CAMBRIDGE CARES

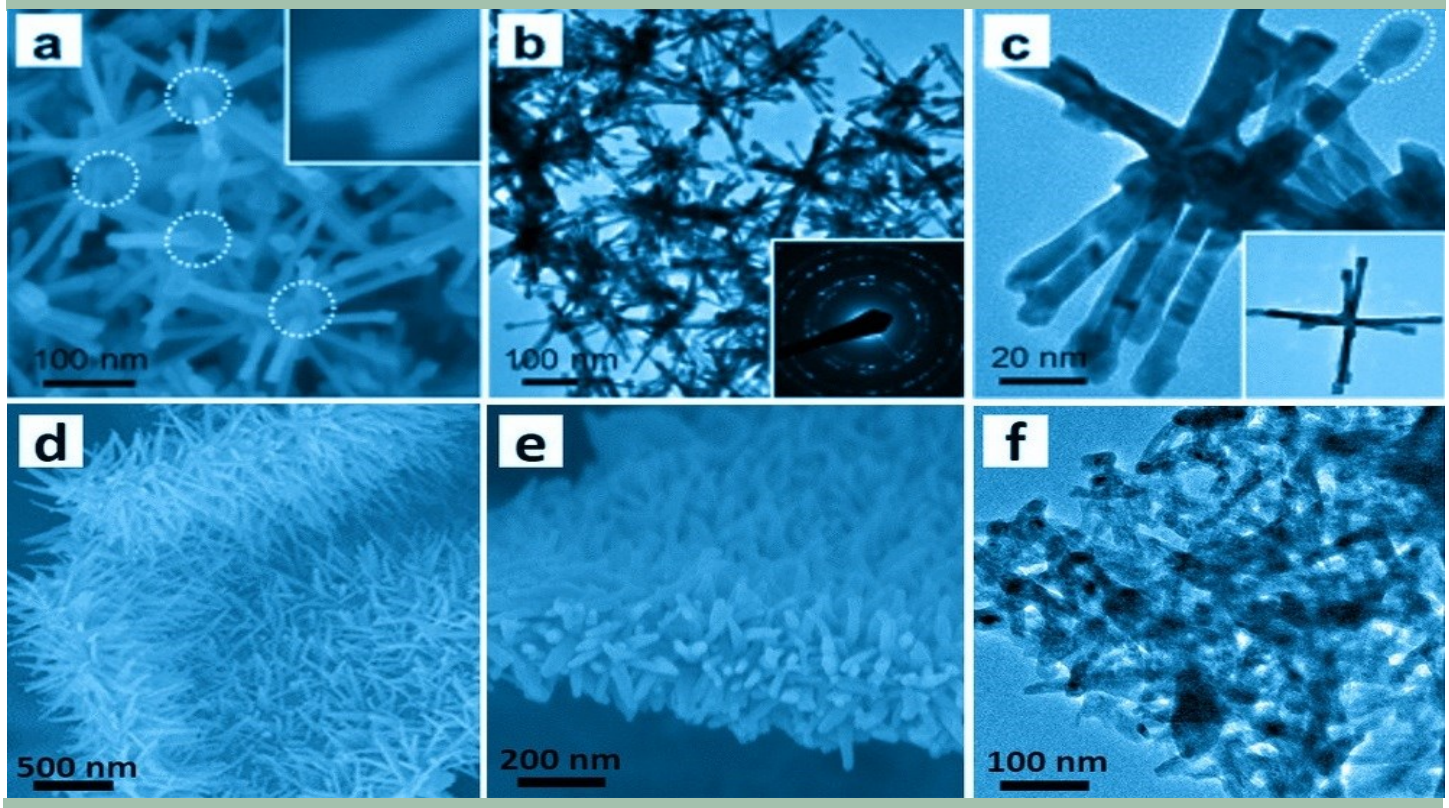
CAMBRIDGE CENTRE FOR ADVANCED RESEARCH IN ENERGY EFFICIENCY IN SINGAPORE LTD.

Biannual Research Report

May - October 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.

September 2015

I am delighted to present the 3rd 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 May 2015, our team has continued to make good progress towards our overarching programmatic goal of investigating technologies and techniques for the reduction of the carbon footprint of chemical industrial parks such as Jurong Island in Singapore. Across our four Interdisciplinary Research Programmes (IRPs) we have now published 91 papers in peer-reviewed journals and conference proceedings. The programme has produced five technology disclosures and currently has two patent applications pending. One of the patents has attracted enquiries from two Singapore-based companies interested in licensing the IP; both opportunities are currently undergoing feasibility studies in collaboration with NTUitive. The links between our IRPs continue to grow – IRP3 and 4 held a productive joint workshop in Cambridge in August 2015 and are working together on several joint workstreams. A second IRP3/4 conference is being planned for January 2016.

During the past six months, it has been particularly exciting to watch the dedicated C4T offices and laboratories in the CREATE Tower in Singapore taking shape as the construction teams have got to work. We are looking forward to the C4T programme members being housed in the new spaces from November 2015 (offices) and February 2016 (laboratories). I anticipate significant benefits for the collaborative efforts between the IRPs once they are sharing space and the new laboratories will give us the opportunity to accelerate various workstreams that require the equipment that will be housed there. It is also important to note that we continue to be kindly housed in temporary space by NTU and remain grateful for their significant support.

We have had a number of new members of the team, including several students joining the programme both in Singapore and Cambridge. There has also been a significant departure from the team as Prof John Dennis (PI, Cambridge, IRP1) stepped down following his recent appointment to the Headship of the Department for Chemical Engineering and Biotechnology, University of Cambridge. At the time of going to press, discussions are at an advanced stage to identify his replacement; we hope to make an announcement shortly. I would like to take this opportunity to thank Prof Dennis for his contribution to the programme and wish him well in his new role.

Our industrial interactions continue to grow. We have secured match-funding for three studentships under the Cambridge-CARES Studentship Scheme – two from Huntsman Tioxide Ltd (a global chemical manufacturer) and one from CMCL Innovations (a supplier of computer-aided engineering solutions to the chemical and automotive industry). Three excellent students have taken up these studentships and will start their courses in October 2015 in Cambridge. I am particularly pleased that one of these students is a 'homegrown' talent. Manoel Manuputty, came to work for C4T as a Project Officer in 2014 and will continue to contribute to the programme through his PhD project.

Finally, I am pleased to report that the C4T International Scientific Advisory Committee had their first teleconference in September 2015 and are expecting to hold their first in-person meeting in Singapore in April 2016. The input of these eminent scientists to the programme is very much appreciated by all C4T members.

I commend this report to you as a demonstration of the continuing contribution of our programme to the problem of how to develop environmentally sustainable chemical industries. Over the next reporting period, I fully expect the scientific excellence of our outputs to continue and strengthen further as we develop ideas and technologies that will influence the next generation of industrial installations, both in Singapore and worldwide.

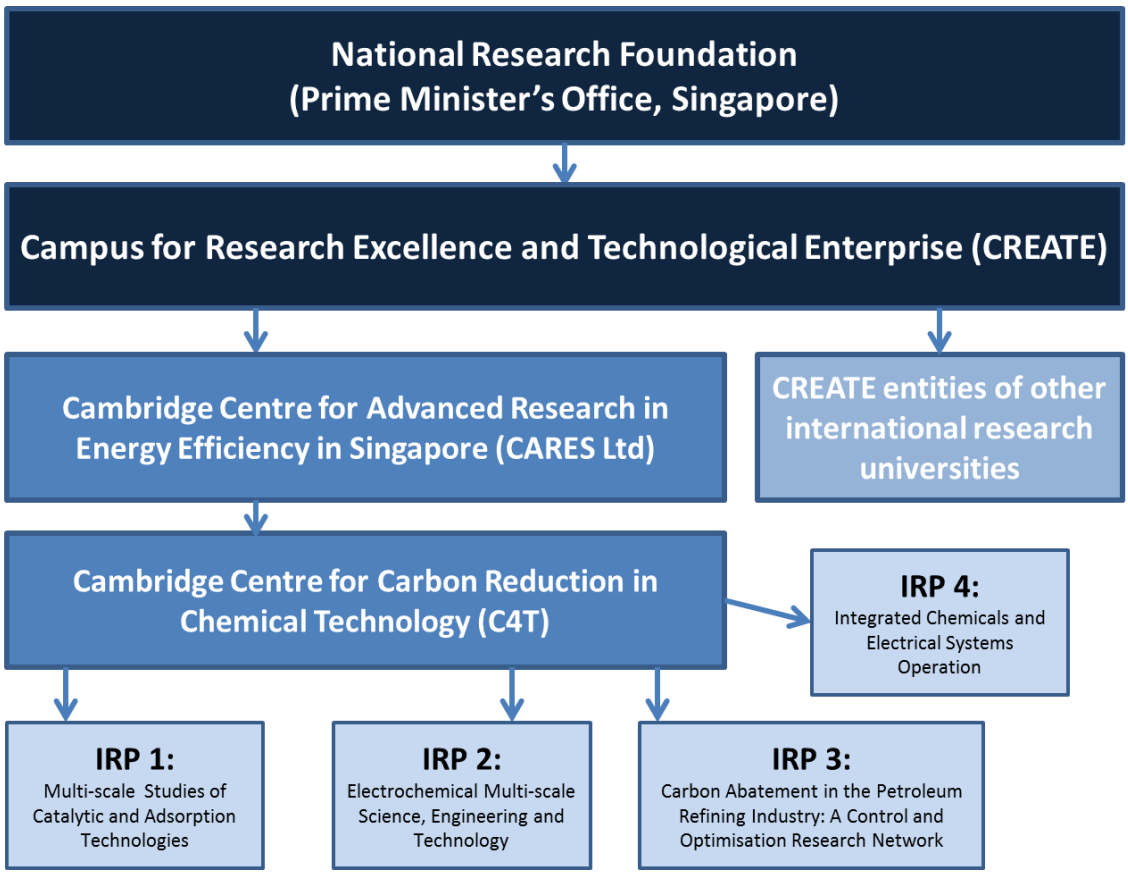
Contents

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.

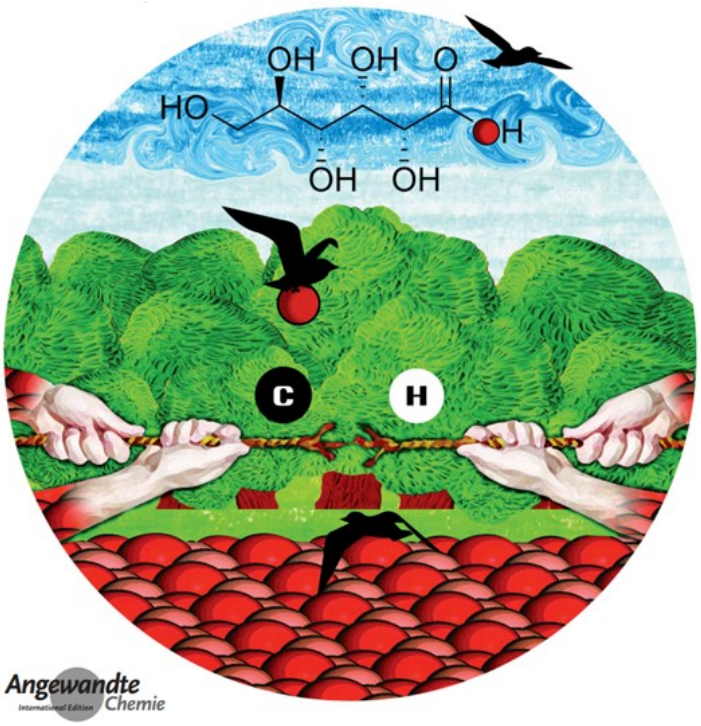
- IRP 1: Multi-Scale Studies of Catalytic and Adsorption Technologies (MUSCAT)
- IRP 2: Electrochemical Multi-scale Science, Engineering and Technology (EMSET)
- IRP 3: Carbon Abatement in the Petroleum Refining Industry: A Control and Optimisation Research Network (CAPRICORN)
- IRP 4: Integrated Chemicals 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 and IRP3: Biomass oxidation: Formyl C–H bond activation by the surface lattice oxygen of regenerative CuO nanoleaves

Prince N. Amaniampong, Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, Samir H. Mushrif . DOI: 10.1002/anie.201503916



Highlights:

- CuO nano-leaves are excellent candidates for glucose oxidation to gluconic acid. The catalyst upon re-oxidation, regains its structure, morphology and activity.
- DFT calculations help to reveal the crucial role of surface lattice Oxygen: Activates the formyl C-H bond and incorporate itself into glucose molecule to oxidize it to gluconic acid.
- Systematic DFT screening on CuO(111), Cu(111) and chemisorbed Oxygen on Cu(111) surfaces demonstrates that lattice Oxygen is superior in formyl C-H activation, and its hydrogen abstraction ability correlates with the adsorption energy.
- It is suggested that lattice oxygen is critical for the oxidation of glucose to gluconic acid, without further breaking glucose into smaller fragments

Abstract:

An integrated experimental and computational investigation reveals that surface lattice oxygen of copper oxide (CuO) nanoleaves activates the formyl C[BOND]H bond in glucose and incorporates itself into the glucose molecule to oxidize it to gluconic acid. The reduced CuO catalyst regains its structure, morphology, and activity upon reoxidation. The activity of lattice oxygen is shown to be superior to that of the chemisorbed oxygen on the metal surface and the hydrogen abstraction ability of the catalyst is correlated with the adsorption energy. Based on the present investigation, it is suggested that surface lattice oxygen is critical for the oxidation of glucose to gluconic acid, without further breaking down the glucose molecule into smaller fragments, because of C[BOND]C cleavage. Using CuO nanoleaves as catalyst, an excellent yield of gluconic acid is also obtained for the direct oxidation of cellobiose and polymeric cellulose, as biomass substrates.

2.2 IRP1: Monodisperse Aluminosilicate Spheres with Tunable Al/Si Ratio and Hierarchical Macro-Meso-Microporous Structure

Yuan Sheng and Hua Chun Zeng. DOI: 10.1021/acsami.5b03011

Highlights

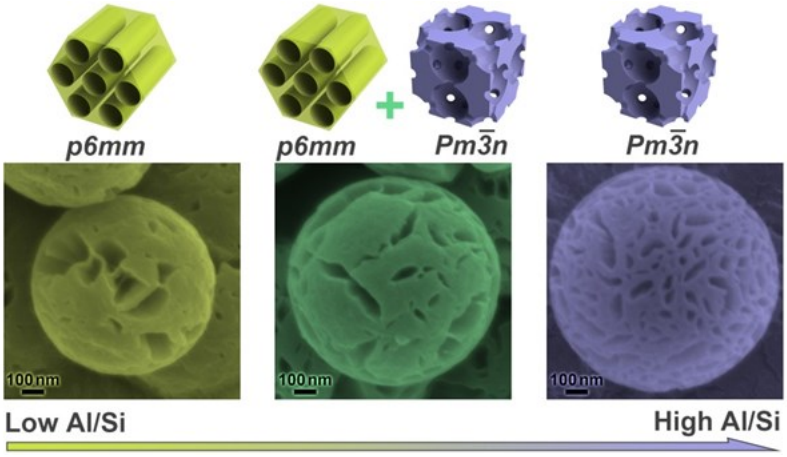
- In order to develop better catalyst supports, introduction of aluminium ions into silica is challenging as it leads to difficulties in morphological control of the product.
- The conflict between morphological control and aluminium incorporation can be resolved through a microemulsion route. Uniform macro-meso-microporous aluminosilicate spheres

can be made in one step.

- Control of composition and hierarchical pore structure of this type of new support are realized by investigating Hofmeister anion effects.
- The developed macro-meso-microporous aluminosilicate spheres can be used as an active catalyst support for heterogeneous catalysis, including hydrogenation of carbon dioxide.

Abstract

For the first time, monodisperse macro-meso-microporous aluminosilicate spheres (MASS) are synthesized in one step at room temperature. Simultaneous tuning of Al/Si ratio (0 -0.35) and the hierarchical pore structure is realized by Hofmeister anion effects of the Al source itself, $[Al(OH)_4]^-$, which change the geometry of CTAB micelles and giant vesicles. The Al is incorporated purely in a tetrahedrally coordinated status, and preliminary results from catalytic experiments show tuned acidity of MASS as a catalyst support for CO_2 hydrogenation to obtain desired products such as methanol or dimethyl ether.



2.3 IRP2: Surface segregation in bimetallic nanoparticles: a critical issue in electrocatalyst engineering

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

Highlights

•This review article (which was featured on the front cover of Small) introduces 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 detail.

•This review summarizes the advantages and disadvantages of surface segregation of bimetallic electrocatalysts and highlights the challenges and future perspectives.

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

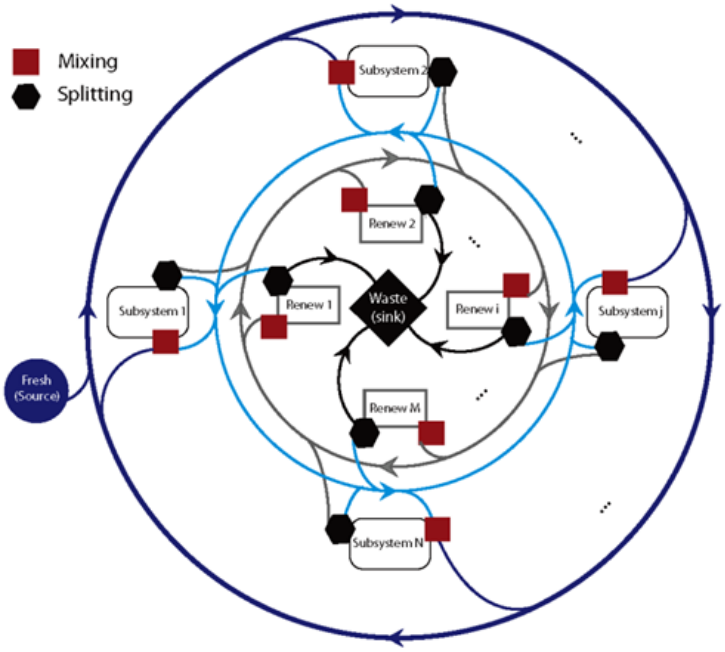
and intermediates during the catalysis. The surface composition can be varied as nanoparticles are exposed to certain environments through the surface segregation. Thermodynamically, the surface segregation is due to the difference of surface energy between two metals. It may lead to the enrichment of 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.

2.4 IRP3: Quantitative tools for cultivating symbiosis in industrial parks; a literature review

Catharine A. Kastner, Raymond Lau, and Markus Kraft. DOI: 10.1016/j.apenergy.2015.05.037

Highlights

- Quantitative tools and methods to cultivate industrial symbiosis exchanges are reviewed.
- A table of existing eco-industrial parks which have been studied is included.
- Alterations in existing infrastructure issues are examined.
- Motivational and restricted information concerns are discussed.



Abstract

The quantitative tools and methods that have been developed to identify and cultivate industrial symbiotic exchanges in existing industrial parks to minimize overall energy and material consumption are reviewed. The issues relevant to adapting an existing park differs from those associated with constructing a new park using eco-industrial principles. Published literature was surveyed for methodologies which identify and establish viable inter-company exchanges for water, heat, power and materials. Studies which address issues associated with infrastructure alterations are specifically highlighted, as well as methods to quantify and manipulate any potential financial and/or ecological benefits gained by adopting proposed eco-industrial measures. Additional topics, such as network analysis, company motivation, confidentiality issues and introduction of new industries or facilities are included. This review surveys current quantitative methodologies that can be applied to the process of adapting established industrial park networks into eco-industrial park systems and case studies which are pertinent to this type of adaptation.

2.5 IRP3 and IRP4: Distributed Moving Horizon Estimation for Power Systems

Tengpeng Chen, Dexiang Zhou, Tri Tran, C. Kastner, K-V. Ling, K-J. Tseng, and J. Maciejowski. Presented to 2015 IEEE Power and Energy Society General Meeting (PES GM'15), Denver, Colorado, July 2015.

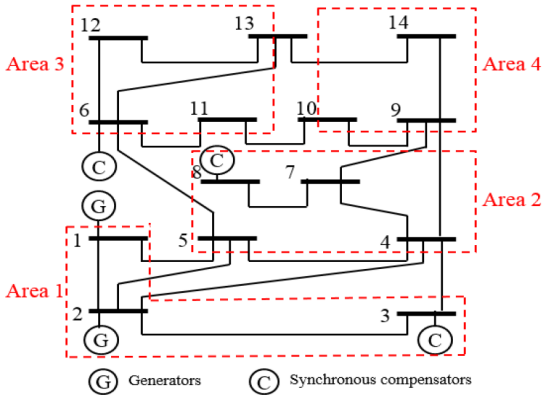


Fig. 1. IEEE 14-bus system.

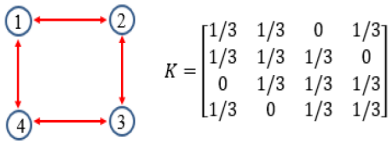


Fig. 2. Communication scheme and matrix K.

