATE Tower and was co-hosted by CARES, Atos and Siemens. The half-day seminar was directed at industry and was focussed on ways in which automation systems and IT could support companies in driving innovation. The meeting looked at using cloud technologies and advanced analytics to transform businesses and organisations into next generation manufacturing companies. Representatives from a number of chemical industry companies attended the seminar, alongside delegates from the National University of Singapore and Nanyang Technological University.

2nd prize at the 12th UK Particle Technology Forum

Kok Foong Lee, supervised by Prof Markus KRAFT, won the second prize of the Young Researcher Award for his presentation 'A multi-compartment population balance model for wet granulation' on 17 September 2014. A total of 40 abstracts were submitted and 6 of them were selected for the Young Researcher Award. Contestants for the Young Researcher Award were required to give a 20-minute oral presentation and the prize winners were judged based on the presentations. This research is directly relevant for work in WP3.3 and WP3.4

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. 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

April 2015

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 are in the process of acquiring a powerful real-time power system simulator.

Research in IRP4 encompasses control methodologies and electrical power systems design based on smart grid technologies to minimize holistically the total energy demand of a network of chemical industry loads such as found on Jurong Island. Optimised and predictive control of two way electrical power flow, to and from the chemical industry loads to stabilise a capacity distribution in the local electrical network is a particular focus. The control aspect being explored include methods of model predictive control suitable for application to power distribution systems, taking account of features such as multiple areas, nonlinear couplings between areas, and distributed control algorithms. Both theoretical and experimental research are being pursued. The key advantage of model predictive control is that operation close to limits can be supported, because operating and safety constraints can be taken account of explicitly by the optimization algorithm. This algorithm needs to solve quite large optimization problems online, which leads to much emphasis on solution speed. Hence some of the IRP4 effort is devoted to speeding up relevant optimization algorithms. Dual to model predictive control is the notion of 'moving horizon estimation'. Research in IRP4 indicates that this can be more effective, when estimating the state of an electrical distribution network, than the standard 'weighted least squares' method. In the area of smart grid management the application of artificial intelligence to predict power system failures and capacity limitations through real time fine grain, 0.1 -0.01 cycle time intervals, data acquisition to enable real time power flow management is a focus area. The data communications and management required to implement such smart grid supervisory agents is also an area of research Experimental validation and verification of the methodologies is being explored is a key feature of ICESO. To enable this a 'hardware in the loop' real time simulation environment which connects physically to a dedicated experimental smart grid, which includes load analogues of chemical plants, is being implemented.

3.4.2 Update on work packages

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

MPC uses numerical optimisation and repeatedly solves a finite-horizon optimisation problem. One obstacle to applying this technology is the time required to solve the onlone optimisation problem. A version of the 'Alternating Directions Method of Multipliers' (ADMM) algorithm for solving quadratic programs has been developed, which allows polytopic constraints without incurring the computational complexity of polytope projection. The main contribution has been a method for choosing the value of a coefficient in the algorithm which has a very big effect on the convergence speed. The algorithm has been implemented on a Field-Programmable Gate Array (FPGA) to allow application at very high sampling and update rates.

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

A post doctoral research fellow has been appointed and is due to start working on this WP from mid April 15.

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

The thrust of the research has been on advancing the concepts of modelling, and through that control and management of electrical power networks with some special features which come into play when they are supplying chemical process plants loads. These are: 1) The possibility of a chemical plant load 'riding through' a fault on the electrical power system which leads to a transient shut down of the electrical power supply and 2) if it were possible to identify the conditions which could lead to 1) above in a segment of the electrical power system, could the co-generation capacity of chemical power plant in that segment be used as a transient generation source to 'stiffen' the grid and avoid the fault. The related question to 2) is whether the chemical process plant could 'ride through' the unavailability of the co-generation supply as in 1). From a modelling perspective a suitable model for a chemical process plant which captures its dynamic behaviour is required. This will be input from research in IRP3. It is therefore around 2) above which most research has been focussed. This in the general context of predicting fault behaviour and managing power flows to avoid faults and recover rapidly if one occurs.

In the context of fault prediction, which is still a very new area in the subject, the approach taken has been based on designing machine learning algorithms based on Support Vector Machines (SVM) for classification and regression and Deep Belief Network (DBN) type of deep neural networks to extract discriminant features in an unsupervised manner. Currently an ensemble deep learning method has been implemented by combining DBN and SVM for both of regression and time series forecasting. The method has been optimized by introducing statistical tests and comparing with other learning algorithms. In the contexts of both power flow management and fault prevention model predictive controllers based on the concept of 'quadratic dissipativity' and Distribution System State Estimation based on inputs from physical small Phasor Measurement Units (PMUs) placed

in the distribution system have been investigated. For the latter case the IEEE 14 bus transmission and IEEE 13 bus distribution systems have been evaluated for PMU placement. As control signals in the system are broadly classified as primary control (fast) and secondary control (relatively slow) based on the time-scale for which control variables are updated. Stochastic optimizations, convex techniques and their hybrid combinations for optimal generation of secondary control decisions are also being investigated

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

The general model based approaches explored in WP4.1 – WP4.3 are to be specifically evaluated within the integrated chemical plant and electrical power system environment of Jurong Island. To achieve this, as a first step, publicly available information has been used to construct a model system of the Jurong Island power network and its connectivity to chemical process plants. Initial evaluation of fault induced behaviour of the electrical network on the exemplar Jurong Island system has been carried out using a commercial software package. An Intelligent network-design & analysis toolbox software is also being developed, which enables automated testing and easy change of different network topologies. The design would use information available regarding Jurong Island network as default configuration.

WP4.4 also encompasses the experimental test bed development for IRP4 as a whole. This is being done primarily by using the existing microgrid facility at NTU. There will also be capability for auxiliary experimentation on the microgrid facility under development at NUS. Development of the C4T-NTU microgrid to enable laboratory replication of critical paths on the Jurong Island network has commenced. The existing system has been upgraded with 13.5kVA synchronous generator and load frequency control implemented on the motor-generator set. Initial evaluation of the WP4.3 paradigm of bi-directional power flow using chemical plant loads are to be mimicked using a synchronous machine which is switched from motor to generator mode operation under specified dynamic conditions. The requirements of instrumenting the microgrid to enable fast (sub millisecond) data acquisition and implementing control strategies based on real time digital simulation have also been studied and assessed in detail. In particular including data from microgrid operation in a 'hardware in the loop' (HIL) real time digital power system simulator and controller has been decided upon as being a core feature of the IRP4 test bed.

WP6: Demonstration of proposed algorithms on pilot scale

To be completed later in the programme using results of other work packages.