Highlights

- A distributed moving horizon estimation (DMHE) algorithm has been applied to the power system state estimation problem.
- Simulations using a standard IEEE 14-bus benchmark system and experiments on a lab microgrid have shown the effectiveness of both MHE and DMHE with constraints, for steady state operation with small variations.
- Enhancement of the algorithms by iterative improvement of the linearisation of the measurement equation has been shown to have improved the state estimation performance.

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 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.

2.6 IRP4: Embedded ADMM-based Quadratic Programming Solver for Model Predictive Control with Polytopic Constraints

Dang Van Thuy, K-V. Ling, and J. Maciejowski. Presented to European Control Conference (ECC'15) , Linz, Austria, July 2015

Highlights

- A new ADMM numerical algorithm for QP solver in embedded systems.
- Application of the newly developed ADMM algorithm to the model predictive control optimization problem with sparse formulation and general inequality constraints.
- Fixed-point arithmetic FPGA implementation with effective step size selections.

Abstract

An algorithm for solving quadratic programming (QP) problems with inequality and equality constraints arising from linear MPC is developed. 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, the developed algorithm can handle the 'sparse' MPC formulation with general inequality constraints. The proposed algorithm is suitable for implementation on embedded platforms where computational resources are limited. The algorithm is also division free when certain fixed matrices are computed off-line. This enables the implementation in fixed-point arithmetic on FPGA. A heuristic rule to select the step size of ADMM for a good convergence rate is also proposed.

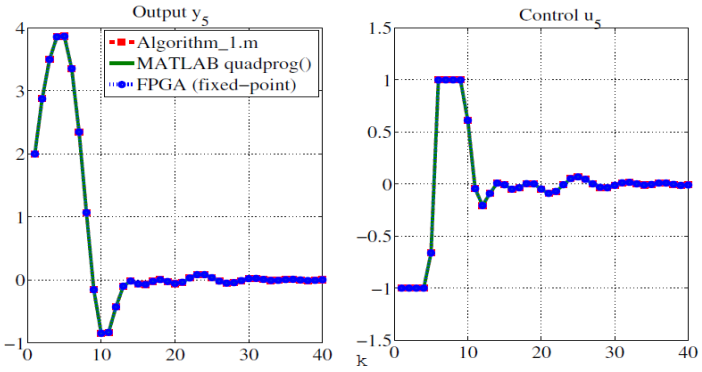
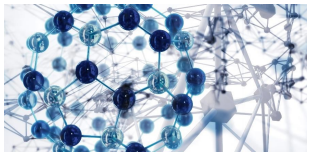


Fig. 2. MPC performance in Spring-Mass system



3.1 IRP1 — MUSCAT

Multi-Scale Studies of Catalytic and Adsorption Technologies

3.2 IRP2 — EMSET

Electrochemical Multi-scale Science, Engineering and Technology

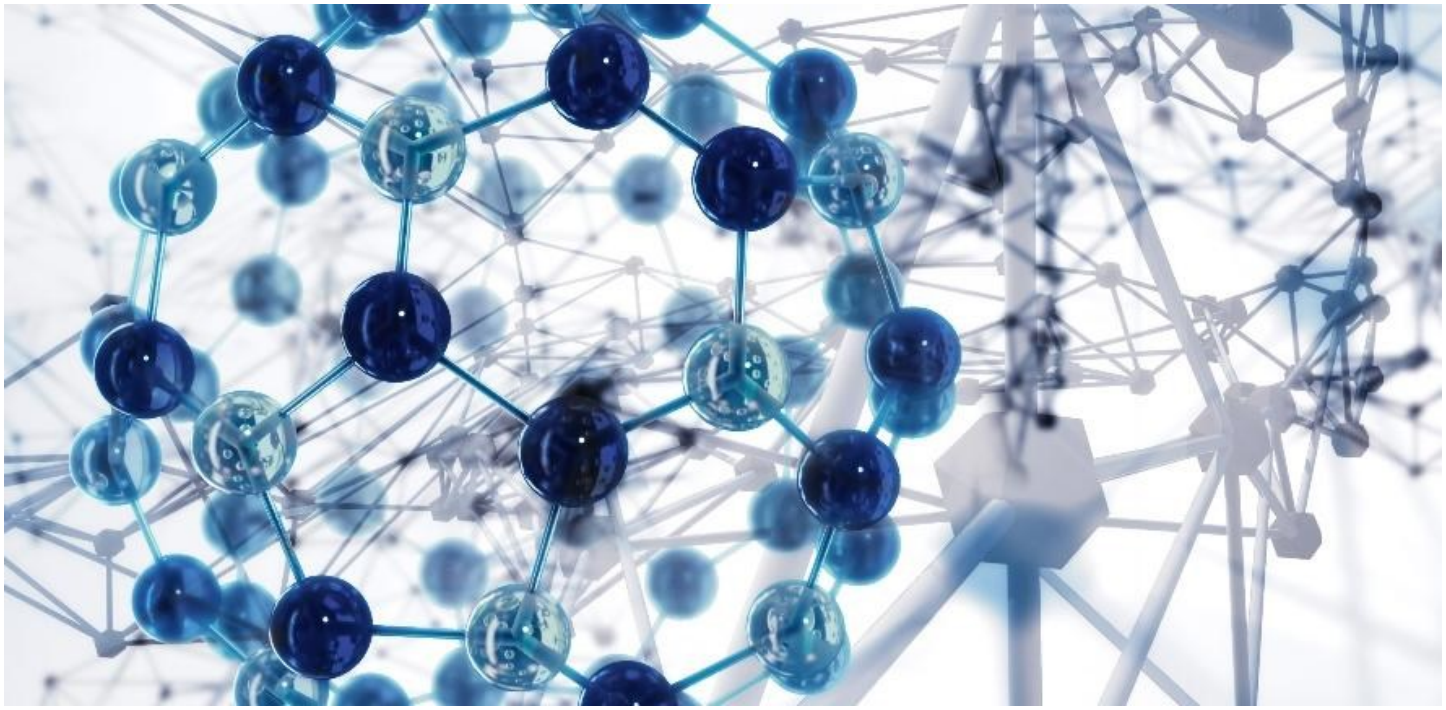
3.3 IRP3 — CAPRICORN

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) - resigned July 2015

Prof Markus KRAFT (Acting Cambridge PI)

Prof Yanhui YANG (NTU)

Prof Hua Chun ZENG (NUS)

Prof. John Dennis,
University of Cambridge
PI, IRP1,
April 2013—July 2015

Prof. Markus Kraft,
University of Cambridge
Acting PI IRP1
September 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 carbon capture (CC) and use of green-house gas emissions). The work packages are 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 CC in the presence of contaminants.
- Modelling of fluidisation and granular solids.

In this reporting period a number of high-quality results have been achieved and published in reputable journals. A detailed description of these exciting outcomes and a list of publication can be found on the next pages.

Following the arrival IRP1's newest Research Fellow , Dr Mark PURDUE (RF, NUS, IRP1), IRP1 research is now happening in the laboratories of all three institutions. The collaboration led by Cambridge yielded novel understandings and applications in high temperature carbon capture processes. At NTU, Professors Yanhui YANG (PI, IRP1, NTU) and Jia Wei CHEW's (Co-I, IRP1, NTU) research groups continued to produce new insights in the fields of catalytic conversion of biomass & waste materials and gas-solid fluidisation, respectively. Professors Hua Chun ZENG (PI, IRP1, NUS) and Shamsuzzaman FAROOQ (Co-I, IRP1, NUS) delivered significant contributions, in their respective areas of expertise, viz. development of novel materials and novel processes for carbon capture technologies.

During the reporting period Professor John DENNIS (former PI, Cambridge, IRP1) has been appointed to be the Head of Department at the Department of Chemical Engineering and Biotechnology at the University of Cambridge. As this represents a substantial increase of workload and responsibility he has decided to resign from the C4T programme. Currently, the programme director Professor Markus KRAFT is leading IRP1 until a suitable new candidate is found. It is anticipated that there will be some restructuring of the IRP1 in the future. Negotiation with a potential successor are very promising.

3.1.2 Update on work packages

Work package 1: Chemical looping with advanced oxide carriers

LIU Wen (SRF, IRP1, NTU & NUS) *et al*. worked collaboratively on research in chemical looping and high temperature carbon capture (also known as calcium looping), resulting in the submission of three manuscripts (Gonzalez et al., 2015; Ismail et al., 2015; Liu et al., 2015). Another application of chemical looping is to produce hydrogen from the steam iron process in a cyclic manner. Accordingly, the collaborative work by Martin CHAN *et al*. has produced publishable results, which are being written up.

In the past six months, HUANG Jijiang (PhD Student, IRP1, NTU) *et al*. have undertaken fundamental research to address the sintering and aggregation problem of the active oxygen carrier under the high temperature during the redox processes by the synthesis of highly dispersed active nanoparticles in ceramic supports. In particular, metal-organic frameworks (MOFs) materials have been prepared to serve as precursors of inert supports, or even the active metal oxides. In general, MOFs material is composed of metal nodes coordinated to organic ligands with regular but tunable microporous structures, high surface area and moderate thermal stability. The micropores can serve as hard templates for the nanoparticles formation with fine grain size, while the unique pore structure and high surface area are expected to achieve high loading of active metal oxides with good dispersion. The fine grain size and good dispersion of active metal oxides may then result in enhanced activity, stability and diminished carbon deposition. Another strategy is to develop a core-shell structured oxygen carrier, of which the core functions as the oxygen tank and the shell as the oxygen transmitter. Accordingly, investigation of various core-shell materials with different activity, stability and oxygen conductivity will be undertaken in the next six months.

Work Package 2: CO_2 methanation and biomass conversion

As the most active and economic catalysts for CO_2 methanation, Nickel based catalysts have been intensively investigated. However, the practical application of Ni based catalysts for CO_2 methanation is greatly compromised by the fact that they often suffer from the formation of coke and sintering of metal particles. Moreover, traceable CO content can be found in CO_2 sources, such as waste gas from power plant, which increases the formation of mobile Ni carbonyls at low temperature, leading to the growth of Ni particles.

YAN Yong (PhD student, IRP1, NTU) *et al*. prepared a novel $NiWMgO_x$ catalyst via a homogeneous precipitation method for CO_2 methanation. The catalyst showed an unexpectedly higher activity than the reference catalysts $NiMgO_x$. In addition, $NiWMgO_x$ catalysts have excellent stability even at temperatures as high as 400^{o}C with almost no activity loss during long-term tests up to 100 h. The fact that $NiWMgO_x$ demonstrated good stability with CO addition in the reaction gas indicates $NiWMgO_x$ is also offers great promise in applications for the methanation of CO_2 from CO-containing sources. Further research should be carried out to study the structure properties and reaction mechanisms over $NiWMgO_x$ catalysts.

DAI Yihu (SRF, IRP1, NTU) *et al*. prepared a series of Ni- and Ru-based catalysts and investigated their catalytic performances towards atmospheric-pressure CO_2 methanation reaction. Ni catalysts with low-metal-loading (<5 wt%) have been focused and Ni species highly dispersed in mesoporous CeO_2, TiO_2 and ZrO_2 matrix are controlled via a special sol-gel method. They revealed poor activities maybe due to difficult redox processes of the Ni species embedded in the support matrix and strong interaction between Ni and the support. Zr-based MOFs (UIO-66) with high surface area and isolated Zr^{4+} species were also employed as support of Ni particles and no obvious enhancement was observed. Carbon nanotubes (CNTs) supported Ru nanoparticles catalysts may be a kind of proper

model catalyst for CO_2 hydrogenation as the surface (oxygen group) of CNTs can be well controlled and the second metal (such as alkalis and noble metals) can be easily added to form alloy phase with Ru. In addition, YAN Yibo *et al*. (2015) recently published a review article concerning CNT catalysts; this paper was a joint effort between researchers from IRP1 and 2, along with other colleagues from NTU.

JIA Chunmiao (PhD student, IRP1, NTU) *et al*. have been studying application of the fluidized bed technology to CO_2 methanation. The methanation reaction is strongly exothermic and the reaction heat must be removed to avoid the sintering of the catalysts. In this case, gas-solid fluidised-bed reactors are more beneficial compared with fix-bed reactors owing to the much higher mass and heat transfer efficiency of the former. The objective of this work is to investigate the application of the fluidized-bed technology to methanation experimentally and by means of computational modelling. Kinetic parameters from experimental measurements will be used as inputs to multi-scale reactor model. After the development of a simplified, 1-D, steady state reactor, the model will be scaled up gradually, eventually to a 3-D dynamic reactor model.

Conversion of biomass and waste materials

An important approach to meet the current needs of energy and chemicals is biorefinery, which may replace human's dependence on fossil fuel resources. Therefore parts of IRP1 are focussing on the development of efficient catalysts to transfer easily available biomass to industrial chemicals.

Among the variety of chemicals, 5-hydroxymethylfurfural(HMF) is considered an important intermediate due to its rich chemistry and potential availability from carbonhydrates such as fructose, glucose, sucrose, cellulose and inulin. It has been identified as a versatile platform molecule which can be converted to valuable chemicals such as 2,5-furandicarboxylic acid (FDCA) 2,5-diformyfuran (DFF) and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), which are suitable starting materials for the preparation of polymeric materials. ZHAO Jun (PhD student, IRP1, NTU) *et al.* (2015) synthesized a series of carbon based solid acid catalysts and carbon-metal oxide composite catalysts applied them in the conversion of biomass to valuable chemicals. The catalysts were characterized by XRD, Raman IR, TGA, SEM and TEM and the reaction conditions were optimized to realize a high yield of the target products.

Biodiesel produced from renewable sources exhibits superior fuel properties, renewability and they are more environmentally friendly than petroleum-based fuel. LI Kaixin *et al*. (2015) (including IRP1 NTU PI YANG Yanhui and IRP3 NTU Co-I Samir MUSHRIF) investigated, a three-step transesterification, catalysed by a pyridinium-based Brønsted acidic ionic liquid (BAIL), for biodiesel production was using density functional theory (DFT) calculations at B3LYP/6-311++G(d) level. DFT results elucidate the detailed catalytic cycle, which involves the formation of a covalent reactant-BAIL-(methanol)n (n=1/3) intermediate and two transition states. Hydrogen bond interactions were found to exist throughout the process of the catalytic cycle, which are of special importance for stabilizing the intermediate and transition states. Therefore, a mechanism involving cooperative hydrogen bonding for BAIL-catalysed biodiesel production was established. The Gibbs free energy profile based on the above mechanism was validated by the subsequent kinetic study. The trend of activation energy from kinetic mathematical models was reasonably consistent with that obtained from the DFT calculations.

Prince AMANIAMPONG et al. (2015) (including IRP1 NTU PI YANG Yanhui and IRP3 NTU Co-I Samir MUSHRIF) undertook an integrated experimental and computational investigation which revealed that surface lattice oxygen of copper oxide (CuO) nanoleaves activates the formyl C-H bond in glucose and incorporates itself into the glucose molecule to oxidize it to gluconic acid. The reduced CuO catalyst regains its structure, morphology, and activity upon reoxidation. The activity of lattice oxygen is shown to be superior to that of the chemisorbed oxygen on the metal surface and the hydrogen abstraction ability of the catalyst is correlated with the adsorption energy. Based on the

present investigation, it is suggested that surface lattice oxygen is critical for the oxidation of glucose to gluconic acid, without further breaking down the glucose molecule into smaller fragments, because of C-C cleavage. Using CuO nanoleaves as catalyst, an excellent yield of gluconic acid is also obtained for the direct oxidation of cellobiose and polymeric cellulose, as biomass substrates.

HE Chao (RF, IRP1, NTU) *et al.* (2015a) performed hydrothermal conversion (HTC) of dewatered sewage sludge (DSS) under sub- and near-critical water to investigate effects of reaction temperature and pressure, moisture content of DSS, and calcium oxide (CaO) additive on evolution profile and characteristics of gas, solid, and liquid products. Although energy recovery rate decreased with increasing temperature and pressure, significant decarboxylation and dehydration reactions led to hydrochars with best fuel quality at 320°C. High moisture content favoured decarboxylation reaction but reduced H_2 and CH_4 yields. Compared to that in the absence of additive, H_2 yield increased almost 6-fold at 380°C and Ca/C molar ratio of 0.2, resulting in 58% H_2 and 26% CH_4 in final fuel gas. The results suggested that mineralization of heteroatomic compounds and dissolution of metals or mineral elements occurred during HTC. Under higher temperature and pressure, heavy metals or mineral elements were prone to be immobilized whereas dehalogenation became more distinct. CaO additive not only facilitated hydrolysis and deamination of organic compounds but also accelerated further fixation of inorganic elements and anions.

In order to reduce considerable emissions of N-containing pollutants from combustion of sewage sludge derived solid fuel, HE Chao (RF, IRP1, NTU) *et al.* (2015b) developed an integrated system of hydrothermal deamination and air stripping was to effectively remove and recover nitrogen from dewatered sewage sludge (DSS). Three characteristic hydrothermal regimes contributing to deamination were identified. Initial hydrolysis of inorganic-N and labile protein-N was responsible for ammonium (NH_4^+-N) released below 300°C/9.3 MPa, whereas deamination of pyridine-N dominated when being raised to 340°C/15.5 MPa. At 380 °C and 22.0 MPa, remarkable deamination of stable protein-N occurred, which was accompanied by formation of more heterocyclic-N compounds and resulted in 76.9% N removal from DSS and 7980 mg/L NH_4^+-N solution. As a result of catalytic hydrolysis and cracking, calcium oxide additive not only accelerated deamination of stable protein-N, pyrrole-N, and pyridine-N, but also favoured transformations of protein-N and quaternary-N to nitrile-N and pyridine-N, respectively, leading to 86.4% total N removal efficiency. The nitrogen transformation reactions and conversion pathways during hydrothermal deamination were proposed and elaborated in detail. Moreover, an efficient air stripping process was coupled to remove and recover ammonia from liquid fraction via ammonium sulphate. Consequently, this system achieved an overall N recovery rate of 62%.

Work Package 3: New materials and MOFs

The research on the development of novel nanostructure materials is undertaken by LI Ping (RF, IRP1, NUS) *et al.* and consists of the following two approaches:

Layered double hydroxides (LDHs) and MOFs nanocomposites

3D flower-like hierarchical-structured LDHs micro/nanospheres, with high surface areas and abundant pores, were prepared via a facile one-pot surfactant-free solvothermal route. A series of MOFs were successfully functionalized on the flakes of the above spheres with uniform size and high dispersion. These nanocomposites have great potential in heterogeneous catalysis and CO_2 adsorption. The related work is currently underway.

Nanocomposites of layered double hydroxides (LDHs) and alloy nanoparticles

Through reactions in confined space, a novel and facile method was developed to prepare LDHs/transition metal alloys. In this project, LDHs/alloy composites with tiny alloy NPs as a nanophase were obtained. A series of binary and ternary alloy nanoparticles were successfully supported

on LDH hosts via this method. The obtained nanocomposites showed high activity in catalytic applications (e.g., C-C cross coupling reaction, CO_2 fixation, hydrogenation reaction and oxidation reaction).

Work Package 4: Multi-scale modelling

Understanding the fundamentals of fluidisation is essential for implementing high temperature solid looping technologies at large scales. YANG Shiliang (RF, IRP1, NTU) *et al.* have conducted the three-dimensional modeling of the gas-solid flow in a spout-fluid bed at the particle-scale level to study its dispersion and residence properties. Furthermore, the scale-up of spout-fluid bed by means of aligning several parallel chambers has been investigated for the purpose of providing some useful baselines to the design, scale-up of this kind of apparatus. Meanwhile, the mechanism for spouting collapse in a 3-D lab-scale double-slot rectangular spouted bed is being explored under the large-scale parallel framework of CFD-DEM coupling approach. Simulation results have demonstrated that large vertical solid flux appears in the central region of each chamber and shows a distribution property strongly related to the slot shape. Furthermore, the slot shape influences the spout-annulus interaction boundary, whereas this effect diminishes obviously with increasing the bed height. Insertion of partition plate enlarges the pressure drop of the system. However, it postpones the collapse the steady fountain in critical operating condition. The related investigation resulted in an acceptance of one manuscript (Yang et al. 2015).

Work Package 5: Fundamentals of adsorption and PSA

Mark PURDUE (RF, IRP1, NUS) is studying the capture of CO_2 using a commercial zeolite. His overall objectives are the characterization of the adsorption of wet flue gas mixtures on commercial adsorbents to allow accurate scale up of pressure swing adsorption processes for the capture of CO2 from industrial flue gas and investigation of the influence of moisture on the adsorption amounts is of particular importance. A literature review of experimental adsorption isotherms for flue gas components on zeolite 13X and silica gel has been made. Studies of flue gas adsorption in zeolite 13X using RASPA molecular simulation software are underway (in cooperation with the Chemical and Biomolecular Engineering Department, NUS). Future studies on silica gel will also be considered. Molecular simulations of wet flue gas adsorption are expected to guide future experiments. The next step is to measure equilibrium isotherm data for CO_2, N_2, H_2O and their mixtures on zeolite 13X and silica gel. Multicomponent breakthrough and adsorption experiments will be performed using pilot plant samples of zeolite 13X. Experiments should incorporate a gas humidifier and mass spectroscopy for outlet gas composition analysis. Then, experimental and molecular simulation results for adsorption isotherms will be compared to identify the most suitable equilibrium model. Molecular simulation results can serve to "patch" together the experimental data points and refine a multicomponent isotherm model to comprehensively cover a wide adsorption data set. Ultimately, the vacuum/temperature swing adsorption process will be simulated and optimised using MATLAB. Multicomponent adsorption will be experimentally investigated at the laboratory scale using dual-adsorbent, two-bed VSA process for CO_2 capture from wet flue gas.

Experimental work will begin when the CREATE laboratory is ready. A PhD student withdrew from his position at the last minute. An offer has been sent out to an alternative PhD student.

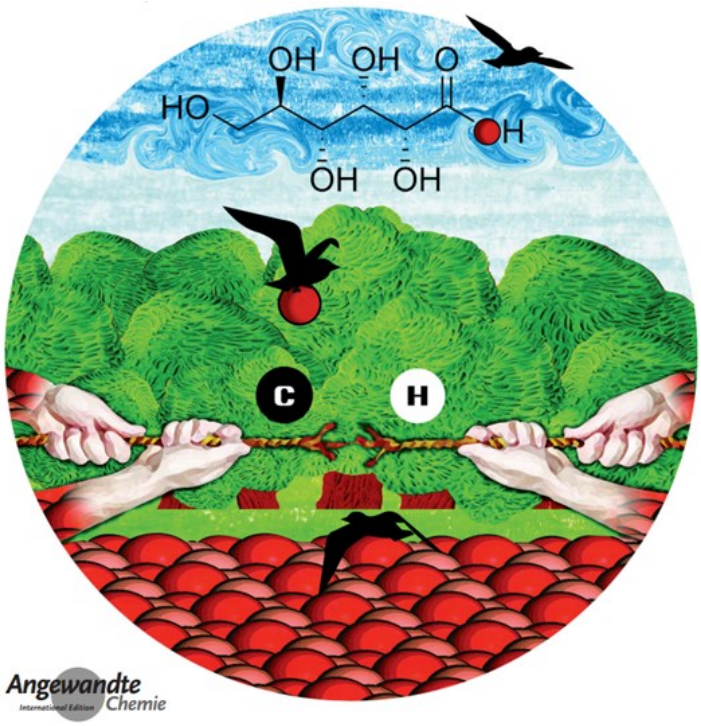
3.1.3 Scientific output of IRP1

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

Biomass oxidation: Formyl C–H bond activation by the surface lattice oxygen of regenerative CuO nanoleaves

Prince N. Amaniampong, Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, Samir H. Mushrif . DOI: 10.1002/anie.201503916

Relevance to the work of the IRP: IRP1 WP1.1 & 1.2



Highlights:

- CuO nano-leaves are excellent candidates for glucose oxidation to gluconic acid. The catalyst upon re-oxidation, regains its structure, morphology and activity.
- DFT calculations help to reveal the crucial role of surface lattice Oxygen: Activates the formyl C-H bond and incorporate itself into glucose molecule to oxidize it to gluconic acid.
- Systematic DFT screening on CuO(111), Cu(111) and chemisorbed Oxygen on Cu(111) surfaces demonstrates that lattice Oxygen is superior in formyl C-H activation, and its hydrogen abstraction ability correlates with the adsorption energy.
- It is suggested that lattice oxygen is critical for the oxidation of glucose to gluconic acid, without further breaking glucose into smaller fragments

Abstract:

An integrated experimental and computational investigation reveals that surface lattice oxygen of copper oxide (CuO) nanoleaves activates the formyl C[BOND]H bond in glucose and incorporates itself into the glucose molecule to oxidize it to gluconic acid. The reduced CuO catalyst regains its structure, morphology, and activity upon reoxidation. The activity of lattice oxygen is shown to be superior to that of the chemisorbed oxygen on the metal surface and the hydrogen abstraction ability of the catalyst is correlated with the adsorption energy. Based on the present investigation, it is suggested that surface lattice oxygen is critical for the oxidation of glucose to gluconic acid, without further breaking down the glucose molecule into smaller fragments, because of C[BOND]C cleavage. Using CuO nanoleaves as catalyst, an excellent yield of gluconic acid is also obtained for the direct oxidation of cellobiose and polymeric cellulose, as biomass substrates.

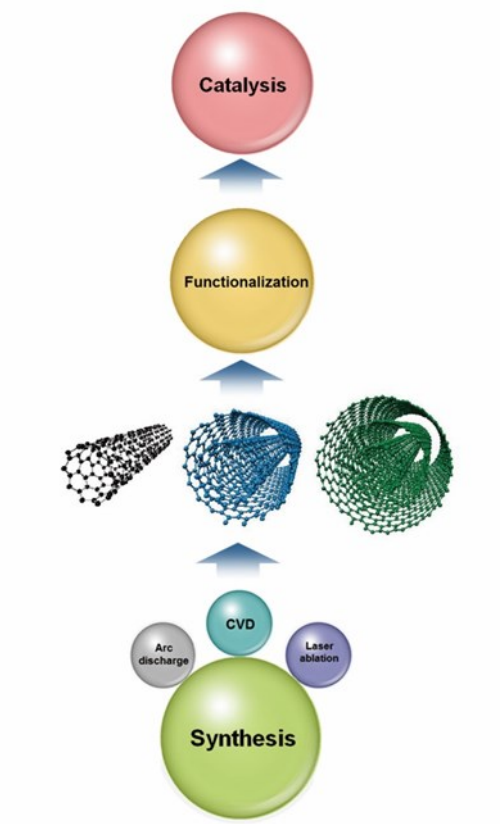
Carbon nanotube catalysts: recent advances in synthesis, characterization and applications

Yibo Yan, Jianwei Miao, Zhihong Yang, Fang-Xing Xiao, Hong Bin Yang, Bin Liu, Yanhui Yang . DOI: 10.1039/C4CS00492B

Relevance to the work of the IRP: IRP1 WP1.2

Abstract:

Carbon nanotubes are promising materials for various applications. In recent years, progress in manufacturing and functionalizing carbon nanotubes has been made to achieve the control of bulk and surface properties including the wettability, acid–base properties, adsorption, electric conductivity and capacitance. In order to gain the optimal benefit of carbon nanotubes, comprehensive understanding on manufacturing and functionalizing carbon nanotubes ought to be systematically developed. This review summarizes methodologies of manufacturing carbon nanotubes via arc discharge, laser ablation and chemical vapor deposition and functionalizing carbon nanotubes through surface oxidation and activation, doping of heteroatoms, halogenation, sulfonation, grafting, polymer coating, noncovalent functionalization and nanoparticle attachment. The characterization techniques detecting the bulk nature and surface properties as well as the effects of various functionalization approaches on modifying the surface properties for specific applications in catalysis including heterogeneous catalysis, photocatalysis, photoelectrocatalysis and electrocatalysis are highlighted.



Mechanistic and kinetic study for biodiesel production catalyzed by an efficient pyridinium based ionic liquid

Kaixin Li, Zhihong Yang, Jun Zhao, Junxi Lei, Xinli Jia, Samir H. Mushrif and Yanhui Yang . DOI: 10.1039/c5gc00976f

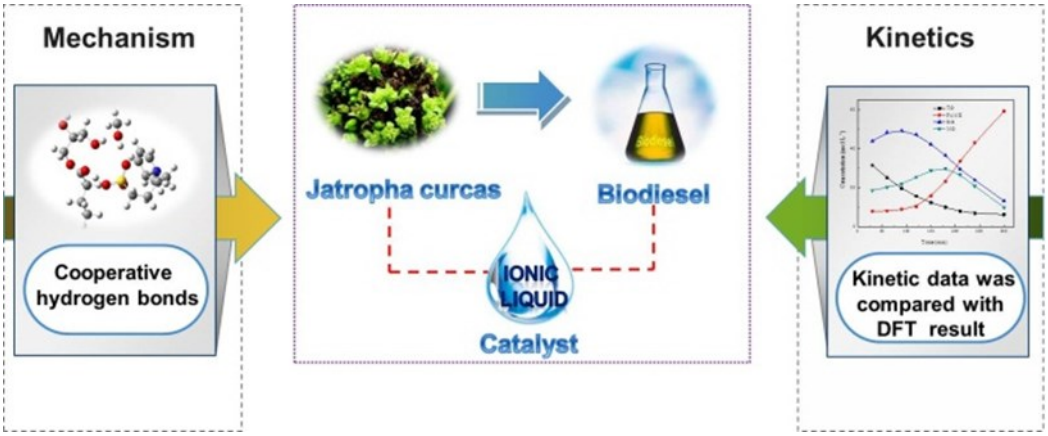
Relevance to the work of the IRP: IRP1 WP1.1 & 1.2

Highlights

- Transesterification catalyzed by a pyridinium-based Brønsted acidic ionic liquid (BAIL) for one -pot biodiesel production was investigated theoretically and experimentally.
- A covalent reactant-BAIL-methanol intermediate and two transition states are formed in the catalytic cycle.
- A mechanism for the BAIL-catalyzed transesterification is proposed for the first time using density functional theory (DFT) calculations, taking into account explicitly the deprotonation of the ILs.
- The DFT computations reveal that the coexistence of intra-molecular and inter-molecular hydrogen bonding is critical to stabilize the intermediate and transition states in the deprotonation and transesterification steps. Thus, specific hydrogen bonding network which plays an important role in deciding the catalytic activity of ILs is identified.
- The subsequent kinetic study shows that the trend of activation energy from kinetic mathematical models was reasonably consistent with that obtained from the DFT calculations.

Abstract

Biodiesel produced from renewable sources exhibits superior fuel properties, renewability and they are more environmentally friendly than petroleum-based fuel. In this paper, a three-step transesterification, catalyzed by a pyridinium-based Brønsted acidic ionic liquid (BAIL), for biodiesel production was investigated using density fnctional theory (DFT) calculations at B3LYP/6-311++G (d) level. DFT results elucidate the detailed catalytic cycle, which involves the formation of a covalent reactant-BAIL-(methanol)n (n=1/3) intermediate and two transition states. Hydrogen bond interactions were found to exist throughout the process of the catalytic cycle, which are of special importance for stabilizing the intermediate and transition states. Therefore, a mechanism involving cooperative hydrogen bonding for BAIL-catalyzed biodiesel production was established. The Gibbs free energy profile based on the above mechanism was validated by the subsequent kinetic study. The trend of activation energy from kinetic mathematical models was reasonably consistent with that obtained from the DFT calculations.



Effective nitrogen removal and recovery from sewage sludge using a novel integrated system of accelerated hydrothermal deamination and air stripping

Chao He, Ke Wang, Yanhui Yang, Prince Nana Amaniampong, Jing-Yuan Wang . DOI: 10.1021/acs.est.5b00652

Relevance to the work of the IRP: IRP1 WP1.1 & 1.2

Highlights

- Three characteristic hydrothermal regimes contributing to deamination were identified.
- Because of catalytic hydrolysis and cracking, CaO not only accelerated deamination but also favored N transformations, leading to 86.4% total N removal efficiency.
- An efficient air stripping process achieved an overall N recovery rate of 62%.

Abstract

In order to reduce considerable emissions of N-containing pollutants from combustion of sewage sludge derived solid fuel, an integrated system of hydrothermal deamination and air stripping was developed to effectively remove and recover nitrogen from dewatered sewage sludge (DSS). Three characteristic hydrothermal regimes contributing to deamination were identified. Initial hydrolysis of inorganic-N and labile protein-N was responsible for ammonium (NH4+-N) released below 300° C/9.3 MPa, whereas deamination of pyridine-N dominated when being raised to 340°C/15.5 MPa. At 380 °C and 22.0 MPa, remarkable deamination of stable protein-N occurred, which was accompanied by formation of more heterocyclic-N compounds and resulted in 76.9% N removal from DSS

and 7980 mg/L NH_4^+-N solution. As a result of catalytic hydrolysis and cracking, calcium oxide additive not only accelerated deamination of stable protein-N, pyrrole-N, and pyridine-N, but also favored transformations of protein-N and quaternary-N to nitrile-N and pyridine-N, respectively, leading to 86.4% total N removal efficiency. The nitrogen transformation reactions and conversion pathways during hydrothermal deamination were proposed and elaborated in detail. Moreover, an efficient air stripping process was coupled to remove and recover ammonia from liquid fraction via ammonium sulfate. Consequently, this system achieved an overall N recovery rate of 62%.

Products evolution during hydrothermal conversion of dewatered sewage sludge in sub- and near-critical water: Effects of reaction conditions and calcium oxide additive

Chao He, Ke Wang, Apostolos Giannis, Yanhui Yang, Jing-Yuan Wang. ***DOI:*** *10.1016/j.ijhydene.2015.03.006*

Relevance to the work of the IRP: IRP1 WP1.1 & 1.2

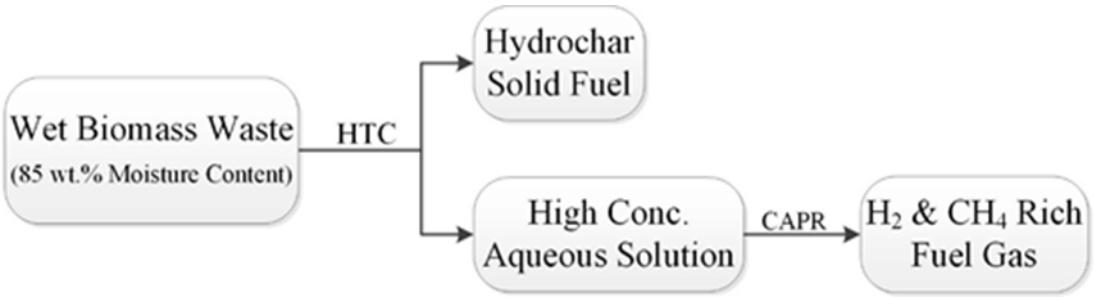
Highlights

- Products evolution in HTC of SS was studied at various conditions and CaO amounts.
- H2 yield could grow nearly 6-fold and accounted for 58% at 380°C after adding CaO.
- Increased temperature promoted dehalogenation and fixation of heavy metals and P.
- High moisture content favored decarboxylation and hydrolysis.
- CaO improved hydrolysis, deamination, and fixation of inorganic elements/anions.

Abstract

In the present study, hydrothermal conversion (HTC) of dewatered sewage sludge (DSS) under sub- and near-critical water has been performed to investigate effects of reaction temperature and pressure, moisture content of DSS, and calcium oxide (CaO) additive on evolution profile and characteristics of gas, solid, and liquid products. Although energy recovery rate decreased with increasing temperature and pressure, significant decarboxylation and dehydration reactions led to hydrochars with best fuel quality at 320°C. High moisture content favored decarboxylation reaction but reduced

H_2 and CH_4 yields. Compared to that in the absence of additive, H_2 yield increased almost 6-fold at 380°C and Ca/C molar ratio of 0.2, resulting in 58% H_2 and 26% CH_4 in final fuel gas. The results suggested that mineralization of heteroatomic compounds and dissolution of metals or mineral elements occurred during HTC. Under higher temperature and pressure, heavy metals or mineral elements were prone to be immobilized whereas dehalogenation became more distinct. CaO additive not only facilitated hydrolysis and deamination of organic compounds but also accelerated further fixation of inorganic elements and anions.



Efficient dehydration of fructose to 5-hydroxymethylfurfural over sulfonated carbon sphere solid acid catalysts

Jun Zhao, Chunmei Zhou, Chao He, Yihu Dai, Xinli Jia, Yanhui Yang. ***DOI:*** *10.1016/j.cattod.2015.07.005*

Relevance to the work of the IRP: IRP1 WP1.1 & 1.2

Highlights

- Sulfonated carbon as synthesized by a modified two-step method under mild condition.
- Spherical shape was preserved which is independent of sulfonation solution concentration.
- This carbon-based solid acid showed excellent activity in fructose dehydration to HMF.
- 90% HMF yield was obtained at 160 °C after 1.5 h reaction time duration.

Abstract

A carbon-based solid acid catalyst was prepared via hydrothermal method using glucose as carbon precursors and aqueous solution of H2SO4 as sulfonation agent. The as-synthesized solid acid catalyst was attempted in the catalytic dehydration of fructose to 5-hydroxymethylfurfural (HMF). The effects of acid site density, reaction time, solvents, catalyst amount, temperature and mole ratio of catalyst to substrate were investigated. Under the optimum reaction conditions, the HMF yield of 90% was achieved in dimethylsulfoxide (DMSO) solvent at 160 °C after 1.5 h reaction time duration. The solid acid catalyst can be separated from the reaction mixture after reaction and reused without

substantial loss in catalytic activity.

Monodisperse Aluminosilicate Spheres with Tunable Al/Si Ratio and Hierarchical Macro-Meso-Microporous Structure

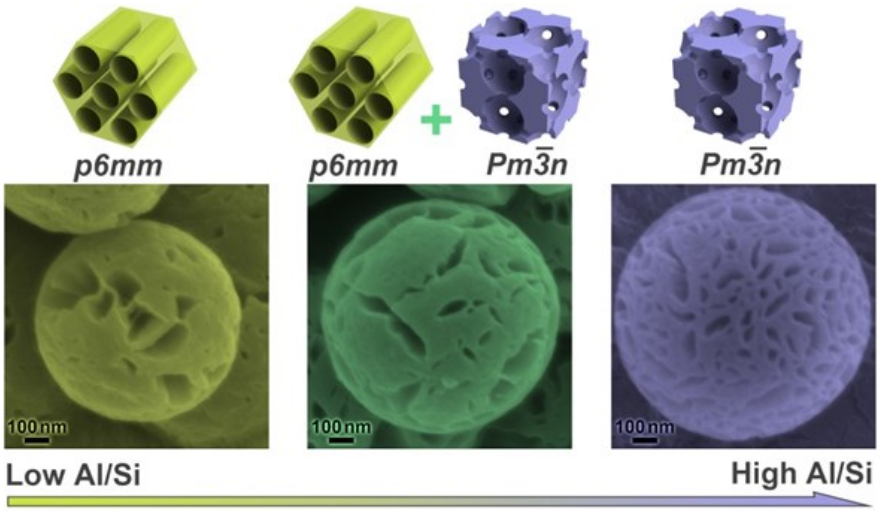
Yuan Sheng and Hua Chun Zeng. DOI: 10.1021/acsami.5b03011

Relevance to the work of the IRP: IRP1 WP1.3

Highlights

- In order to develop better catalyst supports, introduction of aluminium ions into silica is challenging as it leads to difficulties in morphological control of the product.
- The conflict between morphological control and aluminium incorporation can be resolved through a microemulsion route. Uniform macro-meso-microporous aluminosilicate spheres can be made in one step.
- Control of composition and hierarchical pore structure of this type of new support are realized by investigating Hofmeister anion effects.
- The developed macro-meso-microporous aluminosilicate spheres can be used as an active catalyst support for heterogeneous catalysis, including hydrogenation of carbon dioxide.

Abstract



While tremendous success has been seen in the development of ordered mesoporous silica by soft-templated methods, synthesis of hierarchical structures with controllable multi-scale pore networks has remained a challenging topic. On the other hand, introduction of heteroatoms as an effective method of chemically functionalizing silica leads to difficulties in morphological control of the product, and multi-step synthesis has been necessary for functionalized silica particles with hierarchical pore structure and uniform size. The present work demonstrates that the conflict between morphological control and heteroatoms incorporation can be resolved in a CTAB-stabilized toluene-water-ethanol microemulsion system. For the first time, monodisperse macro-meso-microporous aluminosilicate spheres (MASS) are synthesized in one step at room temperature. Simultaneous tuning of Al/Si ratio (0 0.35) and the hierarchical pore structure is realized by Hofmeister anion effects of the Al source itself, [Al(OH)4], which change the geometry of CTAB micelles and giant vesicles. The Al is incorporated purely in a tetrahedrally coordinated status, and preliminary results from catalytic experiments show improved acidity of MASS as a catalyst support.

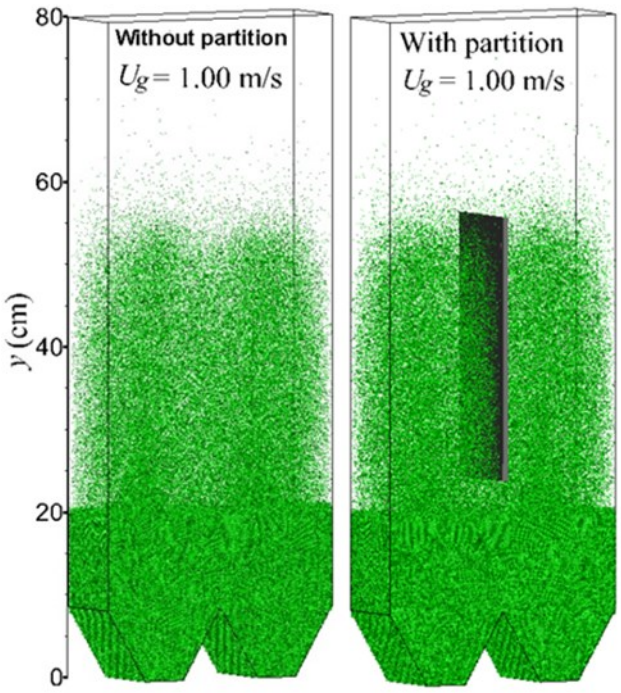
Computational study of spout collapse and impact of partition plate in a double slot-rectangular spouted bed

Shiliang Yang, Ke Zhang, Jia Wei Chew. DOI: 10.1002/aic.14973

Relevance to the work of the IRP: IRP1 WP1.3

Highlights

- Large-scale parallel CFD-DEM coupling approach is adopted to model the three-dimensional double slot-rectangular spouted bed
- Five distinct flow regimes are observed in the bed at different gas velocities.
- Knowledge gained was extended to understand the mechanisms leading to operational instability due to the collapse of a spout
- Vertical partition can successfully prevent interactions between adjacent fountains.