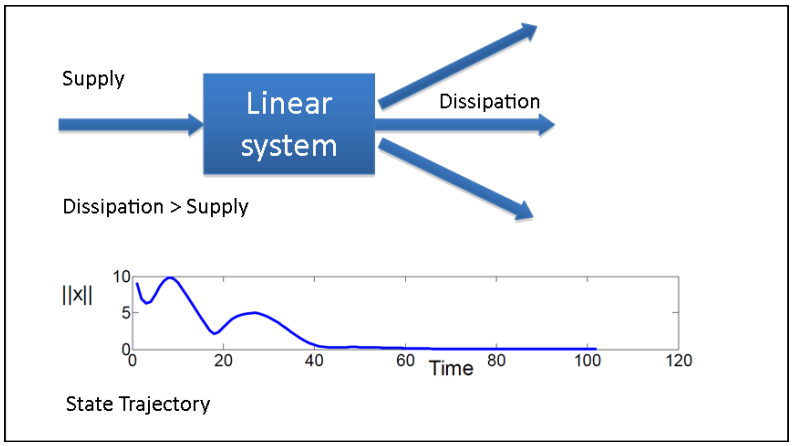
3.4.3 Scientific output of IRP4

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.

Model Predictive Control via Quadratic Dissipativity Constraint

Proceedings of IEEE Conference on Decision and Control (CDC'14) – LA, USA, 15-17 December 2014, pp. 6689-6694. http://control.disp.uniroma2.it/CDC2014/

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



Highlights:

- Quadratic dissipativity constraint (QDC) is used to ensure closed-loop stability.
- Further conditions are enforced to reduce chances of losing feasibility of MPC problem. Iterative feasibility is simultaneously achieved.
- Terminal constraints (ie constraints at the end of the planning horizon) are avoided, thus (i) reducing computational complexity, (ii) increasing the set of feasible initial conditions, (iii) making easier future extensions to decentralised control etc.

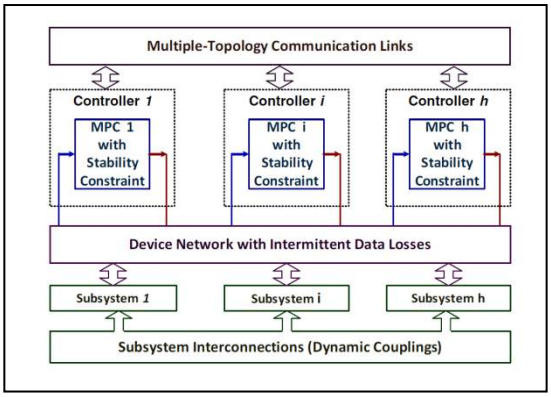
Abstract:

A model predictive control (MPC) scheme is deployed via the quadratic dissipativity constraint (QDC) in this paper. Within the development, two new constraints, one a QDC-based stability constraint, the other an iterative-feasibility constraint, are derived for the model predictive control of linear systems. These two constraints are imposed on the first control vector of the MPC control sequence. The input-and-power-to-state stabilizability (IpSS) – an extension of ISS, and the iterative feasibility are simultaneously achieved as a result of the two mentioned constraints. Previous results on the quadratic dissipativity constraint for unconstrained systems are consolidated in this work, and extended to include the iterative feasibility condition. Since terminal constraints are not employed in this strategy, it has the potential for further extension to distributed or decentralized control of interconnected systems, as well as for other types of MPC such as economic MPC. Numerical simulations with an open-loop unstable interconnected system are provided to demonstrate the effectiveness of the quadratic dissipativity constraint for model predictive control.

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, pp-193-198.http://www.icarcv.org/2014/

Tri Tran, Y. S. Foo Eddy, K-V. Ling, and J. Maciejowski



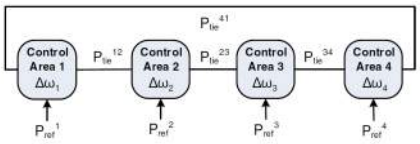


Fig. 2. A four-area power system with tie-lines for power flow control.

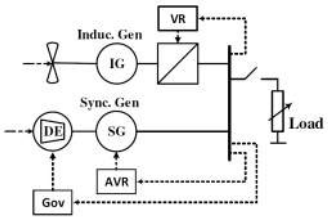


Fig. 6. Isolated wind-diesel power system.

Highlights:

- Simulation studies for MPC via QDC with typical small-signal linear models of power systems are presented.
- A comparison is then provided in the simulation study for the online optimization of MPC via QDC relative to the constrained-state feedback control.

Abstract:

Simulations for model predictive control (MPC) via quadratic dissipativity constraint (QDC) with power system linear models are studied in this work. In MPC via QDC, the optimization is imposed with two additional constraints to achieve closed-loop stability and iterative feasibility simultaneously. Instead of engaging the traditional terminal constraint for MPC, both constraints in MPC via QDC are imposed on the first control vector of the MPC control sequence. As a result, MPC via QDC has the potential for further extension to the network-centric control of power systems. Simulation studies for MPC via QDC with typical small-signal linear models of power systems are presented to demonstrate its efficacy. We also develop a computational strategy for the decentralized static state -feedback control using the same quadratic dissipativity constraint as of the MPC via QDC for linear interconnected systems. A comparison is then provided in the simulation study for the online optimization of qc-MPC relativeto the constrained-state feedback control.

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, pp. 992-997. http://www.icarcv.org/2014/

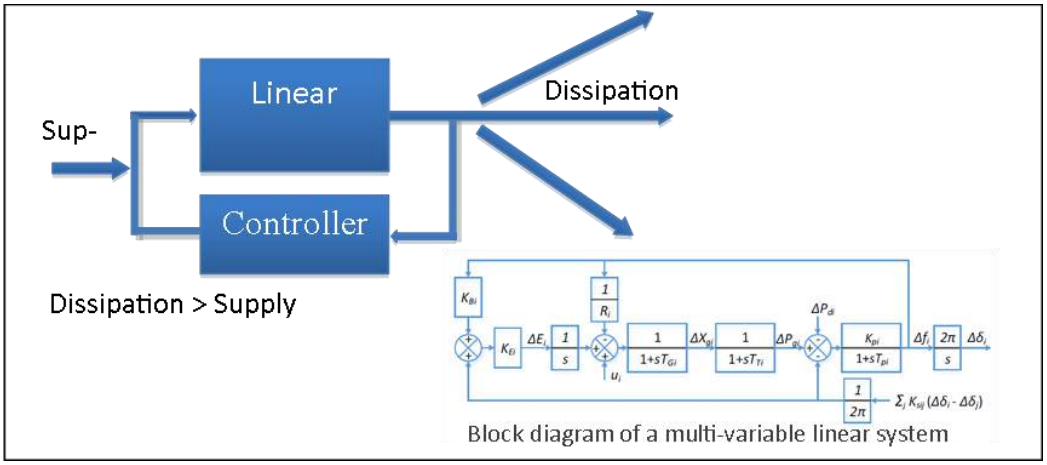
Tri Tran, K-V. Ling, and J. Maciejowski

Highlights:

- The model predictive control of nonlinear systems employing the quadratic dissipativity constraint is developed.
- A compound output vector is engaged to the supply rate. The compound vector shares similar properties of the so-called manifest variable defined in the behaviourial framework for dynamical systems.
- Both the storage function and supply rate of the dissipation inequality are parameterized in this development. The multiplier matrices need to be re-computed at every time step in this approach.

Abstract:

This paper presents a development for the model predictive control (MPC) of nonlinear systems employing the quadratic dissipativity constraint (QDC). In this QDC strategy for nonlinear input-affine systems, a compound output vector is engaged to the supply rate such that the stability condition based on linear matrix inequality (LMI) can be rendered for nonlinear systems. The compound vector shares similar properties of the so-called manifest variable defined in the behaviourial framework for dynamical systems. Unlike linear systems, the LMI-based condition for nonlinear systems has not been much used in the control literature. The present method introduces an application of such a condition to nonlinear systems in this paper. In conjunction with QDC, the MPC recursive feasibility is achieved by having a bounded condition on the local divergence of the Lyapunov function. Both the storage function and supply rate of the dissipation inequality are parameterized in this development. The multiplier matrices need to be re-computed at every time step in this approach. Numerical simulation with a network of two chemical reactors has demonstrated the success of QDC approach in MPC, employing the compound output vector.



Block diagram of a multi-variable linear system

Closed-loop Development for Quadratic Dissipativity Constraint

In Proceedings of IEEE International Conference on Control, Automation, and Information Science (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014, pp. 356-361.

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

Highlights:

- A novel development for a static constrained-state feedback control of interconnected systems, in which the decentralized QDC is employed for assuring the closed-loop stability of the global large-scale system, is presented.
- The input-and-power-to-state stability (IpSS), an extension of the input-to-state stability (ISS), is achieved. Under the realm of IpSS, the system stability does not rely on a monotonically reducing Lyapunov function.

Abstract:

The quadratic dissipativity constraint (QDC), a generalization of the asymptotically positive realness constraint (APRC), has previously been introduced and developed into an enforced stability constraint for the model predictive control schemes. This paper presents the novel development for a static constrained-state feedback control of interconnected systems, in which the decentralized QDC is employed for assuring the closed-loop stability of the global large-scale system. In this work, the input-and-power-to-state stability (IpSS), an extension of the input-to-state stability (ISS), is achieved. Under the realm of IpSS, the system stability does not rely on a monotonically reducing

Lyapunov function. As a result, the proposed method provides a less conservative decentralized control law compared to those synthesized with the traditional Lyapunov stability condition. Simulation studies with small-signal linear models of three typical power systems are presented to demonstrate the effectiveness of the QDC, especially for systems having state constraints.

Dependable Control Systems with Self-Recovery Constraint

In Proceedings of IEEE International Conference on Control, Automation, and Information Science (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014, pp. 153-158. http://iccais2014.gist.ac.kr/

Tri Tran and Q. P. Ha

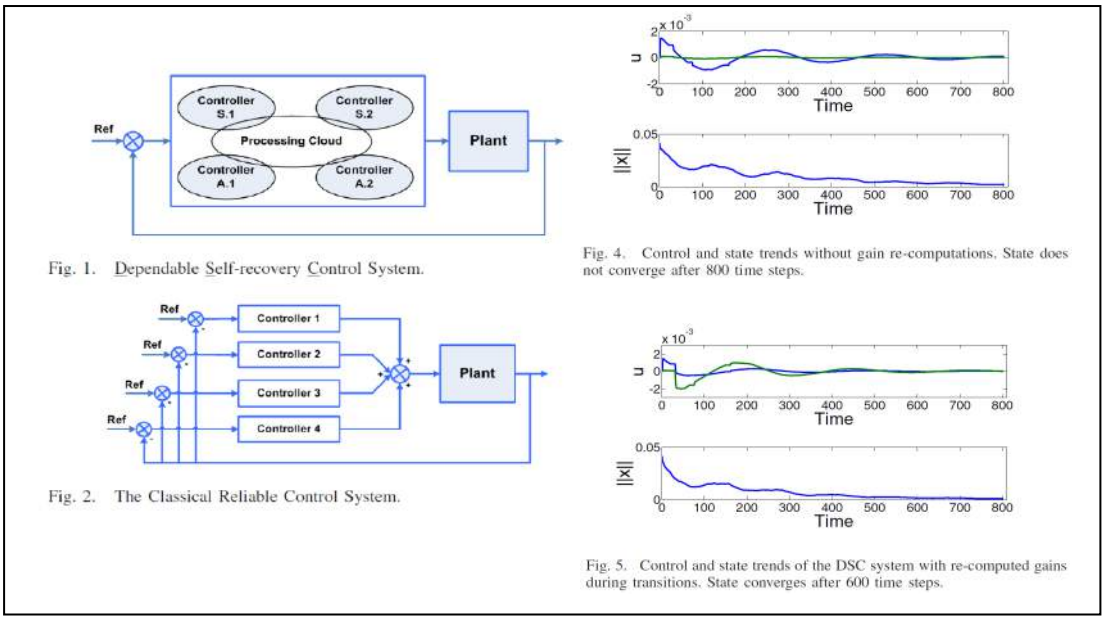


Fig. 1. Dependable Self-recovery Control System.

Fig. 2. The Classical Reliable Control System.

Fig. 4. Control and state trends without gain re-computations. State does not converge after 800 time steps.

Fig. 5. Control and state trends of the DSC system with re-computed gains during transitions. State converges after 600 time steps.

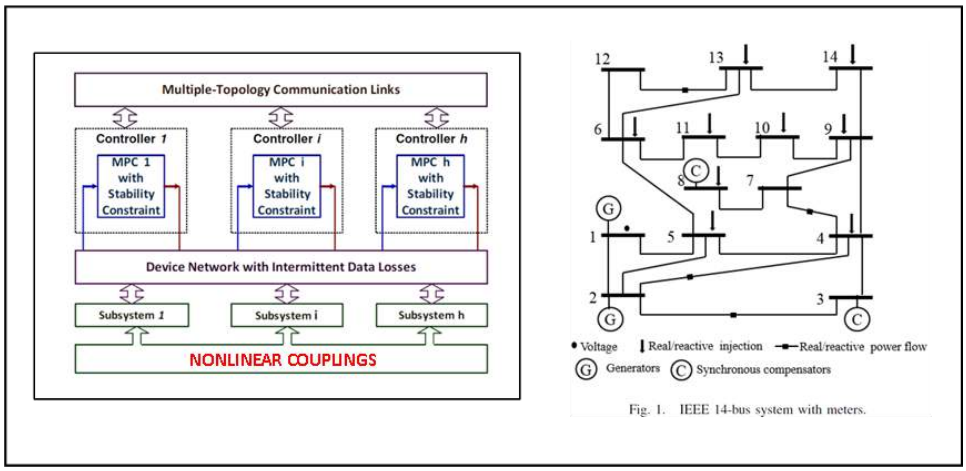
Highlights:

- A novel constrained-state feedback control design method for duty-standby controllers of a dependable control system is presented.
- Dependable control system is a replacement for the classical reliable control system which has been developed for wired and analogue systems.
- As an alternative to the control summation in reliable control systems, only one controller is active at any one time in a dependable control system.
- The proposed solution takes into account both state- and control-incremental constraints.