Abstract

Gas-solid hydrodynamics in a three-dimensional slot-rectangular double-spouted bed was numerically investigated by a combined approach of discrete element method (DEM) and computational fluid dynamics (CFD), and the knowledge gained was extended to understand the mechanisms leading to operational instability due to the collapse of a spout, along with the beneficial impact of inserting a vertical partition plate. The setup investigated has two diverging bases and contains up to 2,590,000 particles. The computational results show different behaviours of pressure drop, in terms of average value, fluctuations and power spectral trends, in the five distinct flow regimes corresponding to various superficial gas velocities. Two types of spout shapes are observed under stable spouting conditions, and the spout sizes are quantified. When one of the spouts chokes then collapses, complex interactions between the chambers are identified. Furthermore, the insertion of a vertical partition plate between two chambers appears to be an effective way to prevent the interactions between adjacent fountains, which is advantageous for improving the operational stability of such systems upon scale-up.

3.1.4 Further Achievements

Technology disclosures and patents

IRP1 has now submitted two technology disclosures, one of which has resulted in a patent and some significant progress towards licensing the IP to two potential industrial collaborators.

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

September 2015

3.2.1 IRP2 Research Overview

The rapid expansion of renewable electricity generation and the long-term availability of low cost 'electrons' from these technologies offers new and exciting opportunities for the electrochemical community. In particular the continued challenges around long-term electron storage means that utilization of electrons generated from renewable sources is becoming increasingly critical. The EMSET focus is targeted directly at these opportunities with a specialism in the discovery, analysis, design and development of electrochemical methodologies which can covert electricity to chemical feedstocks and/or value added chemicals.

Existing electrochemical technologies such as batteries, fuel cells and the extensive chloroalkyl industry clearly demonstrate the possibilities for carbon and energy efficient routes for electricity generation and chemical production. However, broad exploitation of the low cost and low carbon 'electrons' generated from the massive expansion in renewables calls for novel electrochemical technologies, catalyst materials, process routes, electroanalytical measurements and new engineering concepts.

In collaboration with multinational organisations the IRP2 group is taking a 'bottom up' look at each of the key elements that can control the productivity and chemical efficiency of an electrolyser, electrochemical electricity generator or electroanalyser. The IRP2 group in Singapore and Cambridge has recruited skilled researchers and senior academics, with expertise in advanced electrocatalysis, materials synthesis reactor design and numerical modelling to address the above challenges. The strong and positive working relationships between the Cambridge and C4T partners are delivering co-authored publications, exchange of staff regularly between the UK/Singapore and the organization of international training activities.

Current IRP2 activities in WP2.1 (Multi-Scale Electrochemical Modelling and Analysis) are targeted at the development of numerical models and tools to establish high resolution and sensitivity analytical techniques. Strong progress has been made here and we are close to establishing a set of novel tools for highly resolving electroanalytical measurements. In WP 2.2 (Electrode Design and Development), novel electrode materials development and testing continues at a strong pace. The current focus is on feedstocks with hydrogen oxygen, hydrogen peroxide as well as exploring potentially novel biological electrode materials. The toxicology and chemical stability of electrode substrates is also underway. The research collaboration with NTU IRP2 PI Prof Xin WANG, has led to the development of novel catalysts, which will be tested as part of a large scale marine engine project, based at ERIAN in NTU. The focus of WP 2.3 (Electrochemical Reactor Engineering) has been on the development and testing of high throughput reactors and analysers. Collaboration work with the Department of Chemistry at NTU is currently exploring these devices. The potential of IRP2 tehniques and reactor approaches are also currently being discussed for the REIDS project (collaboration led by ERI@N, NTU).

IRP2 continues to have strong industrial support for its research and training activities. Schlumberger Gould Research (SGR) has provided of the order of $1m of in-kind support for reactor development/testing and Methrohm has given in-kind contributions in the form of equipment access and training support. The recent appointment of Cambridge Co-I Jize Yan has strengthened industrial aspects of IRP2 and we expect new developments in the near future.

In addition to the academic research programmes, the IRP2 team has targeted the development of a vertically integrated advanced electrochemical training and education programme. Currently two programmes are running under this activity (i) the Global Chemical Technologies Programe (GCTP) and the Advanced Electrochemical Techniques (AET) Programme. Further details of these can be found later in the report.

3.2.2 Update on work packages

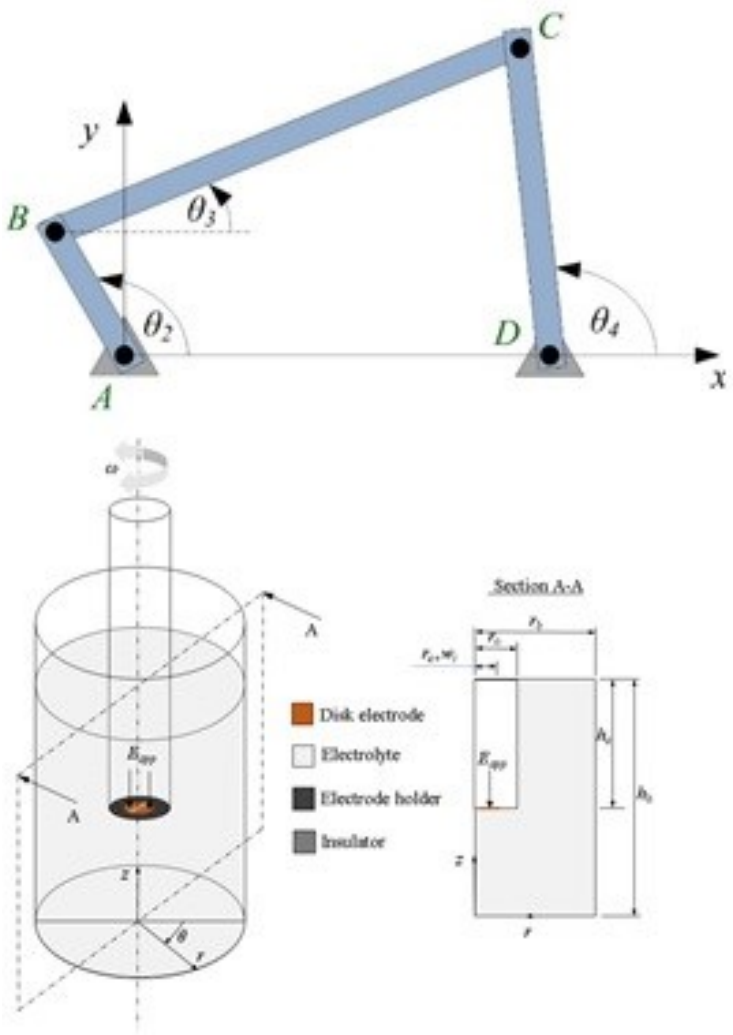


Fig 2.1.1 (a) Four-bar mechanism generating rocking motion, (b) Schematic of the rocking split-disc electrode with the axi-symmetric geometry

Work Package 2.1 Numerical Multi-Scale Electrochemical Modelling and Analysis

The numerical modeling and multiscale analysis work package has focused on the development of experimental protocols to improve the determination of electrolysis pathways and kinetics. These microscopic elements form a critical part of the energy efficiency of an electrolytic or electrochemical power source.

In current investigations a complex rocking motion of an electrode is explored since it has the potential to provide a unique mass transport and complex flow field potentially improving analysis and signal to noise aspects. In tandem with experiments, a mathematical model that aims to capture the essential physics of the rocking motion is derived based on a kinematic analysis of a four-bar mechanism (see Fig.2.1.1a). The rocking motion is then coupled with the transient conservation of mass, momentum, and species that takes it beyond the treatment of a standard rotating disk electrode. The voltammetric response of a dual semi-disc electrode for the oxidation of ferricyanide is predicted by the model at different rocking rates and compared with experiments. Furthermore, the limiting current dependency on the square root of the rocking rate is established. Here, the rocking motion is generated through the four-bar mechanism. A kinematic analysis of the four-bar mechanism is carried out by forming the vector-loop equations. The resulting algebraic equations are solved in Comsol Multiphysics v5.0. Knowing the input angular speed of the link AB, the rocking motion of the link CD is predicted by the analysis. The predicted rocking motion, in turn, serves as a boundary condition for the fluid-flow model. The rocking disk geometry considered in this study is shown in Fig. 2.1.1b.

In brief, the mathematical model accounts for the transient conservation of mass, momentum and species (convective-diffusion equation). It is resolved in 2D axisymmetric geometry and classical Butler-Volmer kinetics describes the electrode reaction. The electrolyte solution is assumed to be incompressible, Newtonian, to have negligible resistance and double-*layer* capacitance, and sufficient salt concentration to eliminate migration. These equations are solved with Comsol Multiphysics v5.0 as well. The voltammetric response predicted by the model agrees well with the experiments with increasing rocking rates. Furthermore, the limiting current varies linearly with the square root of the rocking rate similar to the rotating disk electrodes and as found in experiments. The model has been extended to three dimensions (3D) to account for the generator-collector configuration and simulations are in progress. The 3D simulations take a longer time due to the complexity of the problem. Typically, a run at 50 rpm takes nearly a week to complete due its multiscale nature; we have been working on reducing the computational cost through the introduction of conditional operators and time-step functions in Comsol. For example, the convergence time has been improved significantly: a simulation at 50 rpm took nearly 16 days when we started simulations; this has been reduced to a week now and should

be reduced further in the near future. This will allow for wide-ranging parameter studies for different operating, material and design conditions as well as addition of additional physics.

Two extensions of the model are currently being worked on: first, the inclusion of the flux due to migration of species to improve predictions; and second, to carry out a scaling analysis of the model equations that will provide the various inherent time and length scales which are be useful for model reductions as well as quantifying the underlying physics. The criteria for reaching a pseudo-steady state can be derived through scaling analysis and that solution can further be employed while solving the convective-diffusion equation to obtain the limiting current. Finally, we are considering the following phenomena: quantifying when the 2D symmetry breaks down; inclusion of turbulence models at higher rocking rates; exploring stochastic simulations to understand how sensitive the system is; and extensions to translating electrodes with a moving mesh in a combined Eularian/ Lagrangian reference frame.

Work Package 2.2 Electrode Development and Testing

Electrode development and testing forms part of the Advanced Materials and Electrocatalysis Group in IRP2 which focuses on electrocatalytic aspects of the programme. The group are currently preparing a wide variety of designer nanostructured electro-catalysts for applications such as water splitting in order to harvest sustainable energy sources. Meanwhile, the group is also paying significant attention to the design of efficient gas evolution electrodes. Recent studies have shown that catalysts that are very active for the electrochemical oxidation of formic acid should also be active for the reverse electrochemical reduction of CO2 to formic acid. IRP2 is therefore trying to apply the highly active and durable Pd-based alloy formic acid oxidation catalysts to the electrochemical conversion of CO2 and investigate the alloy effects (ligand, ensemble, and geometric) in the electrocatalytic reduction of CO2.

In the work of Prof Bin LIU (Co-I, NTU, IRP1 and 2), catalytic experiments with high efficiency under mild conditions such as room temperature and normal pressure are underway. The electrocatalytic oxygen evolution reaction (OER) has significant energy efficiency applications as it is critical in processes such as water splitting, fuel cells, and metal-air batteries. The oxygen evolution reaction requires four electrons transfer steps that corresponded the higher activation energy barrier for O-O formation. Transition metals are good alternatives for the noble metal such as IrO2 and RuO2 that are common catalysts on OER. To meet the requirements of electrocatalysts for electrocatalytic reactions with economic purposes, those are cost-effective price, good reaction activity, and low resistivity, the materials in our work have been designed as a core-shell structures. In our design, the conductive core is responsible for charge transfer and the active shell is in charge of reaction activity. Herein, we used the facile chemical bath deposition (CBD) to deposit 1D Co(OH)2 nanorods on the carbon cloth and further improved the OER activity by modification of MOF structure to increase the electrochemical activity surface area and calcination of obtained samples to form cobalt oxide to enhance the conductivity.

Research in collaboration with Prof Zhichuan XU (Co-I, NTU, IRP2) has focused on metal Phosphides and Mo-based nanomaterials. Metal phosphide nanoparticles, such as FeP, CoP and NiP, exhibit semiconductor properties. Their conductivities are usually not very good, which could limit their application in electrochemical catalysis. When these metal phosphides are combined with Cu nanowires, the situation improves significantly opening up new and potentially novel routes for the HER. In this report work is highlighted with Fe-on-Cu NWs and Co-on-Cu NWs which were synthesized by pyrolysis of metal carbonyls in the presence of Cu NWs, subsequently, the metal-on-Cu NWs were converted to metal phosphide-on-Cu NWs. In additional, the firm heterostructure could effectively avoid the drop of metal phosphides during the electrochemical experiment, which could improve the catalytic stability.

Further work has focused on Mo-based bimetallic nanomaterials. According to the volcano plot for

the HER, in order to obtain the optimum value of Gibbs free energy of adsorbed atomic hydrogen on the metallic surface, we tried to synthesize a set of Mo-based bimetallic nanomaterials, such as Mo-Fe, MoCu and MoAu. Mo atoms have strong affinity with H atoms, which dramatically impedes the HER process. Therefore, the second metal can weaken the bonding of Mo and H. Due to this synergy effect, the hydrogen evolution reaction activities are dramatically improved than their counterparts.

Naziah LATIFF (PhD Student, NTU, IRP2) and Prof Martin PUMERA (Co-I, NTU, IRP2) have been investigating the cytotoxicity of layered materials with promising properties for usage in energy related applications such as solar energy conversion, and energy storage devices; namely gallium selenide (GaSe), germanium sulphide (GeS), and black phosphorus. This is important in view of the rising research and possible commercialization of these materials as little is known currently on their toxicological effects. Two papers have been submitted and accepted; “Toxicity of layered semiconductor chalcogenides: beware of interferences”, and “The Cytotoxicity of Layered Black Phosphorus”. In addition the main factor(s) governing the increased performance seen in both p- and n-type doped graphenes for two important energy-related applications have been studied; for use in electrochemical capacitors (ECs) as well as electrocatalysts for hydrogen evolution reaction (HER) in fuel cells. This is important for the construction of graphene-based electrodes for ECs and HER catalysts. This project is currently in progress.

Work Package 2.3 Electrochemical Reactor Engineering: Cogeneration and Electrosynthesis

The reactors groups are currently exploring electrocatalytic processes and electrochemical analysis. Bahareh KHREZI (RF, NTU, IRP2) has been working with both Martin PUMERA (Co-I, NTU, IRP2) and Richard WEBSTER (Co-I, NTU, IRP2), on different aspects of reactor research.

In her work with Martin PUMERA, Bahareh has been been working on catalytic micro/nanomotors. These micro/nanomotors operate based on the propulsion principle, which is the catalytic decomposition of fuel, typically H_2O_2, on platinum (Pt) surfaces to create oxygen bubbles that subsequently propel the devices. There has been a recent increase of interest in self-propelled catalytic micro/nanomotors. Self-propelled micro/nanomotors are at the forefront of nanotechnology research. These artificial machines are expected to be able to engage in various tasks, ranging from drug delivery to environmental remediation and discovery of natural resources.

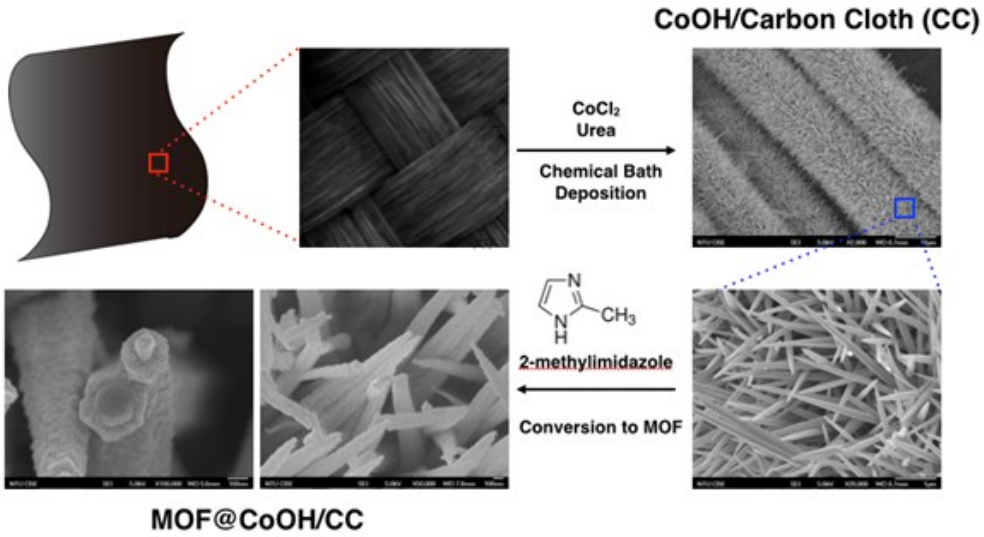
Study of motion and transport of micro/nanomotors within microfluidic channels represent a critical step toward designing integrated microdevices, powered by autonomous transport (instead of pressure or electrical-driven bulk flow).

In separate investigations Bahareh KHREZI (RF, NTU, IRP2) and Richard WEBSTER (Co-I, NTU, IRP2) have been exploring electrochemical sensing applications with an initial focus on gas sampling. The group has successfully analysed samples to study the composition of inorganic and organic components. As part of the electroanalysis programme work has been recently published highlighting the annual pollution caused by the Hungry Ghost Festival.

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.

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

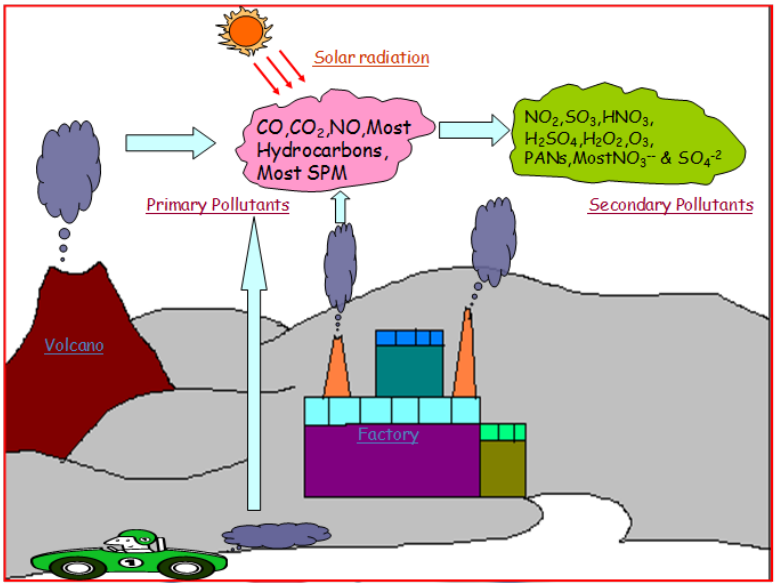


H. –Y. Wang, Y. –Y. Hsu, R. Chen, T. –S. Chan, H. B. Chen and B. Liu . DOI: 10.1002/aenm.201500091

Abstract

Efficient and earth abundant electrocatalysts for high-performance oxygen evolution reaction (OER) are essential for the development of sustainable energy conversion technologies. Here, a new hierarchical Ni–Co oxide nanostructure, composed of small secondary nanosheets grown on primary nanosheet arrays, is synthesized via a topotactic transformation of Ni–Co layered double hydroxide. The Ni^{3+}-rich surface benefits the formation of NiOOH, which is the main redox site as revealed via in situ X-ray absorption near edge structure and extended X-ray absorption fine structure 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 dec^{-1} in alkaline media. The improvement in the OER activity can 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.