Abstract:

A novel constrained-state feedback control design method for duty-standby controllers of a dependable control system is presented in this paper. The dependable control system is a replacement for the classical reliable control system which has been developed for wired and analogue systems. As an alternative to the control summation in reliable control systems, only one controller is active at any one time in a dependable control system. This will make it compatible with the duty-standby architecture of dependable computer systems that run the control algorithm. The automated managing of duty-standby controllers is challenging, especially in wireless sensor and actuator networks,

owing to the scarcity of both information and processing resources. The solutions proposed in this paper are effective and feasible, taking into account both state- and control-incremental constraints, and simply involving a static state-feedback strategy to minimize the computational demand in implementations. The state feedback gains are synthesized to fulfil the strict requirement on the two incremental constraints. As a result of that, the duty-standby controllers will be able to operate independently, while assuring the closed-loop system stability with a newly introduced self-recovery constraint.



State Feedback Control of Explicitly-Bounded Nonlinearly-Coupled Interconnected Systems

Proceedings of IEEE International Conference on Control, Automation, and Information Science (ICCAIS'14) – Gwangju, South Korea, 2-5 December 2014, pp. 247-252.
Tri Tran

Highlights:

- The partial strategy here is different and only employs local and coupling feedbacks. The state feedback gains are pre-computed from the LMI optimization problems formulated from the quadratic bound presented by Siljak et al. together with the closed-loop and open-loop dissipative conditions for every subsystem and for the global system..
- The Lyapunov function is allowed to increase locally and intermittently. It is is thus promisingly non-conservative for a decentralized control strategy.

Abstract:

The nominal linear subsystem state-space model having nonlinear couplings is used in this work. The quadratic dissipativity constraint approach, previously introduced and developed for the model predictive control of interconnected systems, is deployed here with a static state-feedback strategy. We re-use the derivation for a quadratic bound on the nonlinear coupling in a newly derived stability condition for the decentralized excitation control of multiple-machine power systems. The state feedback gains are pre-computed from the LMI optimization problems formulated from this stability condition in combination with the open-loop dissipative condition for the global system and the closed-loop dissipative condition for subsystems. The resulting static state-feedback gain can be used in the feedback policy for a distributed model predictive control scheme, when it is required to push the system towards tighter constraints for various economic objectives.

Moving Horizon Estimation on a Chip

Proceedings of IEEE International Conference on Automation, Robotics, Control and Vision (ICARCV'14) – Singapore, 9-11 December 2014, pp. 431-437. http://www.icarcv.org/2014/

Thuy V. Dang and K-V. Ling

Highlights:

- An FPGA implementation of ADMM (Alternating Direction Method of Multipliers) which solves the QP (Quadratic Programming) problem arising from Moving Horizon Estimation is reported.
- The first order QP solver is cheaper and easier to implement in embedded systems such as FPGA which has limited hardware resources.
- Both fixed point and floating point arithmetic on the Xilinx Zynq-7000 XC7Z020-1CLG484C AP SoC and clocks at 50 MHz have been successfully implemented.

Abstract:

Second order Quadratic Programming (QP) solvers such as interior-point method (IPM) require the solution of a system of linear equations at every iteration and could be a factor limiting the implementation of IPM to miniaturized devices or embedded systems. In contrast, first order QP solvers such as alternating direction method of multipliers (ADMM) does not require the solution of a system of linear equations. Thus first order QP solver is cheaper and easier to implement in embedded systems such as FPGA which has limited hardware resources. In this paper an FPGA implementation of ADMM which solves QP problems arising from Moving Horizon Estimation is proposed to demonstrate the "MHE on a Chip" idea. Our design has been implemented in both fixed-point and floating point arithmetic on the Xilinx Zynq-7000 XC7Z020-1CLG484C AP SoC and clocks at 50 MHz.

Distributed Moving Horizon Estimation for Power Systems

Accepted forIEEE Power and Energy Society General Meeting (PES GM' 15) – Denver, Colorado, 26-30 July 2015. http://www.pes-gm.org/2015/

T. Chen, D. Zhou, Tri Tran, K-V. Ling, and J. Maciejowski.

Highlights:

- A Distributed Moving Horizon Estimation (DMHE) algorithm, previously developed in the control literature, is applied to the power system state estimation (PSSE) problem.
- At each time step the state of the whole system is estimated locally by exchanging measurements with neighbours and updating consensus weights.
- DMHE converges to the centralized solution of moving horizon estimation (MHE) within a certain number of time steps.
- Constraints on states and noise are explicitly employed in DMHE.
- Numerical simulations in Matlab and experiments on CERL microgrid both show better results than those from Weighted Least Squares (WLS).

Abstract:

We adapt and apply a known algorithm for Distributed Moving Horizon Estimation (DMHE) to power systems. In this distributed approach, the power system is partitioned into several control areas. At each time step the state of the whole system is estimated locally in each area, by solving a local optimization problem. A consensus weights update step is performed in which the covariance matrix

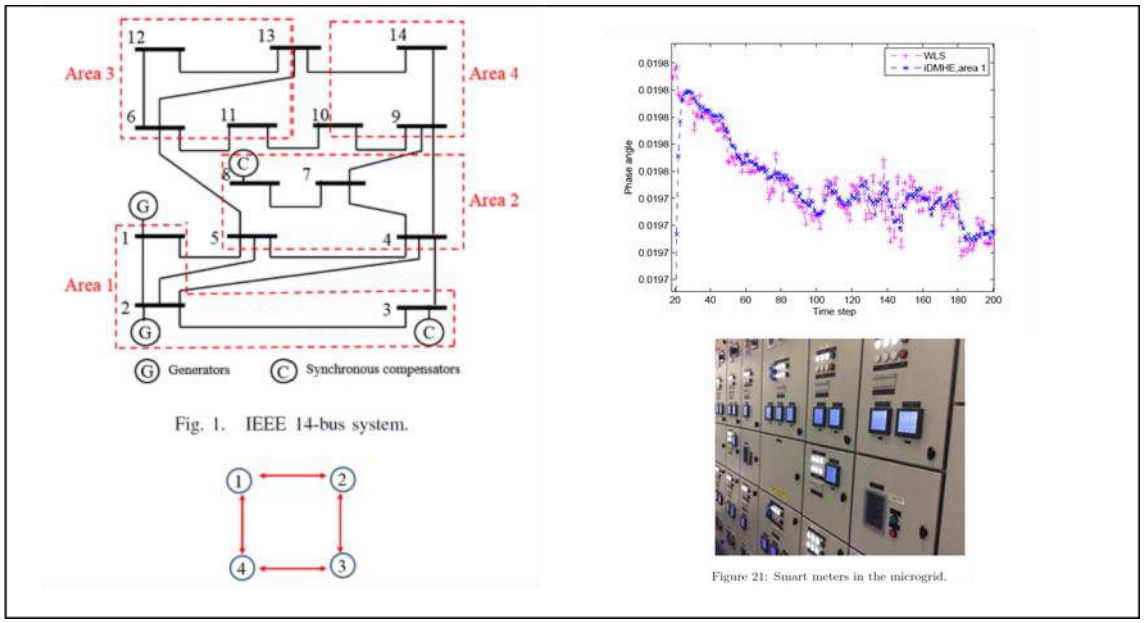


Fig. 1. IEEE 14-bus system.

of the initial penalty is dynamically computed to ensure convergence of DMHE algorithm. DMHE converges to the centralized solution of moving horizon estimation (MHE) within a reasonable number of time steps. Numerical simulations with the IEEE 14-bus system and experiments on a lab microgrid show better results than those obtained from the standard approach using weighted least squares (WLS), if known constraints on states and noise are exploited.

Embedded ADMM-based QP Solver for MPC with Polytopic Constraints

Submitted to European Control Conference (ECC' 15) – Linz, Austria, 15-17 July 2015. http://www.ecc15.at/

Thuy V. Dang, K-V. Ling,, and J. Maciejowski

Highlights:

- An ADMM-based algorithm for QP with inequality and equality constraints arising from MPC problems was proposed.
- By introducing slack variables, the algorithm is greatly simplified because the projection is onto a positive orthant rather than a general polytopic set. The algorithm can handle general inequality constraints without the complexity of polytope projection.
- Heuristic methods based on 2-norm and max-norm criteria to select the step-size of the ADMM iteration for optimal good convergence rates.
- The algorithm has simple computational structure, as well as being division-free
- if some offline computations are performed, it allows an efficient implementation, with fixed-point arithmetic, on embedded platforms such as an FPGA.

Abstract:

We propose an algorithm for solving quadratic programming (QP) problems with inequality and equality constraints arising from linear MPC. The proposed algorithm is based on the 'alternating direction method of multipliers' (ADMM), with the introduction of slack variables. In comparison with algorithms available in the literature, our proposed algorithm can handle the so-called sparse MPC formulation with general inequality constraints. Moreover, our proposed algorithm is suitable for implementation on embedded platforms where computational resources are limited. In some

cases, our algorithm is division-free when certain fixed matrices are computed offline. This enables our algorithm to be implemented in fixed-point arithmetic on a FPGA. In this paper, we also propose heuristic rules to select the step size of ADMM for a good convergence rate

Symmetry Between A Trajectory Advisor in Model Predictive Control and Admissible Measurement Checker in Moving Horizon Estimation

Submitted to Chinese Control Conference (CCC' 15) – Hangzhou, China, 28-30 July 2015. http://www.sice.jp/ccc-sice2015/

D. Zhou and K-V Ling

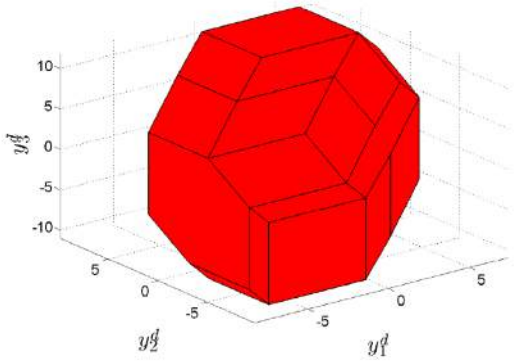


Figure 4: The set of admissible measurement.

Highlights:

- The trajectory advisor was obtained from computing the initial feasible set of an equivalent Model Predictive Control (MPC) regulatory problem. By invoking the symmetry between MPC and Moving Horizon Estimation (MHE), the initial feasible set in the MPC tracking problem is re-interpreted to obtain the admissible measurement checker.
- The admissible measurement checker can be used to determine the feasibility of the MHE before the actual constrained optimization is carried out.
- The requirement for online computation of both the trajectory advisor and admissible measurement checker is high, nonetheless. The admissible measurement checker is potentially able to identify a fault or to detect an outlier for measurement or sensor errors.
- Some subtle differences between MPC and MHE are highlighted in this paper. Examples which illustrate the trajectory advisor in MPC and the admissible measurement checker in MHE are also given.

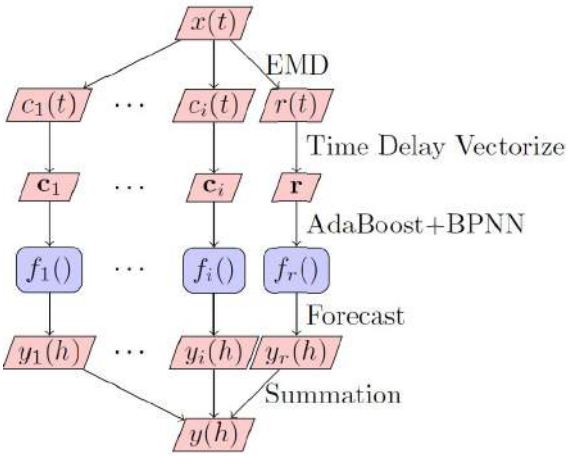
Abstract:

Both Model Predictive Control (MPC) and Moving Horizon Estimation (MHE) are optimization-based methods where a constrained optimization problem is solved at each time instant. The recursive feasibility of MPC is key to prevent the state from being driven into a "blind valley" where the constrained optimization problem could become infeasible. One strategy to guarantee the recursive feasibility of MPC is to compute an initial feasible set from which the controller is always feasible. In this paper we propose a trajectory advisor, which is obtained from the initial feasible set, for the MPC tracking problem. By symmetry, the MHE problem can be reformulated as an equivalent MPC tracking problem and the trajectory advisor can be re-interpreted and used as an admissible measurement checker. The trajectory advisor can be used to provide MPC feasible trajectory online. The admissible measurement checker can be used to determine the feasibility of the MHE before the actual constrained optimization is carried out. The online computation needed for both the trajectory advisor and admissible measurement checker is moderate.

Empirical Mode Decomposition based AdaBoost-Backpropagation Neural Network Method for Wind Speed Forecasting

in Proc. IEEE Symposium on Computational Intelligence and Ensemble Learning (CIEL'14), 2014.

Ye Ren, XuehengQiu& P. N. Suganthan



Highlights

- As small errors in wind speed forecasting will be amplified to a large error in wind power by wind turbine, higher accuracy can reduce the power system instability, and improve the efficiency of wind energy.

- This paper has proposed an Empirical Mode Decomposition based Adaptive Boosting-Backpropagation Neural Network (EMD-AdaBoost-BPNN) model for wind speed time series forecasting.

- The performance of the algorithm is evaluated using twelve wind speed time series datasets, and has been compared with six benchmark models. The comparisons based on Wilcoxon signed rank test and Diebold-Mariano test have shown the advantages of the proposed method.