Annual air pollution caused by the Hungry Ghost Festival

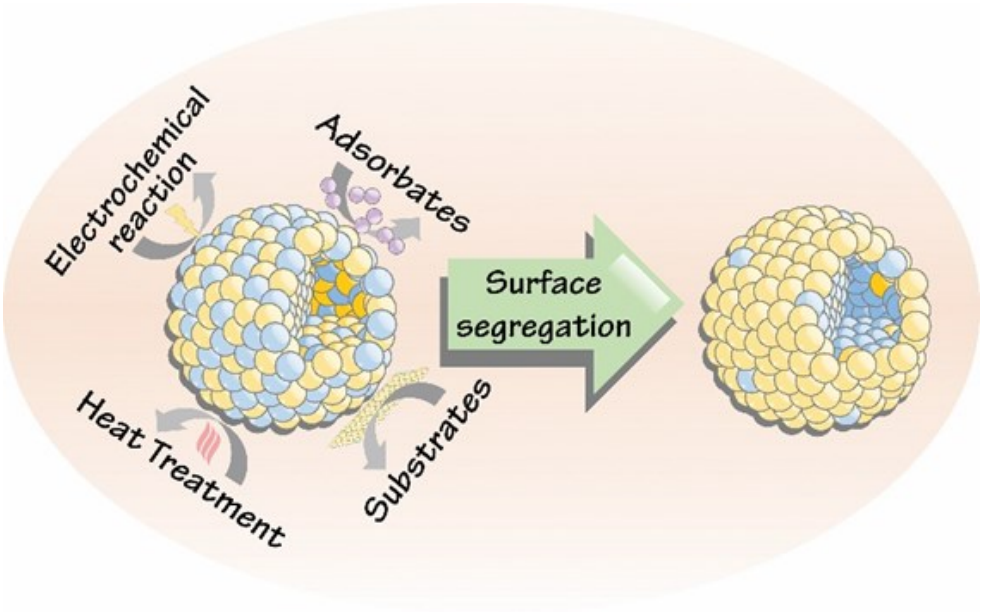


B. Khezri, Y.Y. Chan, L.Y.D. Tiong, R.D. Webster,

DOI: 10.1039/C5EM00312A

Abstract

Burning of joss paper and incense is still a very common traditional custom in countries with a majority Chinese population. The Hungry Ghost Festival which is celebrated in the 7 month of the Chinese calendar is one of the events where joss paper and incense are burned as offerings. This study investigates the impact of the Ghost Month Festival (open burning event) on air quality by analysis of the chemical composition of particulate matter (PM) and rainwater samples collected during this event, compared with data collected throughout the year, as well as bottom ash samples from burning the original joss paper and incense. The results showed that the change in the chemical composition of the rainwater and $PM_{2.5}$ (PM ≤ 2.5 μm) atmospheric samples could be correlated directly with burning events during this festival, with many elements increasing between 18% and 60% during August and September compared to the yearly mean concentrations. The order of percentage increase in elemental composition (in rain water and $PM_{2.5}$) during the Hungry Ghost Festival is as follows: Zn > Ca > K > Mg > Fe > Al > Na ~ Mn ~ Ti ~ V > Cu > As > Ni > Co > Cd > Cr > Pb. The chemical composition of the original source materials (joss paper and incense for combustion) and their associated bottom ash were analysed to explain the impact of burning on air quality.



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

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

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

Highlights

•This review article introduces the most recent and important progress of the surface segregation in bimetallic nanoparticles and the impacts in electrocatalysis.

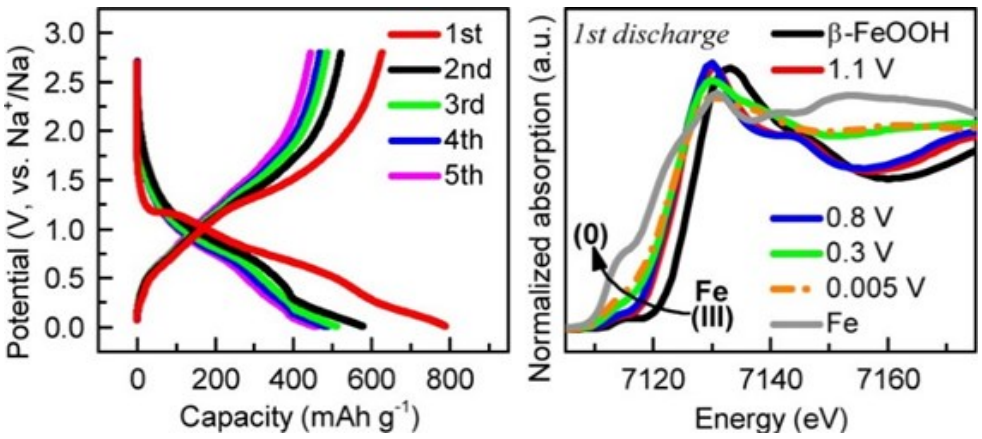
•Typical segregation inducements and surface characterization techniques are discussed in detail.

•This review summarizes the advantages and disadvantages of surface segregation of bimetallic electrocatalysts and highlights the challenges and future perspectives.

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 sur-

face 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.



β-FeOOH: An Earth-Abundant High-Capacity Negative Electrode Material for Sodium-Ion Batteries

Linghui Yu, Luyuan Paul Wang, Shibo Xi, Ping Yang, Yonghua Du, Madhavi Srinivasan, and Zhichuan J. Xu. DOI: 10.1021/acs.chemmater.5b01747

Relevance to the work of the IRP: IRP2 supports leading-edge research in the electrochemical fields. This project focuses on the electrochemical application in the field of Sodium-ion batteries.

Highlights

•β-FeOOH is a very promising low-cost anode material, with a high reversible capacity (>500 mAh g^{-1} during initial cycles).

•The 5 nm β-FeOOH has more serious kinetic restrictions, and thus lower capacities, while it shows better cycling stability.

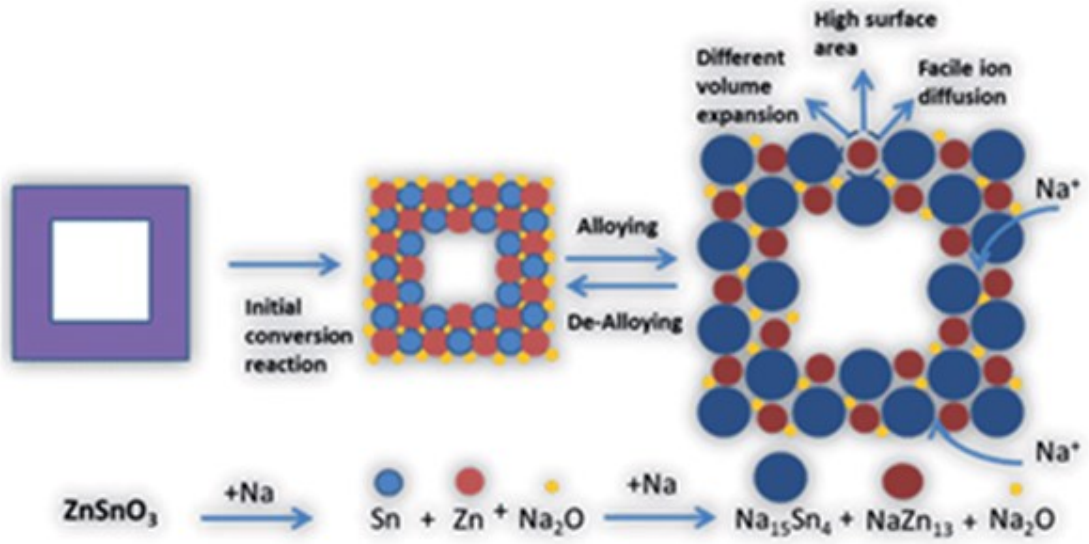
Abstract

Thanks to the great earth abundance and excellent energy density of sodium, sodium-ion batteries are promising alternative energy storage devices for large-scale applications. Developing cheap, safe, and high-capacity sodium-ion battery anode materials is one of the critical challenges in this field. Here, we show that β-FeOOH is a very promising low-cost anode material, with a high reversible capacity (>500 mAh g^{-1} during initial cycles). The fundamental characteristics associated with the discharge/charge processes, in terms of the redox reactions, formation/deformation of the solid electrolyte interface (SEI) layers, and structural and morphological changes, are comprehensively investigated. In addition, a comparison study shows that the smaller-sized FeOOH has more serious kinetic restrictions, and thus lower capacities, while it shows better cyclability than the bigger one. Origins of the large overpotential are discussed, and it is suggested that the overpotential should be mainly due to the features of the surface-concentration-dependent potential and the slow diffusion of Na^+; in addition, the presence of the SEI layers may also contribute to the overpotential.

Polycrystalline zinc stannate as an anode material for sodium-ion batteries

Luyuan Paul Wang, Yi Zhao, Chao Wei, Chuiling Wong, Madhavi Srinivasan, and Zhichuan J. Xu. DOI: 10.1039/C5TA02734A

Relevance to the work of the IRP: IRP2 supports leading-edge research in the electrochemical fields. This project focuses on the electrochemical application in the field of Sodium-ion batteries.



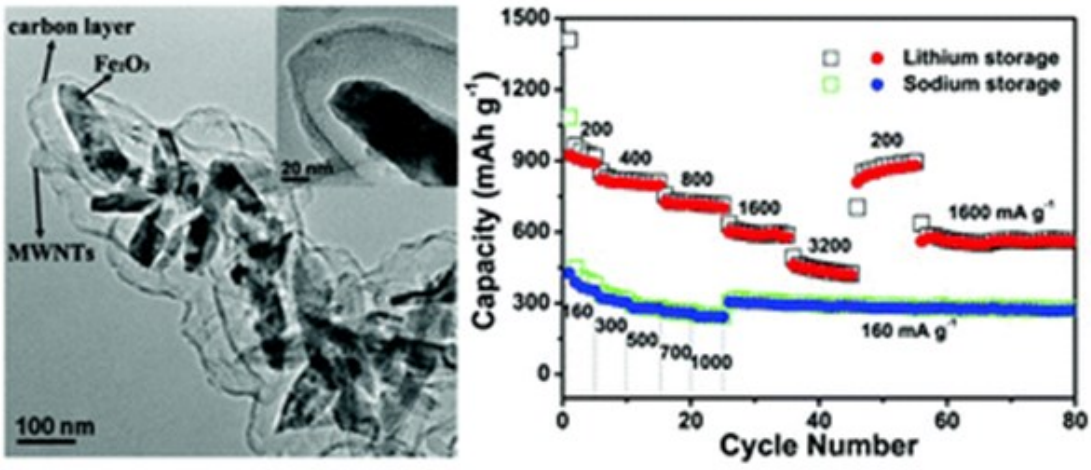
Highlights

•The electrochemical performance of polycrystalline $ZnSnO_3$ as an anode material was demonstrated for the first time in NIBs

•The hollow cubes were able to deliver a reversible capacity of 315 mA h g^{-1} when cycled at a current density of 30 mA g^{-1} within a voltage window of 0.01–3.00 V vs. Na^+/Na.

Abstract

In this work, we report for the first time the electrochemical performance of polycrystalline $ZnSnO_3$ as an anode material for sodium ion batteries (NIBs). The as-synthesized cubes were found to be derived from the self-assembly of $ZnSnO_3$ nanoparticles. A hollow interior was subsequently obtained through a facile etching reaction. A reversible capacity of 315 mA h g^{-1} (~0.3 V *vs.* Na^+/Na) was obtained when cycled between 0.01 and 3.00 V *vs.* Na^+/Na at 30 mA g^{-1}. A decent capacity retention of 92% was also observed after 100 cycles when tested at 250 mA g^{-1}. The $ZnSnO_3$ hollow cubes were found to demonstrate superior electrochemical performance when compared with both $ZnSnO_3$ solid cubes and manually blended ZnO–SnO_2. The enhanced performance is believed to be attributed to the even distribution of Zn and Sn metallic nanoparticles following the first conversion process, which, conversely, is unachievable in manually blended ZnO–SnO_2. Additional free space owing to different volume expansions during alloying of Zn and Sn easily permits diffusion of Na^+ to the interior of the microcube, giving rise to enhanced capacity and cyclability.



Yolk–shell Fe_2O_3 @ C composites anchored on MWNTs with enhanced lithium and sodium storage

Yi Zhao, Zhenxing Feng, and Zhichuan J. Xu. DOI: 10.1039/C5NR01281C

Relevance to the work of the IRP: IRP2 supports leading-edge research in the electrochemical fields. This project focuses on the electrochemical application in the field of lithium-ion and Sodium-ion batteries.

Highlights

•A novel architecture with yolk–shell Fe_2O_3 ⊙ C composites anchored on MWNTs has been designed and fabricated for high performance LIBs and NIBs.

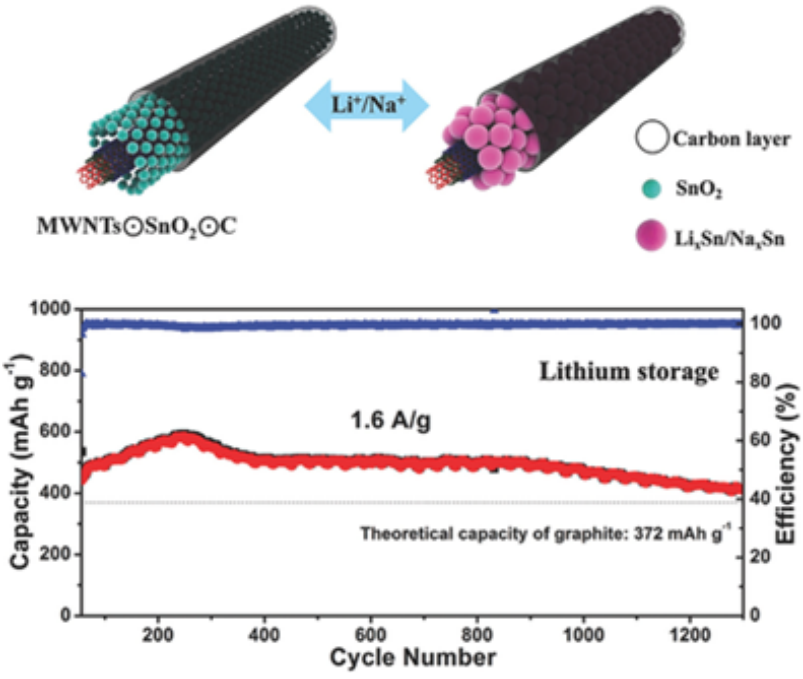
•For lithium storage, this electrode was able to retain high specific capacities of 1024 and 502 mA h g^{-1} after 360 cycles, when cycled at 200 and 2000 mA g^{-1}, respectively.

•For sodium storage, this composite also delivered excellent rate capabilities and good cycling stability.

Abstract

A unique architecture with yolk–shell Fe_2O_3 @ C composites attached to the surface of MWNTs is designed. Benefiting from the good electrical conductivity of MWNTs and carbon layers, as well as the large void space to accommodate the volume expansion/extraction of Fe_2O_3 during battery cycling, the obtained MWNT@Fe_2O_3 @ C exhibited outstanding lithium and sodium storage performance.

Reserving Interior Void Space for Volume Change Accommodation: An Example of Cable-Like MWNTs@SnO_2@C Composite for Superior Lithium and Sodium Storage



Yi Zhao, Chao Wei, Shengnan Sun, Luyuan Paul Wang, and Zhichuan J. Xu. DOI: 10.1002/advs.201500097

Relevance to the work of the IRP: IRP2 supports leading-edge research in the electrochemical fields. This project focuses on the electrochemical application in the field of lithium-ion and Sodium-ion batteries.

Highlights

•A novel architecture with nanostructure of multi-walled carbon nanotubes-in-SnO_2-in-carbon layer composites anchored on MWNTs has been designed and fabricated for high performance LIBs and NIBs.

•After 100 successive discharge/charge cycles, the MWNTs@SnO_2@C composite still delivered a high discharge capacity of 944 mAh g^{-1}, which was superior than most of the reported SnO_2 based composites.

Abstract

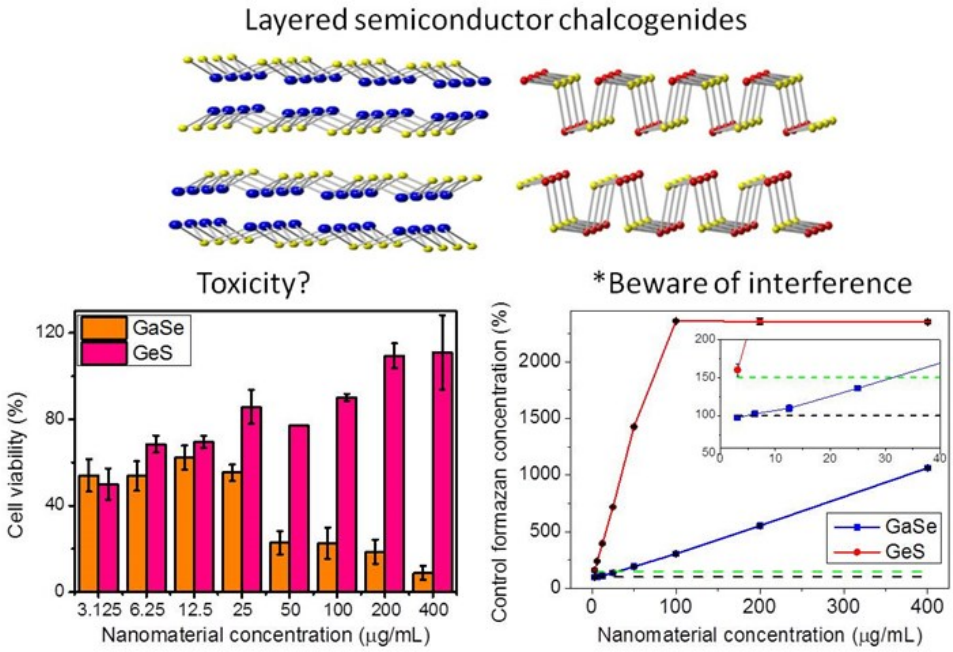
Reserving interior void space in the cable-like structure of multiwalled carbon nanotubes-in-SnO_2-in-carbon layer (MWNTs@SnO_2@C) is reported for the first time. Such a design enables the structure performing excellent for Li and Na storage, which benefit from the good electrical conductivity of MWNTs and carbon layer as well as the reserved void space to accommodate the volume changes of SnO_2.

Toxicity of layered semiconductor chalcogenides: beware of interferences

Naziah Latiff, Wei Zhe Teo, Zdenek Sofer, Štěpán Huber, Adrian C. Fisher and Martin Pumera. DOI: 10.1039/C5RA09404F

Relevance to the work of the IRP: This project focuses on the development of safe materials for important energy applications.

Highlights



- Human lung carcinoma epithelial cell line (A549) was used for this investigation since lungs are likely to be the first point of contact with the body when layered semiconductor chalcogenides (GaSe, GeS) enter through inhalation.
- Following a 24 h exposure of A549 cells to different concentrations of GaSe and GeS, their cell viabilities were determined using two well-established cell viability assays; water-soluble tetrazolium salt (WST-8) and methyl-thiazolyldiphenyl-tetrazolium bromide (MTT).
- Test materials can significantly interfere with the WST-8 and MTT cell viability assays, and control experiments were conducted to ensure reliability of data obtained.
- GeS interfered significantly with the two cell viability assay reagents tested.
- GaSe was found to be relatively more toxic than another group of layered chalcogenides; exfoliated transition metal dichalcogenides (MoS_2, WS_2, WSe_2).

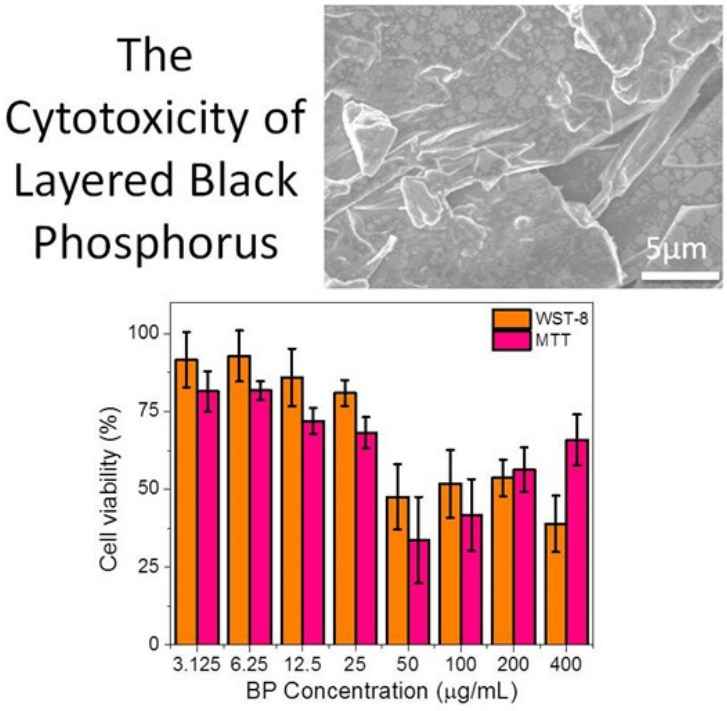
Abstract

The absence of bandgap in graphene has opened exploration in a new class of 2D nanomaterials: layered semiconductor chalcogenides. Research has found that they have promising properties which are advantageous for applications in a wide range of fields such as solar energy conversion, field effect transistors, optoelectronic devices, energy storage, and is expanding into biomedical applications. However, little is known about their toxicity effects. In view of the possibility of employing these materials into consumer products, we investigated the cytotoxicity of two common layered semiconductor chalcogenides, namely GaSe and GeS, based on cell viability assessments using water- soluble tetrazolium salt (WST-8) and methyl-thiazolyldiphenyl-tetrazolium bromide (MTT) assays after a 24 h exposure to varying concentrations of the nanomaterials on human lung carcinoma epithelial cells (A549). The cytotoxicity results indicated that GaSe is relatively more toxic than another group of 2D layered chalcogenide: transition metal dichalcogenides (MoS_2, WS_2, WSe_2). On the other hand, GeS appeared to be non-toxic, with the concentration of GeS introduced having a positive correlation with the cell viability. Control experiments in cell-free conditions revealed that both GaSe and GeS interfered with the absorbance data gathered in the two assays, but the interference effect induced by GaSe could be minimized by additional washing steps to remove

the nanomaterials prior to the cell viability assessments. In the case of GeS, however, the interference effect between GeS and both assay dyes were still significant despite the washing steps adopted, thereby giving rise to the false cytotoxicity results observed for GeS. Therein, we wish to highlight that control experiments should always be carried out to check for any possible interferences between the test specimen and cell viability markers when conducting cell viability assessments for cytotoxicity studies

The Cytotoxicity of Layered Black Phosphorus

Naziah M. Latiff, Wei Zhe Teo, Zdenek Sofer, Adrian C. Fisher, and Martin Pumera. DOI: 10.1002/chem.201502006



Relevance to the work of the IRP: This project focuses on the development of safe materials for important energy applications.