Abstract:

Wind speed forecasting is a popular research direction in renewable energy and computational intelligence. Ensemble forecasting and hybrid forecasting models are widely used in wind speed forecasting. This paper proposes a novel ensemble forecasting model by combining Empirical mode decomposition (EMD), Adaptive boosting (AdaBoost) and Backpropagation Neural Network (BPNN) together. The proposed model is compared with six benchmark models: persistent, AdaBoost with regression tree, BPNN, AdaBoost-BPNN, EMD-BPNN and EMD-AdaBoost with regression tree. The comparisons undergoing several statistical tests and the tests show that the proposed EMD-AdaBoost-BPNN model outperformed the other models significantly. The forecasting error of the proposed model also shows significant randomness.

Ensemble Deep Learning for Regression and Time Series Forecasting

Xueheng Qiu, Le Zhang, Ye Ren, P. N. Suganthan & Gehan Amaratunga

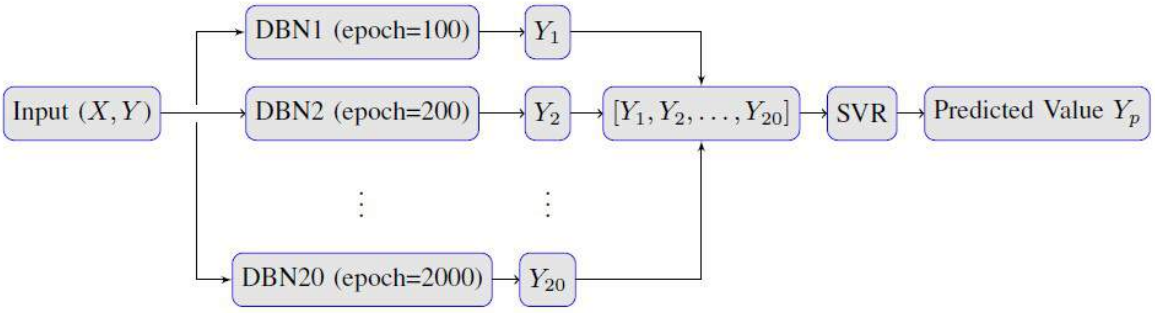
in Proc. IEEE Symposium on Computational Intelligence and Ensemble Learning (CIEL'14), 2014.

Highlights:

- Electricity load demand forecasting is important but challenging as the data is highly nonlinear.
- The paper has proposed an ensemble deep learning method by combining Deep Belief Network and Support Vector Regression for both of regression and time series forecasting.
- The performance of the algorithm is evaluated using three electricity load demand datasets, one artificial time series dataset and three regression datasets. The proposed method has shown its advantages by outperforming four benchmark methods.

Abstract:

An ensemble of deep learning belief networks (DBN) is proposed for regression and time series forecasting. Another novel contribution is to aggregate the outputs from various DBNs by a support vector regression (SVR) model. We show the advantage of the proposed method on three electricity load demand datasets, one artificial time series dataset and three regression datasets over other benchmark methods.



Differential Evolution with Two Subpopulations

Nandar Lynn, R. Mallipeddi & P. N. Suganthan

in Proc. SEMCCO (Swarm, Evolutionary and Memetic Computing) 2014.

Highlights

- A differential evolution with two subpopulations is proposed in the paper.
- The proposed DE algorithm is applied to solve the unit commitment problem.

Abstract:

Differential evolution with two subpopulations is proposed for balancing exploration and exploitation capabilities. The first population is responsible for exploring over the search space to find good regions using only its own subpopulation. The second sub-population is responsible for exploiting good regions. The exploitation-oriented sub-population is permitted to make use of the whole population to select best solution candidates to generate offspring. Hence, this heterogeneous one-way information transfer allows the exploration sub-population to maintain diversity even when exploitation group converges. This is an efficient realization of population based algorithm enabling simultaneous use of highly exploitative and explorative characteristics simultaneously. Hence, this approach can be an effective substitute for memetic algorithms in the real-parameter optimization domain. The performance of the algorithm is evaluated using the shifted and rotated benchmark problems. To verify the performance of the proposed algorithm, it is also applied to solve the unit commitment problem by considering 10 and 20 unit power systems over 24 hour scheduling period.

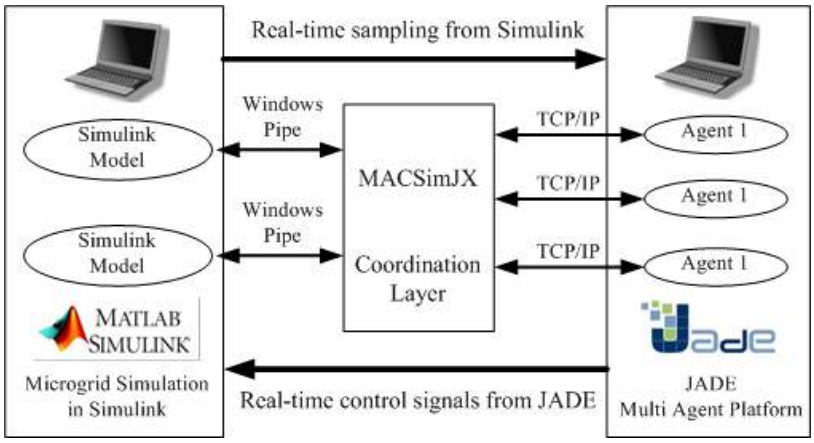
Multi-Agent System for Distributed Management of Microgrids

Foo Eddy, Y.S.; Gooi, H.B.; Chen, S.X.

Power Systems, IEEE Transactions on, vol.30, no.1, pp.24-34, Jan. 2015.doi: 10.1109/TPWRS.2014.2322622.

Highlights

- Using agents to represent both distributed generations (DGs) and loads to participate in a local microgrid electricity market.



- Agents are assigned tasks/objectives to perform various functions e.g. scheduling, coordination and market clearing
- The agent objectives can be either biased towards one side i.e. DGs or loads, or unbiased which will affect the outcome of the market clearing.
- Simulated response of the DGs and loads were done to verify the stable operation of the microgrid after market clearing.
- Proposed distributed agent control can be implemented on the petrochemical plants in Jurong Island to reduce carbon emissions as part of the IRP4 requirements.

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.

3.4.4 Other achievements and news

Technology disclosures

IRP4 has made three technology disclosures during this reporting period. All are currently being assessed by NTUitive for patent suitability.

Visiting Scholar

Dr Anthony TRAN was awarded the Honorary Visiting Scholar position to the University of Technology, Sydney (UTS), Australia in October 2014, hosted by the Faculty of Engineering and IT.

A.1 Publications

An * indicates publications that were included in the May—Oct 2014 Biannual Research Report as 'in press', which have since been published.

A.1.1 IRP1— MUSCAT

- *Azadi, P., Brownbridge, G., Kemp, A.I., Mosbach, S., Dennis, J.S., Kraft, M. 2015. Microkinetic modelling of Fischer-Tropsh synthesis over cobalt catalysts. *ChemCatChem* 7(1), 137-143. doi: 10.1002/cctc.201402662
- Dai, Y., Wang, Y., Liu, B., Yang, Y. 2015. Metallic Nanocatalysis: An Accelerating Seamless Integration with Nanotechnology. *Small*, 11(3), 268-289. doi: 10.1002/smll.201400847
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- Pore, G.H. Ong, C.M. Boyce, M. Materazzi, J. Gargiuli, T. Leadbeater, A. J. Sedermana, J. S. Dennis, D. J. Holland, A. Ingram, P. Lettieri, D. J. Parker. 2015. A Comparison of Magnetic Resonance, X-ray and Positron Emission Particle Tracking Measurements of a Single Jet of Gas Entering a Bed of Particles. *Chemical Engineering Science*, 122, 210-218. doi:10.1016/j.ces.2014.09.029
- Yuan Sheng and Hua Chun Zeng. 2015. Single-Walled 3*d* Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts. *Chem. Mater.*, 27, 658−667. *DOI:* 10.1002/chem.201405697
- Guowu Zhan, Christopher C. Yec, and Hua Chun Zeng*. 2015. Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts. *Chem. Eur. J.* 2015, 21, 1882–1887. *DOI:* 10.1002/chem.201405697

A.1.2 IRP2— EMSET

- Rong Chen, Hsin-Yi Wang, Jianwei Miao, Hongbin Yang and Bin Liu . 2015. A Flexible High-Performance Oxygen Evolution Electrode with Three-Dimensional $NiCo_2O_4$ Core-Shell Nanowires. *Nano Energy*, 2015, 11, 333-340.
- Chencheng Dai, Peng Song, Jay D. Wadhawan, Adrian C. Fisher, Nathan S. Lawrence . 2015. Screen Printed Alizarin-based Carbon Electrodes: Monitoring pH in Unbuffered Media. *Electroanalysis*, 2015, in press .
- Fong-Lee Ng, Muhammad Musoddiq Jaafar, Siew-Moi Phang, Zhijian Chan, Nurul Anati Salleh, Siti Zulfikriyah Azmi, Kamran Yunus, Adrian C. Fisher & Vengadesh Periasamy . 2015. Reduced Graphene Oxide (rGO) Anodes for Potential Application in Algae Biophotovoltaic Platforms. *Nature Scientific Reports, 2015, **4**,* in press .
- Nan Li, Hai-Bo Wang, Larissa Thia, Jing-Yuan Wang and Xin Wang . 2015. Enzymatic-reaction induced production of polydopamine nanoparticles for sensitive and visual sensing of urea .

Analyst, 2015,140, 449-455. DOI: 10.1039/C4AN01900H

- Hanbin Liao, Adrian Fisher, and Zhichuan J. Xu. *2015.* Surface segregation in bimetallic nanoparticles: a critical issue in electrocatalyst engineering . *Small,* in press. DOI: 10.1002/smll.201403380
- Shengnan Sun and Zhichuan J. Xu. 2015. Composition dependence of methanol oxidation activity in nickel–cobalt hydroxides and oxides: an optimization toward highly active electrodes . *Electrochimica Acta,* Volume 165, Pages 56–66
- P. Vengadesh, G. P. M. K. Ciniciato, C. Zhijian, M. Musoddiq, A. C. Fisher and K. Yunus . 2015. Capillary force assisted fabrication of DNA templated silver wires. *RSC Advances,* 2015, **5**, 8163 .
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- Peng Xiao , Xiaoming Ge , Haibo Wang , Zhaolin Liu , Adrian Fisher , and Xin Wang. 2015. Novel Molybdenum Carbide–Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution . *Advanced Functional Materials*, 25:10, 1520-1526. DOI: 10.1002/adfm.201403633
- Bao Yu Xia, Hao Bin Wu, Nan Li, Ya Yan, Xiong Wen (David) Lou, and Xin Wang . 2015. One-Pot Synthesis of Pt–Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties . *Angewandte Chemie International Edition*. 54:12, 3797-3801. DOI: 10.1002/anie.201411544
- Ya Yan, BaoYu Xia, Nan Li, Zhichuan Xu, Adrian Fisher and Xin Wang . 2015. Vertically oriented MoS_2 and WS_2 nanosheets directly grown on carbon cloth as efficient and stable 3-dimensional hydrogen-evolving cathodes . *J. Mater. Chem. A,* 2015,3, 131-135. DOI: 10.1039/c4ta04858j
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- Linghui Yu, Shibo Xi, Chao Wei, Wenyu Zhang, Yonghua Du, Qingyu Yan, and Zhichuan Xu . *2015.* Superior Lithium Storage Properties of β-FeOOH. *Advanced Energy Materials,* Volume 5, Issue 6, March 18, 2015

A.1.3 IRP3 — CAPRICORN

- Ming Pan, Janusz Sikorski, Catharine A Kastner, Jethro Akroyd, Sebastian Mosbach, R. Lau, and Markus Kraft. 2015. Applying Industry 4.0 to the Jurong Island Eco-industrial Park. *Energy Procedia*, (2015).

- Kok Foong Lee, Sebastian Mosbach, Markus Kraft, and Wolfgang Wagner. 2015. A multi-compartment population balance model for high shear granulation. *Computers and Chemical Engineering* 75, 1-13, (2015). http://dx.doi.org/10.1016/j.compchemeng.2015.01.009
- Daniel Nurkowski, Stephen J. Klippenstein, Yuri Georgievskii, Marco Verdicchio, Ahren W. Jasper, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. 2015. Ab initio Variational Transition State Theory and Master Equation Study of the Reaction (OH)3SiOCH2 + CH3 <-> (OH) 3SiOC2H5. *Zeitschrift fuer Physikalische Chemie*, in press, (2015). http://dx.doi.org/10.1515/zpch-2014-0640
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- Wei Zhang, Tianhua Zhou, Jindui Hong, Yunxiang Pan, Rong Xu. 2015. Water-Soluble PVP-Modified MoS_x Nanoparticles as Highly Efficient Catalyst for Photocatalytic H_2 Evolution from Aqueous Solution. *ChemSusChem* (in revision)

A.1.4 IRP4— ICESO

- *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, pp. 6689-6694.
- *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, pp. 193-198.
- *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, pp. 992-997.