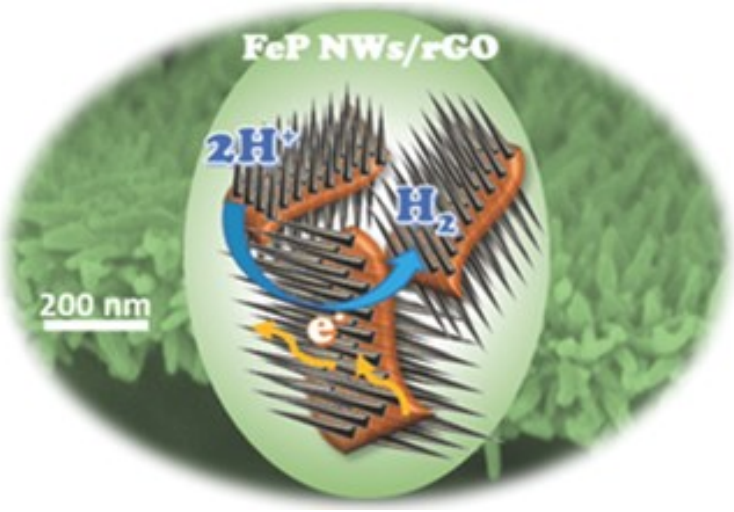
Highlights

- Human lung carcinoma epithelial cell line (A549) was used for this investigation since lungs are likely to be the first point of contact with the body when layered black phosphorus enters through inhalation.
- Following a 24 h exposure of A549 cells to different concentrations of black phosphorus, their remaining cell viabilities were determined using two well-established cell viability assays; water-soluble tetrazolium salt (WST-8) and methyl-thiazolyldiphenyl-tetrazolium bromide (MTT).
- Test materials can significantly interfere with the WST-8 and MTT cell viability assays, and control experiments were conducted to ensure reliability of data obtained.
- Black phosphorus was observed to have a generally intermediate toxicity between that of graphene oxides and exfoliated transition-metal dichalcogenides (MoS_2, WS_2, WSe_2).
- This relatively low toxicity paves the way to utilization of black phosphorus.

Abstract

Black phosphorus (BP), the latest addition to the family of 2D layered materials, has attracted much interest owing to potential optoelectronics, nanoelectronics, and biomedicine applications. Little is known about its toxicity, such as whether it could be as toxic as white phosphorus. In response to the possibility of BP employment into commercial products and biomedical devices, its cytotoxicity to human lung carcinoma epithelial cells (A549) was investigated. Following a 24 h exposure of the cells with different BP concentrations, cell viability assessments were conducted using water-soluble tetrazolium salt (WST-8) and methylthiazolyldiphenyltetrazolium bromide (MTT) assays. The toxicological effects were found to be dose-dependent, with BP reducing cell viabilities to 48% (WST-8) and 34 % (MTT) at 50 mg mL^{-1} exposure. This toxicity was observed to be generally intermediate between that of graphene oxides and exfoliated transition-metal dichalcogenides (MoS_2, WS_2, WSe_2). The relatively low toxicity paves the way to utilization of black phosphorus.

Construction of Efficient 3D Gas Evolution Electrocatalyst for Hydrogen Evolution: Porous FeP Nanowire Arrays on Graphene Sheets



Ya Yan , Larissa Thia , Bao Yu Xia , Xiaoming Ge , Zhaolin Liu , Adrian Fisher and Xin Wang. DOI: 10.1002/advs.201500120

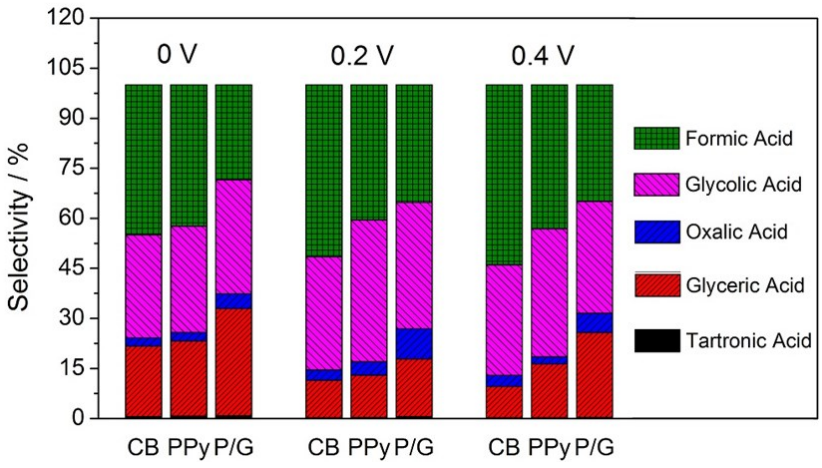
Relevance to the work of the IRP: IRP2 supports leading-edge research in the fields of electrocatalysis and electrochemical characterization. The project focusses on the development of new catalysts for fuel cell related applications.

Highlights

- Designing 3D hierarchical nanocomposite of vertically aligned porous FeP nano-wires (NWs) on reduced graphene oxide (rGO)
- Construction of efficient hydrogen evolution catalyst
- Attractive to extend this nanostructuring strategy to other functional nanocomposites by combining different dimensional nanomaterials

Abstract

We introduced a facile method to construct hierarchical nanocomposites by combining one dimensional (1D) iron phosphide (FeP) nanowires with 2D reduced graphene oxide (rGO) nanosheets. Porous FeP nanowire arrays are aligned vertically on rGO substrate by pseudomorphic transformation of the as-formed hierarchical FeO(OH) NWs/rGO intermediate. Benefit ting from the unique structure, the FeP NWs/ rGO composite catalyst achieves high activity, stable electrolysis towards HER. It is found the vertically oriented porous FeP NWs on rGO is a ideal catalytic structure for gas evolution because of the improved electrode/electrolyte interaction and efficient utilization of the catalysts. This study offers a straightforward way to design efficient gas evolution materials at the nanoscale level. Extension of this nanostructuring strategy to other functional nanocomposites is attractive by combining different dimensional nanomaterials.



Pd Nanoparticles on Carbon Nitride-Graphene for the Selective Electro-Oxidation of Glycerol in Alkaline Solution

Haibo Wang, Larissa Thia, Nan Li, Xiaoming Ge, Zhaolin Liu, Xin Wang. DOI: 10.1021/acscatal.5b00183

Relevance to the work of the IRP: IRP2 supports leading-edge research in the fields of electrocataly-

sis and electrochemical characterization. The project focusses on the development of cogeneration of high value chemical and electricity using glycerol fuel cell.

Highlights

- Pd nanoparticles supported on CN_x/Graphene is developed as an electrocatalyst for glycerol oxidation.

Abstract

A hybrid support consisting of carbon nitride and graphene (CN_x/G) is prepared by annealing polypyrrole/GO at 800 ^{o}C. Pd nanoparticles (NPs) are then loaded onto the support by a microwave-polyol method. Pd-CN_x/G is used as a catalyst for glycerol electro-oxidation in 0.5 M NaOH aqueous solution. Electrochemical characterization and product analysis by high performance liquid chromatography show that, compared to Pd NPs supported on carbon black, Pd NPs on support containing nitrogen atoms has the ability to promote selectivity towards three carbon products as well as increase activity. The main factors influencing the selectivity and activity are also discussed.

3.2.4 Other Activities and Achievements

Advanced Electrochemical Techniques Training Course

The inaugural Advanced Electrochemical Techniques Programme (AETP), was hosted by IRP2 in August 2015. The course was attended by local industrialists, C4T researchers from Singapore and the UK, and instrument manufacturer Metrohm. The objective of the course was to provide advanced lectures, seminars and hands on experiments for industrialists and scientists who use or wish to use electrochemical methods for their research or industrial applications.

The programme began on the 11th August with a series of introductory lectures from Prof. Frank Marken (University of Bath) and Dr Adrian Fisher (University of Cambridge) on the fundamentals of electrochemistry. Topics covered included key principles and controlling processes that govern electrochemical reactions, with a focus on electron transfer theory, mass transport (diffusion, convection, migration), coupled chemical reaction mechanisms & solid state electrochemistry. The afternoon was dedicated to hands on training sessions orientating delegates to the essential aspects of good experimental design and advanced analysis.

Day two was focussed on advanced electroanalysis, with lectures from Prof Richard Webster (NTU) and Dr Adrian Fisher. The afternoon was dedicated to experimental training with laboratory sessions carried out at the NTU laboratories of Richard Webster. Day three focused on applied electrochemical systems and their experimental analysis. Members of Prof Prof Erik Birgersson's group (NUS) and Dr Adrian Fisher's group delivered lectures and software analysis training in applied electrochemical problems. The final day provided a series of guest lectures allowing delegates to be exposed to current challenges and opportunities within the electrochemical sector. Prof Jim Yang Lee (NUS) and Prof Frank Marken gave overviews of the electrochemical energy storage sector and sensors area using nanoscale electrodes.

The course was kindly sponsored by Methrohm, who provided staff support from their Europe, Singapore, Thailand and Indonesia offices, as well instruments, software and hardware training sessions and a delicious dinner for all the course participants.

Global Chemical Technologies Programme 2015

IRP2 once again hosted a successful visit from the students of the Global Chemical Technologies Programme. The programme began with a visit to the CREATE Campus on the 1st July 2015, where the delegates were given an introduction to CREATE and the research activities of C4T. In the afternoon the students were hosted by the University of Berkeley, with Dr Matthew Sherburne presenting the Berkeley programmes SinBer BEST and SinBerRISE. This was followed by a research workshop hosted by the C4T programme where C4T Research Fellows presented aspects of their ongoing activities as part of the programme.

The following day the programme moved to NUS. Professor Jim Yang Lee (PI, NUS, IRP2) gave an introduction to NUS and key research activities on the campus. In the afternoon the programme visited the A*STAR Institute of Chemical and Engineering Sciences on Jurong Island. Dr Ann Chow presented the key objectives of the A*STAR institutes and gave a broad overview of the research activities of ICES and the opportunities to either study or work with the institute in the future. The students were then taken on an extensive tour of the institute to see the impressive research and pilot plant facilities that are housed at ICES. The GCTP programme continued on the 3rd July, with a visit to NTU. Students where given an overview of NTU research and undergraduate programmes by Professor Xin Wang. This was followed by presentations and research tours including visits to the laboratories in the School of Chemical and Biomedical Engineering, Department of Chemistry and Department of Materials.

Honours and Memberships

- Prof Richard WEBSTER (Co-I, NTU, IRP2) was made a Fellow of the Royal Society of Chemistry

Grants

- Prof. WANG Xin has been awarded a grant by the Singapore Maritime Institute as Principal investigator with the amount of S$950,000. The project title is: Development of a total solution of exhaust gas cleaning system(EGCS) and its installation for dry cargo carriers. This project is in collaboration with a few industrial partners, including Nippon Yusen Kabushiki Kaisha/ Monohakobi Technology Institute , Nippon Kaiji Kyokai (ClassNK), and Alfa Laval, Japan. Using the knowledge gained from C4T work, Prof. Wang's group will focus on CO_2 reduction and capture to compensate the CO_2 emissions due to energy consumption by EGCS.

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

September 2015

3.3.1 IRP3 Research Overview

IRP 3 presents three main strategies to reduce carbon emissions in the chemical industry. The first element is based on a process system engineering approach in which we want to create a virtual environment for chemical processes in an industrial park. We will use this environment as a platform to study the impact of carbon reduction technologies and also make use of mathematical models to improve efficiency of the implemented processes. The second element investigates the fuel of present and future engines with respect to the emissions produced in present and future internal combustion engines. We also want to understand how a particular demand of fuel components influences the operation of a refinery. In other words if a future fuel consists of particular fractions of refinery products or biofuels what chemical processes need to be added to or modified in a refinery. Thirdly, connecting to IRP1 and IRP2, we study how we can use flame synthesis of nanoparticles to scale up the production of potential heterogeneous catalysts. Flame synthesis is a very cheap method to produce nanoparticles which can easily be scaled-up. In the first instance we want to understand and control the process of producing thin films of titania and silica particles.

Probably the most exciting result in this reporting period is the launch of the first interactive version of the “J-Park simulator”. This is exciting for two reasons. It marks a joint effort between IRP3 and IRP4 and is the first ever simulation environment of an industrial park of the size of Jurong Island on the web. Although it is in a very early stage it allows to study the electrical power grid on the island. For further details go to: www.jparksimulator.com.

This work package also benefitted during the reporting period from the work of Daryl YONG, an intern from the NUS Global Engineering Programme. Daryl further developed the "J-Park Simulator" Java web application.

The last six months have been very successful developing links with industrial sponsors. In particular the new Cambridge CARES studentships proved to be a successful funding tool. Huntsman Tioxide and CMCL Innovations have both made cash contribution to co-fund three studentships. One more studentship is likely to be funded by Johnson Matthey. These studentships cover aspects of the nanoparticle work in IRP3. More exciting collaborations with ExxonMobil and DSO are on the horizon.

In addition, members of IRP 3 attended and organized various conferences. There was a conference on the development of the “J-Park simulator” in Cambridge, attended by both Singapore and Cambridge-based C4T members from IRP3 and 4. Prof Karimi and PhD student Pulkit Chhabra were involved in the 13th International Conference on Carbon Dioxide Utilisation (ICCDU) at NUS. I had the chance to give (with Dr Heiko Aydt, TUM CREATE) the inaugural session of the Monthly Seminar Series by CREATE PIs, an event programme which promotes the interaction between the different CREATE entities.

In the coming months, IRP3 is looking forward to accelerating development of the J-Park Simulator and the opportunity to step up our experimental programme, once the CREATE labs become operational in 2016.

3.3.2 Update on work packages

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

Two papers have been published relating to Jurong Island as an eco-industrial park. The first paper presents a literature review of existing eco-industrial parks and methodologies which can be used in the process of identifying and introducing cooperation in industrial parks. The second paper explores how to apply the ideas of Industry 4.0, i.e. full virtualisation of industry, to Jurong Island. A third paper, on hierarchical multi-level modelling and optimisation of eco-industrial parks, is in the process of being finalised and is due to be submitted for publication in the very near future.

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

Four papers have been submitted: One is concerned with soot produced from a wall film of fuel in internal combustion engines – a source of emissions that is relatively poorly understood. The second paper considers mixtures of certain fuels, and how the mixture composition influences sooting propensity and soot particle characteristics. The third paper investigates the structure of soot particles formed in flames of relevant transportation fuels by means of high-resolution transmission electron microscopy. The fourth paper sheds further light on the structure of the polycyclic aromatic hydrocarbons (PAHs) constituting soot particles through optical band gap diagnostics. In addition, one paper has been published on numerically simulating such PAHs in certain types of flame setups. Another paper previously submitted, on sooting propensity of surrogates for the aromatic fractions of diesel and gasoline fuels, has now appeared in print.

Prof Wenming YANG (Co-PI, NUS, IRP3) and WU Shaohua (PhD student, NUS, IRP3) are investigating the performance and emissions formation of various fuels in internal combustion engines and transportation. A three dimensional numerical simulation platform by combining KIVA 4 and CHEMKIN is being developed, detailed chemical reaction mechanisms have been developed for fossil diesel, biodiesel and their blends. An experimental setup is being built-up to investigate the formation mechanism of soot in the flame of various fuels.

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

Two previously submitted papers in the area of chemical kinetics of some precursors in the formation of titania and silica nanoparticles in flames have now appeared in print. A third paper presenting an improved and reduced kinetic mechanism of the oxidation of a silicon nanoparticle precursor is in the process of being finalised and is due to be submitted for publication in the very near future.

A particle burner and a soot burner have been purchased from Stanford University and have been assembled in borrowed lab space at NTU. WANG Weijing (RF, NTU, IRP3) will visit Stanford for several weeks in September 2015 to learn from the group there about techniques. On his return, WANG Weijing will take forward the Singapore-based work in WP3.3 on the flame synthesis of nanoparticles. CARES is currently in discussion with Johnson Matthey about a possible studentship in this area.

WP 3.4: Modelling and optimisation of unit operations

A paper has been published in which a computational method capable of dealing with spatial inhomogeneities in particle processes is developed. Such inhomogeneities are ubiquitous in real-world unit operations. Another publication, on a fluidised bed gasifier unit operation, has now appeared in print.

Prof Iftekhar KARIMI (PI, NUS, IRP3), Sushant GARUD (PhD student, NUS, IRP3) and Pulkit CHHABRA (PhD student, NUS, IRP3) have worked on developing an Aspen Plus model for a case study on biodiesel plant. This involves measuring kinetic data for biodiesel reaction and parametrizing the Aspen model using MODS. In addition, they have looked at ways to develop better surrogate models more efficiently. After much effort, they now have a working Aspen model for the biodiesel process under study. The key highlight is the use of a more reasonable fluid package in Aspen Hysys for this complex organic system. Interfacing errors with the Python interface have been eliminated and the model seems ready for parameterization studies. The experimental setup required for measuring the kinetics of the biodiesel reaction is also in place, and the experiments have just begun. A novel smart and adaptive algorithm for sampling input data for surrogate model development has also been developed.

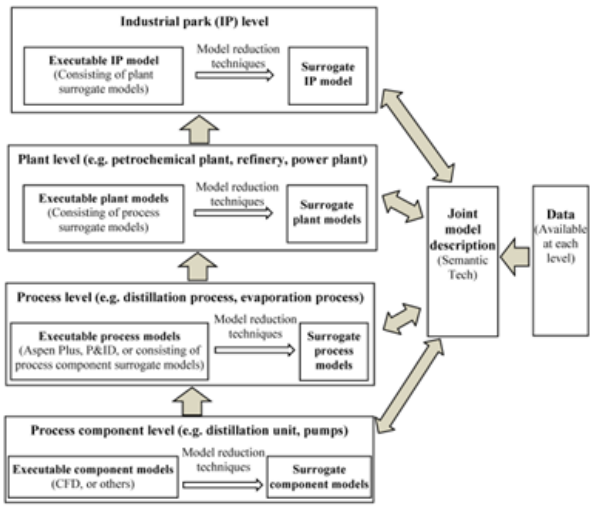
WP 3.5: Automated model development and experimental design/decision support

One of the papers published on Industry 4.0 in this period elaborates on virtualisation, high-performance computing, expert systems, and semantic web technologies and thus sketches out a road-map how to fully automate modelling and ultimately operating (which includes decision support) an eco-industrial park such as Jurong Island.

This work package also benefitted during the reporting period from the work of Daryl YONG, an intern from the NUS Global Engineering Programme. Daryl further developed the "J-Park Simulator" Java web application that integrates spatial information with a PowerWorld simulation of the power network.

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 . DOI: 10.1016/j.egypro.2015.07.313

Relevance to the work of the IRP: WP1, WP5

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.

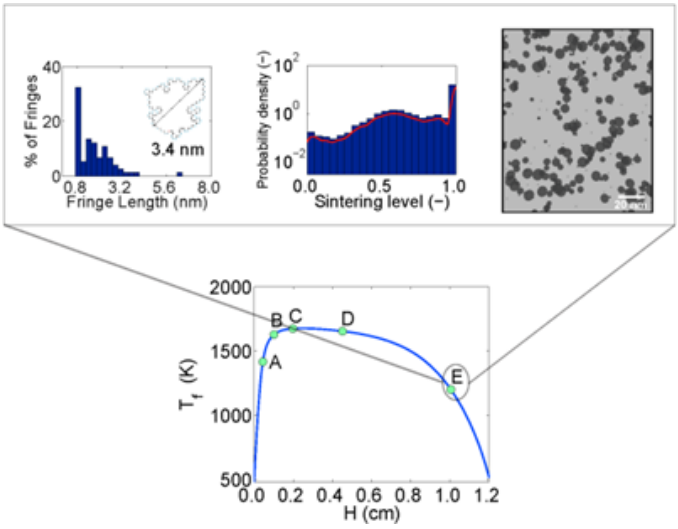
Abstract

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.

Numerical simulation and parametric sensitivity study of particle size distributions in a burner-stabilised stagnation flame

Edward K.Y. Yapp, Dongping Chen, Jethro Akroyd, Sebastian Mosbach, Markus Kraft, Joaquin Camacho, and Hai Wang. *DOI: 10.1016/j.combustflame.2015.03.006*

Relevance to the work of the IRP: WP2



Highlights

- Detailed population balance model used to perform a parametric sensitivity study
- Soot morphology and its effect on the interpretation of mobility size measurements

Abstract

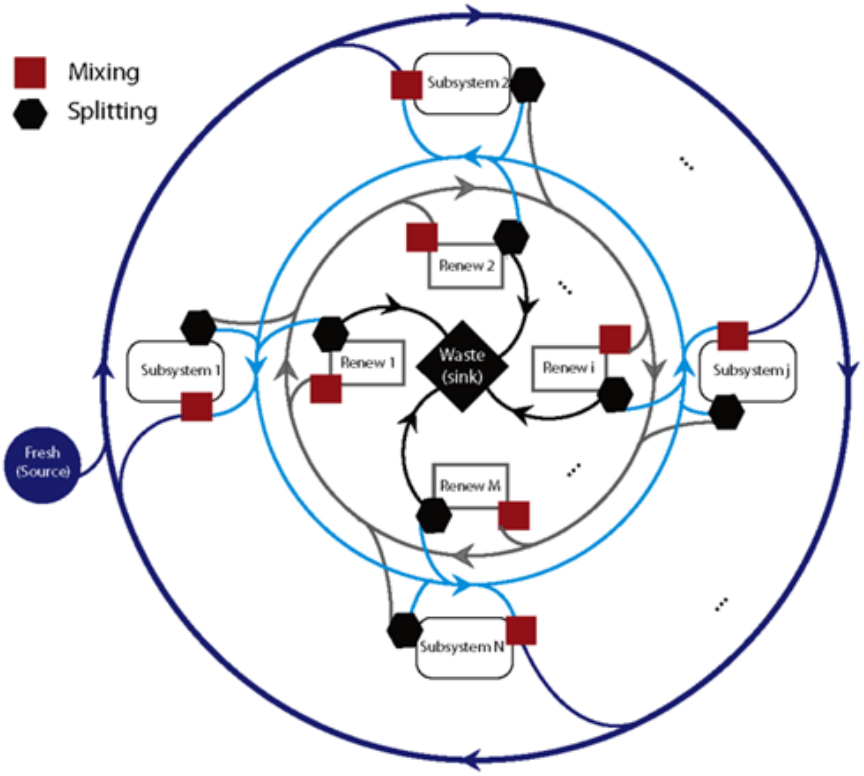
A detailed population balance model is used to perform a parametric sensitivity study on the computed particle size distributions (PSDs) for a laminar premixed ethylene burner-stabilised stagnation flame. The soot morphology in the post-flame region is studied using computed sintering level distributions, fringe length analysis of the polycyclic aromatic hydrocarbons (PAHs) within the primary soot particles, and TEM-like projections of aggregates. The computed PSDs were sensitive to the minimum particle inception size, the coagulation rate and the inception species concentration. Changes in the particle inception size and the coagulation rate led to an overall shift in the position of the coagulation peak. Only changes in the inception species concentration led to a systematic shift in both the position of the trough between the modes of the bimodal PSD and the coagulation peak at larger diameters. Given the overall model, varying the inception species concentration with each burner-stagnation plate separation was the only means possible to achieve a satisfactory agreement between the experimental and computed PSDs. This study shows that further work is required to better understand the soot precursor chemistry, the inception of soot particles. Additional work may also be needed in the area of experimental mobility sizing for the flame studied here.

Quantitative tools for cultivating symbiosis in industrial parks; a literature review

Catharine A. Kastner, Raymond Lau, and Markus Kraft. DOI: 10.1016/j.apenergy.2015.05.037

Relevance to the work of the IRP: WP1

Highlights



- Quantitative tools and methods to cultivate industrial symbiosis exchanges are reviewed.
- A table of existing eco-industrial parks which have been studied is included.
- Alterations in existing infrastructure issues are examined.
- Motivational and restricted information concerns are discussed.

Abstract

The quantitative tools and methods that have been developed to identify and cultivate industrial symbiotic exchanges in existing industrial parks to minimize overall energy and material consumption are reviewed. The issues relevant to adapting an existing park differs from those associated with constructing a new park using eco-industrial principles. Published literature was surveyed for methodologies which identify and establish viable inter-company exchanges for water, heat, power and materials. Studies which address issues associated with infrastructure alterations are specifically highlighted, as well as methods to quantify and manipulate any potential financial and/or ecological benefits gained by adopting proposed eco-industrial measures. Additional topics, such as network analysis, company motivation, confidentiality issues and introduction of new industries or facilities are included. This review surveys current quantitative methodologies that can be applied to the process of adapting established industrial park networks into eco-industrial park systems and case studies which are pertinent to this type of adaptation.

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

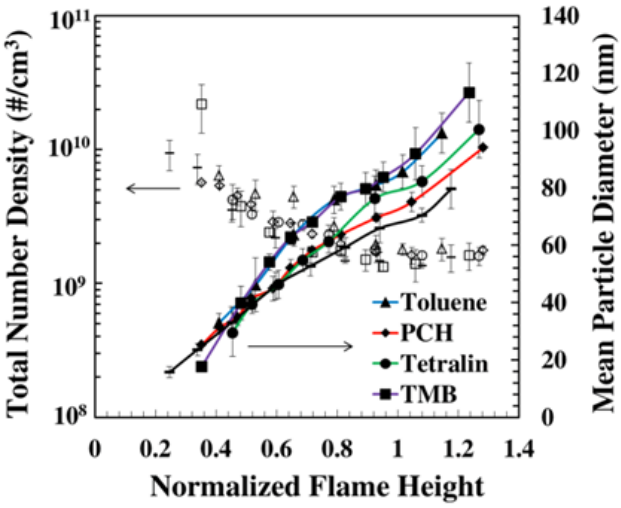
Maria Botero, Sebastian Mosbach, Jethro Akroyd, and Markus Kraft. DOI: 10.1016/j.fuel.2015.02.108

Relevance to the work of the IRP: WP2

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.

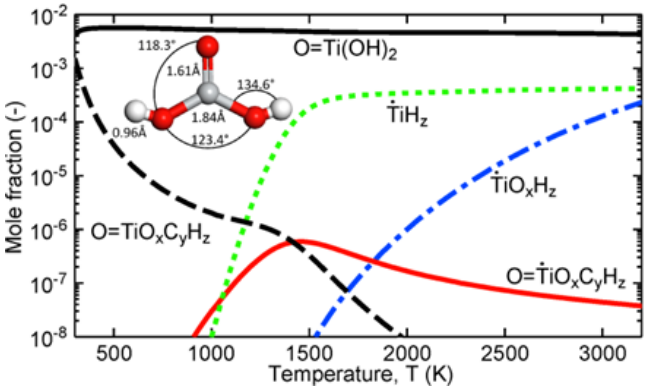
- Aromatic fuels substituted with larger aliphatic chains produce particles with smaller mean diameters.



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. DOI: 10.1021/acs.jpca.5b01721

Relevance to the work of the IRP: WP3

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.

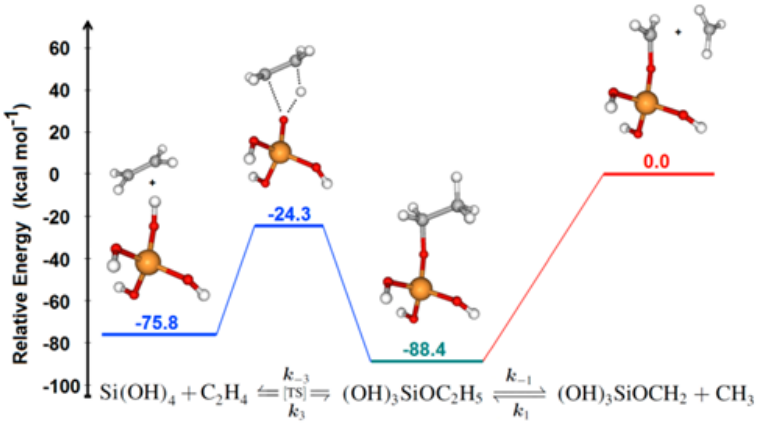
Ab initio Variational Transition State Theory and Master Equation Study of the Reaction (OH)3SiOCH2 + CH3 <-> (OH)3SiOC2H5.

Daniel Nurkowski, Stephen J. Klippenstein, Yuri Georgievskii, Marco Verdicchio, Ahren W. Jasper, Jethro Akroyd, Sebastian Mosbach, and Markus Kraft. DOI: 10.1515/zpch-2014-0640

Relevance to the work of the IRP: WP3

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.

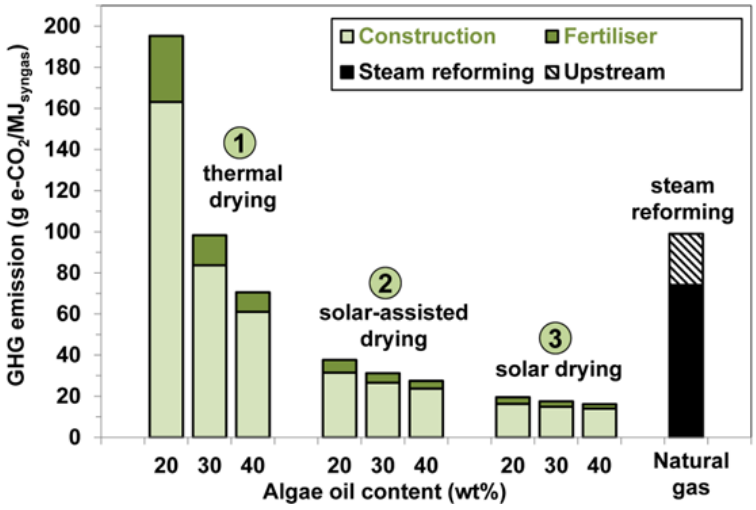
Simulation and life cycle assessment of algae gasification process in dual fluidized bed gasifiers.

Pooya Azadi, George Brownbridge, Sebastian Mosbach, Oliver R. Inderwildi, and Markus Kraft. DOI: 10.1039/C4GC01698J

Relevance to the work of the IRP: WP1, WP4

Highlights

- Algae-derived syngas production using dual fluidised 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).

3.3.4 Other achievements and news

Global Engineering Programme Internship

In May 2015, C4T welcomed the first intern to the team. Daryl YONG, a first year Electrical Engineering undergraduate at the National University of Singapore, joined C4T's IRP3 for three months. Daryl is part of an elite NUS programme, the Global Engineering Programme (GEP), which places exceptional students on an accelerated pathway and offers opportunities for applied learning outside of the traditional teaching environment.

During his 12-week internship with CARES C4T, Daryl worked with members of IRP3 and 4 to continue development of the "J-Park Simulator" Java web application that integrates spatial information with a PowerWorld simulation of the power network.

Prof Markus Kraft gives inaugural Monthly CREATE seminar

On May 8th 2015, Prof Markus Kraft (CARES Director and Cambridge PI, IRP3) led (with Dr Heiko Aydt, TUM CREATE) the inaugural session of the Monthly Seminar Series by CREATE PIs. The seminar series promotes the interaction between the different CREATE programmes.

Prof Kraft's talk presented new insights into the implementation of Industry 4.0 technologies (novel mathematical and computer-based methods) for designing and optimising an eco-industrial park (EIP) similar to Jurong Island in Singapore. Industry 4.0 translation to an EIP 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 work Prof Kraft leads in C4T 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.

Industry collaboration—ExxonMobil

Prof XU Rong (Co-PI, NTU, IRP3) is expecting to start a project entitled "Synthesis and surface functionalization of carbon materials and related composite materials for catalysis and separations in petroleum and natural gas industries" in September 2015. The project will be supported with US$100,000 of funding from ExxonMobil and will link directly with C4T.

IRP3 and 4 conference held in Cambridge

In August 2015, members of IRP3 and 4 (Research Fellows and PhD students from Cambridge, NTU and NUS) met in Cambridge for a series of workshops hosted by Prof. Markus Kraft (PI, Cambridge, IRP3) to push forward their work on the 'J-Park Simulator' for the optimisation of industrial parks. The C4T members had a number of productive meetings and also met with colleagues from Cambridge Computational Modelling Ltd (CMCL), a local Cambridge company who will be sponsoring a studentship under the Cambridge-CARES Studentship Scheme from October 2015. During their visit, the IRP3 and 4 members were hosted at Churchill College by Prof Markus Kraft and Dr Jethro Akroyd (SRF, Cambridge, IRP3).

IRP3 student on Graduate Student Organising Committee for the 13th International Conference on Carbon Dioxide Utilisation

Pulkit Chhabra (PhD student, NUS, IRP3) was part of the Graduate Student Organising Committee for the 13th International Conference on Carbon Dioxide Utilisation (ICCDU), which was held at NUS in July 2015. This event brought together delegates from 32 countries to discuss the latest updates in the field of carbon dioxide utilization.

IRP3 and 4 collaboration with REIDS project—Semaukau Island

IRP3 and 4 are currently working closely together to explore the possibility of a collaboration with ERI@N regarding the renewable energy integration demonstration microgrid (REIDS) at Semaukau Island using the tools and methodologies developed from the J-Park Simulator. A preliminary electrical diagram for REIDS has been developed and further research on the technical specifications of the equipment will be done in order to fully model and represent the entire electrical network.

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

September 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.

IRP4 is addressing questions related to coordination of electrical and thermal power generation, distribution and consumption. The possibility and impact of introducing renewable generation, in addition to traditional generators, are being investigated. Also heterogeneous structure of the power system, including the incorporation of microgrids as subsystems, is being studied. At present, various problems are being addressed, both standard power system problems and new ones which arise as a result of these various possibilities. Major questions which have been identified are: (1) Is it appropriate to maintain the traditional time-scale hierarchy for controlling power systems, when the range of time constants of equipment is being reduced, and computational algorithms are getting more powerful? (2) One strategy which has been proposed, for coping with renewable generation, is to configure interface inverters such that all generators behave like traditional synchronous generators – so-called ‘virtual power plants’; is this really the best way to proceed? (It seems unlikely.) A range of problems is being considered, from automatic voltage control to optimal despatch problems, with both centralized and decentralized control structures being investigated.

3.4.2 Update on work packages

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

Model Predictive Control uses numerical optimisation and repeatedly solves a finite-horizon optimisation problem. One obstacle to applying this technology is the time required to solve the online optimisation problem. Work on the fast 'Alternating Directions Method of Multipliers' (ADMM) algorithm for solving quadratic programs was already reported in the previous report, and is being developed further to provide a more complete and systematic procedure for implementation – for example, how to decide on appropriate fixed-point precision in an FPGA implementation.

Work is also continuing on the 'Quadratic Dissipativity Constraint' (QDC) introduced into MPC by Anthony TRAN (SRF, NTU, IRP4). This stabilises the closed-loop behaviour of MPC, without requiring the conventional 'terminal constraint', which is very difficult and time-consuming to compute. The efficacy of QDC has been demonstrated on a growing number of examples involving electric power distribution problems. However, QDC is still not thoroughly understood, so fundamental work is continuing in parallel with simulation-based investigations.

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

Dr Bhagyesh PATIL (RF, NTU, IRP4) was recruited to IRP4 at the beginning of this reporting period. His expertise is in global optimisation, including mixed-integer problems, which is central to the application of MPC to nonlinear and hybrid systems. He is already applying this to the control of a mixed-cycle gas-turbine power generator (with Ashok KRISHNAN – PhD student with Prof. Gooi, NTU, IRP4). Dr PATIL is also undertaking a comparative study of various global optimisation algorithms, seeking to identify those which are particularly suitable for use with MPC and electric power applications.

The use of Multiplexed MPC for multi-area power distribution networks has been investigated, although to date using linear models only.

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

As already mentioned in the WP1 report above, a number of investigations of specific power distribution problems are underway, applying MPC. The 'QDC' constraint is used in most of these. In addition to control problems, the estimation of the state of a power network is being investigated using 'Moving Horizon Estimation', which is the dual of MPC. This is shown to have some benefits compared with the conventional method used by the power industry ('weighted least squares') because known constraints on possible values can be exploited to improve the estimation quality. It has also been shown that estimation can be made more robust to outliers by assuming measurement errors to follow a 't-distribution' instead of the commonly used Gaussian (normal) distribution. A recursive version of the estimator has been derived for this case, and shown to coincide with the Kalman Filter in the special case of Gaussian errors.

In addition, work is continuing under the supervision of Prof Sanjib PANDA (PI, NUS, IRP4) to explore the problem of distorted voltage at the Point of Common Coupling. Microgrids are impacted by distorted voltage at the Point of Common Coupling (PCC) especially in a weak grid caused by the drawing of harmonic currents by the nonlinear loads, such as chemical process loads. They thereby

affect the neighbouring loads too. When sufficient local generation, such as the photovoltaic generation is present, this issue can be mitigated by using the local source as a harmonic power injector for the nonlinear loads. The physical feasibility of such injection is achievable through power-electronic inverters. A technique, Selective Harmonic Optimization, is proposed to optimally switch the inverter to attain the desired waveform of injected current. This could prevent nonlinear loads within the grid from drawing harmonic power from other connected grids. It would also maintain quality of waveforms at the PCC.

Development of a platform for easily configurable microgrid simulation model is also being worked on (led by Prof Sanjib PANDA, PI, NUS, IRP4 and involving Dr Joymala MOIRANGTHEM, RF, NUS, IRP4). It is an intelligent network-design and analysis toolbox using MATLAB software which includes code-assisted library of data-encapsulated components. This design facilitates distributed computing and control of the simulated model with easy manual testing. It also makes steady-state analysis and secondary control of the model very flexible.

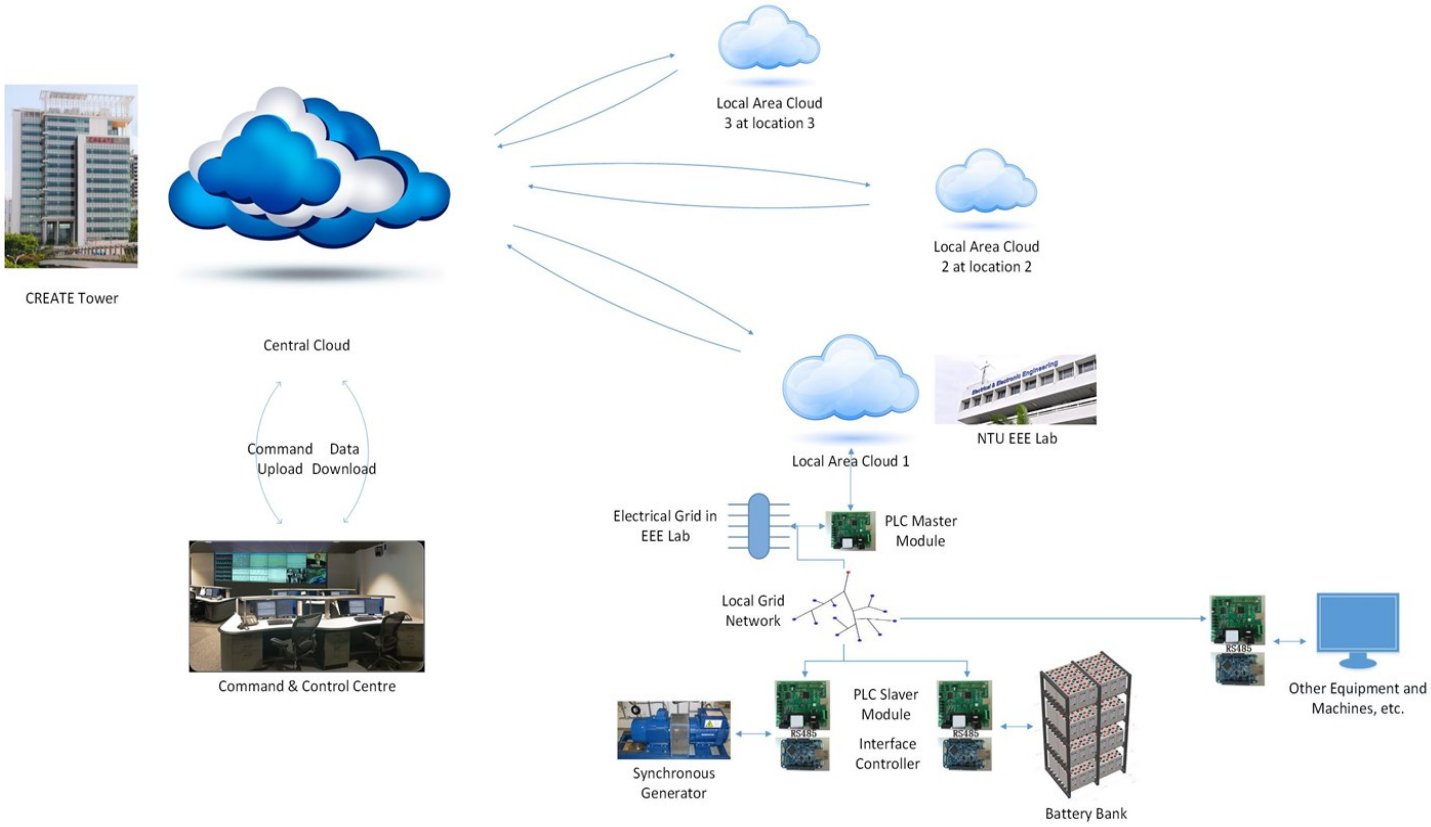
WP4: Modelling of chemical process load and local generator-based electrical network akin to Jurong Island

The main progress on treating chemical plants as active generating agents in a power network as well as loads has been focussed on incorporating such a model system into the C4T-NTU Smart Grid. The initial methodology has been to use a programmable electronic load which can simulate generation and load conditions. In the medium term this will be coped with the Hardware In the Loop real time digital power system simulator which is to be purchased. Evaluation and tender invitations for such a system have now taken place. A model electrical network for Jurong Island has also now been completed and is currently being used to evaluate power flow constraints and different fault scenarios.