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- *Tran, Tri and Ha Q. P. (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, pp. 87-92.
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- *Dang, V Thuy and Ling, K-V (2014) Moving Horizon Estimation on a Chip. *Proceedings of IEEE International Conference on Automation, Robotics, Control and Vision* (ICARCV'14) – Singapore, 9-11 December 2014, pp. 431-437.
- Chen, T., Zhou, D, Tran, Tri, Ling, K-V, and Maciejowski J (2015) Distributed Moving Horizon Estimation for Power Systems. Accepted for*IEEE Power and Energy Society General Meeting* (PES GM' 15) – Denver, Colorado, 26-30 July 2015.
- Dang, V Thuy, Ling, K-V, and Maciejowski, J. (2015) Embedded ADMM-based QP Solver for MPC with polytopic constraints. Submitted to *European Control Conference* (ECC'15) – Linz, Austria, 15-17 July 2015.
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- Zhou, D, Ho, W-K, Ling, K-V, and Maciejowski, J (2015) Moving Horizon Estimation for ARMAX Processes with T-distribution Noise. To be submitted to *IFAC Automatica* Elsevier journal, March 2015.
- Ye Ren, XuehengQiu& P. N. Suganthan, "Empirical Mode Decomposition based AdaBoost-Backpropagation Neural Network Method for Wind Speed Forecasting", *in Proc. IEEE Symposium on Computational Intelligence and Ensemble Learning (CIEL'14)*, 2014.
- XuehengQiu, Le Zhang, Ye Ren, P. N. Suganthan & Gehan Amaratunga, "Ensemble Deep Learning for Regression and Time Series Forecasting", *in Proc. IEEE Symposium on Computational Intelligence and Ensemble Learning (CIEL'14)*, 2014.
- Nandar Lynn, R. Mallipeddi & P. N. Suganthan, "Differential Evolution with Two Subpopulations", in *Proc. SEMCCO (Swarm, Evolutionary and Memetic Computing) 2014*.
- Yu, Qing-Guo Wang, Dan Zhang and Zhongwei Jin, System Identification in Presence of Outliers, submitted to IEEE Transactions on Cybernetics.
- Foo Eddy, Y.S.; Gooi, H.B.; Chen, S.X., "Multi-Agent System for Distributed Management of Microgrids," *Power Systems, IEEE Transactions on*, vol.30, no.1, pp.24-34, Jan. 2015.doi: 10.1109/TPWRS.2014.2322622.

- Foo Eddy, Y.S.; Gooi, H.B.; Chen, S.X., "Multi-Agent System for Distributed Management of Microgrids," *Accepted for future presentation in IEEE Power and Energy Society (PES) General Meeting, Denver,USA, 26-30 July 2015.*

A.2 Invited talks and conference presentations

A.2.1 IRP1— MUSCAT

- **Conference presentation by Prof. Y. YANG**.

"Au-Pd bimetallic nanoparticle catalysts and their application in selective oxidation", Invited talk: 1st International Symposium on Catalytic Science and Technology in Sustainable Energy and Environment, Oct. 2014, Tianjin, PRC

- **Conference presentation by Prof J. CHEW**

A. Cahyadi, J.W. Chew, R. Cocco, R. Karri and C.M. Hrenya, "Review of Cluster Characteristics in Gas-Solid Fluidized Bed Systems", AIChE Annual Meeting, Atlanta, GA, 2014.

A.2.2 IRP2— EMSET

- **Conference presention by Dr Peng SONG, Dr Bahareh KHERZI and Dr Karthik SOMASUNDARAM**

Drs SONG (CARES RF Cambridge), KHEZRI (CARES RF, NTU) and SOMASUNDARAM (CARES RF, NUS) attended and presented current IRP2 research activities at a conference in Cambridge in April 2015. This meeting, organised by Catalysis@Cambridge, explored fundamental challenges to academia and industry in catalysis and highlighted recent discoveries and new approaches to catalysis and catalytic reaction engineering . It also provided an opportunity for exchange of ideas and networking with industry partners. IRPs 1 and 3 also presented at the conference.

- **Conference presentation by Prof LIU Bin**

Prof LIU Bin presented IRP2 material at the 249th ACS Annual meeing held in Denver in March 2015. The title of his talk was "1D core-shell semiconductor nanowire arrays for photoelectrochemical water splitting".

A.2.3 IRP3— CAPRICORN

- **Conference presentations by Prof Markus KRAFT et al:**
- Kok Foong LEE, Sebastian MOSBACH, Markus KRAFT, Wolfgang WAGNER, "A multi-compartment population balance model for wet granulation", *UK Particle Technology Forum,* 17 Sep 2015, UK. (talk)
- Markus KRAFT, "Carbon Reduction in Chemical Technology", Sustainability, Environment & Energy Research (SEER) @ NUS 2014, 23 Sep 2015, Singapore. (Panel member and talk)
- *EURAXESS Links ASEAN*, Session: Europe as a global research player, Moderators: Prof M Kraft, CARES C4T & Mr T Bretschneider, EADS Innovation Works Singapore. (Moderator)

- Markus KRAFT, "Jurong Island , eco-industrial park and the internet of things", *Manufacturing Client Innovation Forum ATOS Siemens*, 4 Nov 2014, Singapore. (Plenary talk)
- Markus KRAFT, *World Economic Forum. Global Agenda Council Nanotechnology*, 9-11 Nov 2014, Abu Dhabi.
- Markus Kraft, Ming Pan, Janusz Sikorski, Catharine A. Kastner, Jethro Akroyd, Sebastian Mosbach, Raymond Lau, "Applying Industry 4.0 to the Jurong Island Eco-industrial Park", *7. International Conference on Applied Energy*, 29-31 Mar 2015, Abu Dhabi. (Panel member, Session Chair, Talks)
- Brandon Yong, Jiming Pang, Catharine Kastner, Markus Kraft, Raymond Lau, "Towards the development of carbon dioxide emission landscape in Singapore", *7. International Conference on Applied Energy*, 29-31 Mar 2015, Abu Dhabi. (Panel member, Session Chair, Talks)
- **Presentation by Prof XU Rong**

  Tianhua Zhou, Jindui Hong, Yunxiang Pan, Jianyu Han, Rong Xu: Design of Hybrid Photocatalyst Systems for Solar Fuel Production, *The 4th International Symposium on Solar Fuels and Solar Cells*, 21-24 Oct 2014, Dalian, China.

A.2.4 IRP4— ICESO

- **Presentations of IRP4 work by Dr Anthony TRAN at the following conferences**:

  ICCAIS'14 in Gwangyu, South Korea, 2-4 Dec 2014

  ICARCV'14 in Singapore, 10-12 Dec 2014.

  IEEE CDC'14 in Los Angeles, USA, 15-17 Dec 2014.

- **Conference Special Session organized by Dr Anthony TRAN**

  Anthony TRAN will organise a Special Session (5 papers) at the ISSAT MCSE'15 conference (Modelling of Complex Systems and Environments -http://www.issatconferences.org/mcse2015.html) in Vietnam, June 2015.

- **Forthcoming conference presentations by Prof Jan MACIEJOWSKI**

  Jan MACIEJOWKI is an Associate Editor for the IFAC Safeprocess Symposium (Paris, September 2015) and for the IFAC System Identification Symposium (Beijing, October 2015). He has been invited to give the opening lecture at the Turkish Automatic Control Conference TOK'15 in Denizli, Turkey, in September 2015.

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