An important and novel aspect of WP4 is to examine power flow and other electrical parameters on a Jurong Island – like system in real time and to predict/gauge risks of faults occurring. With such prior 'knowledge' system power flow reconfiguration and direction of chemical plant generating capacity on to the grid in real time is also to be explored. For such a system to work an 'inelligent' network monitoring system has to be developed. Deep artificial neural networks are being studied for such a system. Initial work has been directed at looking at historic data and predicting load demand in real time. The other aspect which is important is reliable real time data availability. For this the approach being followed is to sample network electrical parameters through distributed micro power measure units (PMUs). Such data in turn needs to be transmitted to a central data storage and analysis node (s). For this both wireless and wired power line communications with redundancy is being examined. A hybrid wired/wireless communication system has been successfully developed and is currently undergoing evaluation.

WP4 – Detailed description of Data Gathering system for Jurong Island-like smart grid system

The monitoring and control system consists of two levels: the far end level and the local area network. The far end is the central controller in display and control center. This controller is able to access all of the date generated from its lower level that is the local area network controller. There are private cloud (data storage) covering controllers from both levels. The local area controller controls locally connected machines for command & control applications. The power-line communication modules are used by local controller to communicate with electrical connected machines. The Power-line communication modules are linked to each conventional machine using multiple-standard interface through programming microcontroller. The microcontroller can adapt the protocols from machines to establish smooth communications between power-line communication modules and machines.



To achieve the demonstrative purpose for IRP4, an industrial solution for future Grid monitoring and control system has been developed. The system includes a command & control and display central controller; a private cloud for data storage, backup and retransmission; power-line communication modules for local area communications; mBed microcontroller for multiple-standard interface to control hardware for grid connected electrical machines; and blue-tooth for short distance wireless communication to achieve physical web. The illustrative schematic can be seen below.

Currently, Dr Yuhao SUN (SRF, NTU, IRP4) et al have completed the development of Power-line Communication system for command and control applications in the Smart Grid. The merit of this technology is to achieve robust communications without using additional communication wires. This communication system is also one of the IoT components to achieve local area data acquisition. The hardware of the communication system has been designed, built and tested. All functions are working correctly.

Working frequency bands 3kHz – 450 kHz

The max speed: 500 kbps; sufficient for most command and control applications in local area network

Matlab GUI has been programmed to control the communication system (an advanced microcontroller controlled version is under development)

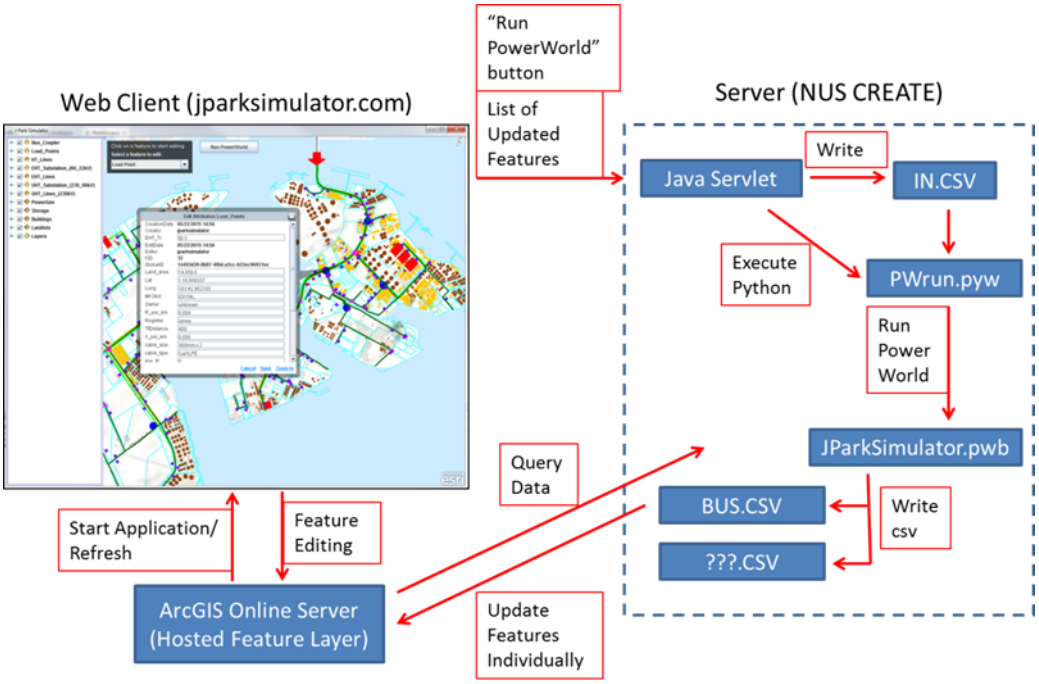
Instantaneous message transmission achieved by MAC optimisation for high priority data transmission (under development).

Private cloud has been set up to verify system operation. The private central and local area clouds are used to store and process gathered data. This part has been implemented by using a 12 TB network attached storage. This will provide data storage capability at industrial standards in terms of security and robustness.

Cloud stored data at both levels can be accessed by other systems and operators from anywhere at anytime using IOS system protocols.

Ongoing work

The IRP4 team are in the process of developing:



1. Advanced microcontroller based PLC control system to achieve fast response.

2. Multiple-standard interface between the controller and the conventional electrical machines in the EE lab.

3. A command & control and display central controller

WP4 – Detailed description of NTU Smart Grid development

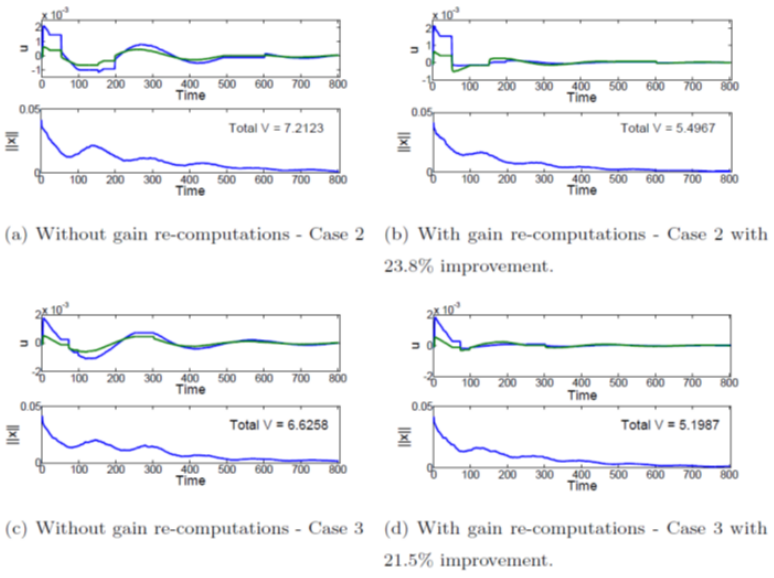
The IRP4 Smart Grid Development Team have made progress on the following:

- Successfully designed and developed the Automatic Generation Control (AGC), Load Frequency Control (LFC) and Voltage Excitation Control module for the 13.5kVA synchronous generator located in the microgrid facility at NTU.
- Integrated a 13.5kW three-phase AC programmable loadinto the NTU microgrid facility. The programmable load is used to simulate the kW/kvar demand characteristics of the chemical plant load in Jurong Island. Further investigations will be done to evaluate the performance of the developed AGC, LFC and voltage excitation control modules.
- A tender for the real time digital simulator is currently being processed. The real time digital simulator will further strengthen our research by validating in real-time, the proposed control algorithms as well as fault and transient stability analysis.
- A proposed 209-bus electrical network model has been developed for Jurong Island. The proposed electrical model is based on the data deriving from the geographical information system (GIS) of Jurong Island. The team is currently working closely with IRP3 to develop an interactive web-based interface for simulating the electrical process of Jurong Island which is termed "J-Park Simulator". Another research aspect of the J-Park Simulator is to study the effects of the dimensionality and the quality of the surrogate models arising from the electrical network parameterization. The results will be reported in the upcoming Asia Clean Energy Summit, RE Asia Conference 2015, Singapore.
- The IRP4 team is also working with IRP3 to develop the equivalent electrical models for the chemical processes in Jurong Island. The equivalent electrical models will then be integrated to the proposed 209-bus electrical network where various simulation studies e.g. fault analysis, transient stability analysis will be carried out.

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.

Dependable Control Systems with Internet of Things



(a) Without gain re-computations - Case 2 (b) With gain re-computations - Case 2 with 23.8% improvement.

(c) Without gain re-computations - Case 3 (d) With gain re-computations - Case 3 with 21.5% improvement.

Figure 14: DSC system - Different transition time instants and intervals.

Tri Tran and Q.P. Ha. DOI: 10.1016/j.isatra.2015.08.008

Highlights

- A dependable self-recovery control (DSC) architecture that utilizes Internet of Things (IoT) connectivity and dependable control systems (DepCSs) are presented as an alternative to the widely perceived DCS architecture for the industrial computerized-control systems.
- A novel state feedback control method for DepCS applying the self-recovery constraint with respect to variable increments. The state feedback gain is re-computed at every duty-standby switching-over incidences. The gain re-computation ensures that the incremental constraint is satisfied and the control performance is not degraded.

Abstract

This paper presents an Internet of Things (IoT) enabled dependable control system (DepCS) for continuous processes. In a DepCS, an actuator and a transmitter form a regulatory control loop. Each processor inside such actuator and transmitter is designed as a computational platform implementing the feedback control algorithm. The connections between actuators and transmitters via IoT create a reliable backbone for the duty and standby processors of a DepCS, wherein only one processor is responsible for manipulating the plant at any one time. The centralized input-output marshalling hardware sub-system is not required in De-pCSs. A development for state feedback control synthesis for DepCS applying the self-recovery constraint is presented in the second part of the paper. Simulation with an isolated wind-diesel power system and the automatic generation control of a power system demonstrates the result.

Iterated moving horizon estimation for power systems

Tengpeng Chen, Tri Tran, Dexiang Zhou, W-K. Ho, and K-V. Ling. DOI: 10.1109/ICCAIS.2014.7020573

Highlights

- WLS, EKF-based, MHE algorithms for PSSE problem are presented.
- Iterations are employed to improve the accuracy of the approximated linear measurement model using Taylor series expansion.
- Numerical simulations in Matlab for IEEE 14-bus benchmark system are summarized and reported.
- Constraints on state are explicitly included to improve the estimation result.

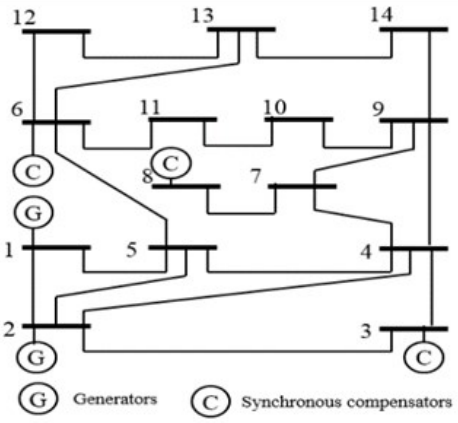


Figure 1: IEEE 14-bus system.

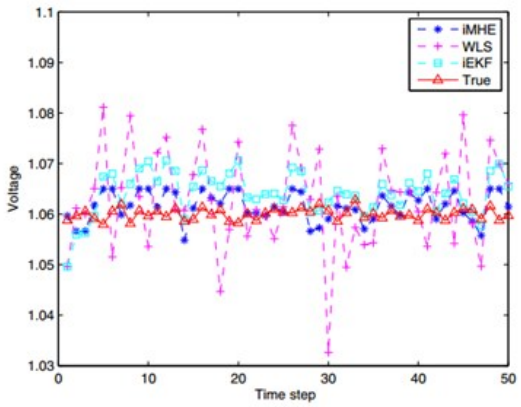


Fig. 5. Voltage of Bus 1 in IEEE 14-bus system of simulation 3 for iMHE with constraints using larger Q^{-1}.

Abstract

The iterated moving horizon estimation (iMHE) algorithm is applied to the power systems in this paper. The approximated measurement model is used in the iterative MHE optimization problem. We show in this paper that the iMHE with constraints provide superior results compared to those from the WLS in simulations for the IEEE 14-bus system. The steady state operation of the power system is considered in this simulation study, wherein there are only small variations of variables around their steady states. An extended Kalman filter based algorithm with iteration is also studied in this paper. Simulation results of the iterated EKF-based algorithm show some improvements from the WLS, but are not as good as the constrained iMHE.

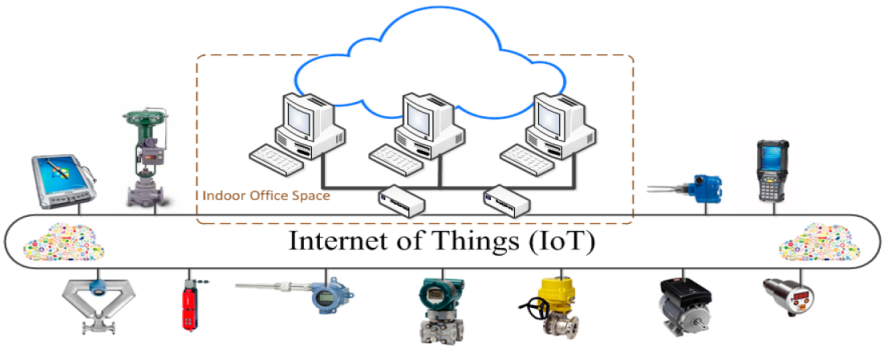


Fig. 12. An IoT enable distributed computerized-control system.

A New Architecture for Reliable Computerized-Control System via IoT Enabled Connectivity

Tri Tran. Presented to 1st ISSAT International Conference on Modelling of Complex Systems and Environment (MCSE'15), Danang, Vietnam, June 2015

Highlights

- IoT (Internet of Things) enabled 1-layer architecture for computerized-control systems.
- Marshalling and input/output hardware subsystems are not required in the new architecture.
- The installation and implementation cost will be reduced tremendously.

Abstract

A collapsed architecture for Distributed Control Systems (DCSs) in industry is proposed in this paper. This new system structure is developed on the ground of peer-to-peer communication and cloud-based computing technologies. The centralized marshalling and input/output (I/O) interface systems

of a traditional DCS are not required in the proposed architecture. The middle-ware and hierarchical communication architecture is collapsed into one layer employing the Industrial Internet of Things (IIoT) technology. The quantitative reliability of the new system is achieved by using multiple processors integrated into the smart transmitters and actuators in the field, far away from the control room. The installation, implementation, testing, operation and maintenance costs will tremendously be reduced by the newly proposed IIoT based architecture.

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

Dang Van Thuy, K-V. Ling, and J. Maciejowski. Presented to European Control Conference (ECC'15) , Linz, Austria, July 2015

Highlights

- A new ADMM numerical algorithm for QP solver in embedded systems.
- Application of the newly developed ADMM algorithm to the model predictive control optimization problem with sparse formulation and general inequality constraints.

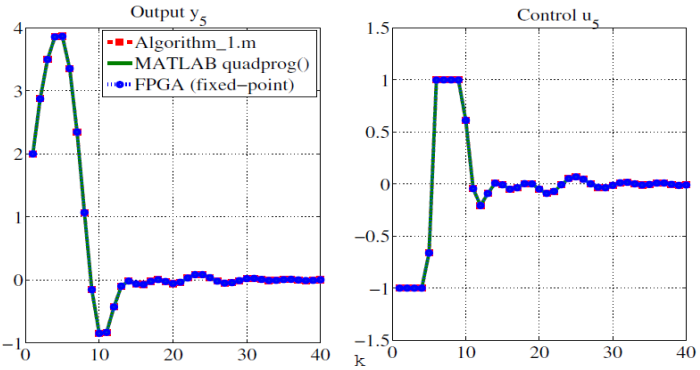


Fig. 2. MPC performance in Spring-Mass system

- Fixed-point arithmetic FPGA implementation with effective step size selections.

Abstract

An algorithm for solving quadratic programming (QP) problems with inequality and equality constraints arising from linear MPC is developed. 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, the developed algorithm can handle the 'sparse' MPC formulation with general inequality constraints. The proposed algorithm is suitable for implementation on embedded platforms where computational resources are limited. The algorithm is also division free when certain fixed matrices are computed off-line. This enables the implementation in fixed-point arithmetic on FPGA. A heuristic rule to select the step size of ADMM for a good convergence rate is also proposed.

A Miniature Distributed Power Hardware-In-The-Loop (dPHIL) Power System Simulator with Reduced Voltage and Reduced Power Components

Tri Tran and M-H. Nguyen. Presented to 1st ISSAT International Conference on Modelling of Complex Systems and Environment (MCSE'15), Danang, Vietnam, June 2015

Highlights

- A new concept of distributed power hardware-in-the-loop reduced-voltage simulator (dPHIL RVS) as a new platform for research experimentations on multiple time-scale control, estimation and optimization algorithms for future grids.
- The miniature reduced voltage and reduced power components are used in the dPHIL RVS to alleviate the unaffordable cost for power system real-time simulators.
- Distributed embedded system and several three-phase back-to-back power inverters as the generation sources, interconnected by the inductors and resistors emulating the transmission lines.

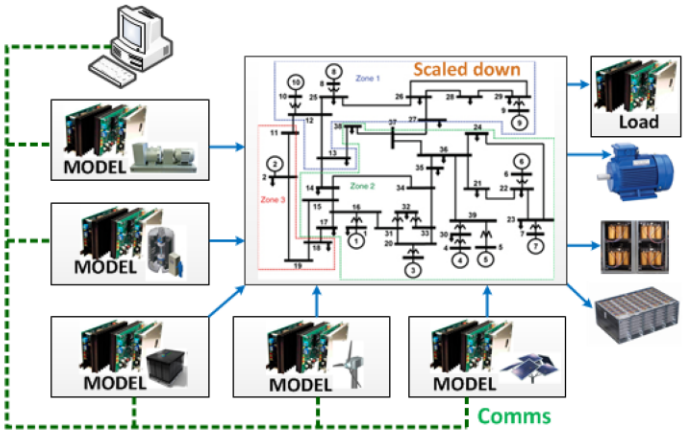


Fig. 3. The presenting dPHIL simulator.

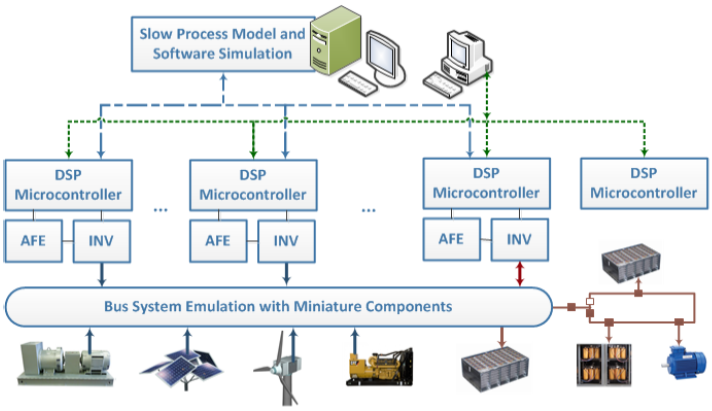


Fig. 6. Block diagram of dPHIL simulator.

Abstract

The distributed power hardware-in-the-loop (dPHIL) simulator provides a three phase alternating-current (AC) voltage miniature power system that is an open platform for research experimentation. It encompasses, but is not limited to, power system multiple time scale control, estimation and optimization, which specifically covers real-time control, supervisory control, economic optimization and energy management. Functionalities for fault detection, system recovery, real-time intersystem communication and interfaces with non-electrical system simulators are also accommodated for. The dPHIL is a reduced-voltage and reduced-power emulation system, characterized by 60 Vac rms line voltage, with small generation sources and emulated generation sources. A distributed microcontroller/FPGA based computer system is the backbone of the dPHIL. The new and existing communication protocols from the power system field can be installed in a dPHIL simulator. The system is not designed for operational training purpose, but for the first stage testing and verifying new distributed algorithms. Power systems with islanded and grid-connected microgrids and distributed renewable energy sources are fully facilitated by the presenting dPHIL simulator.

Distributed Moving Horizon Estimation for Power Systems

Tengpeng Chen, Dexiang Zhou, Tri Tran, C. Kastner, K-V. Ling, K-J. Tseng, and J. Maciejowski. Presented to 2015 IEEE Power and Energy Society General Meeting (PES GM'15), Denver, Colorado, July 2015.

Highlights

- A distributed moving horizon estimation (DMHE) algorithm has been applied to the power system state estimation problem.

- Simulations using a standard IEEE 14-bus benchmark system and experiments on a lab microgrid have shown the effectiveness of both MHE and DMHE with constraints, for steady state operation with small variations.
- Enhancement of the algorithms by iterative improvement of the linearisation of the measurement equation has been shown to have improved the state estimation performance.

Abstract

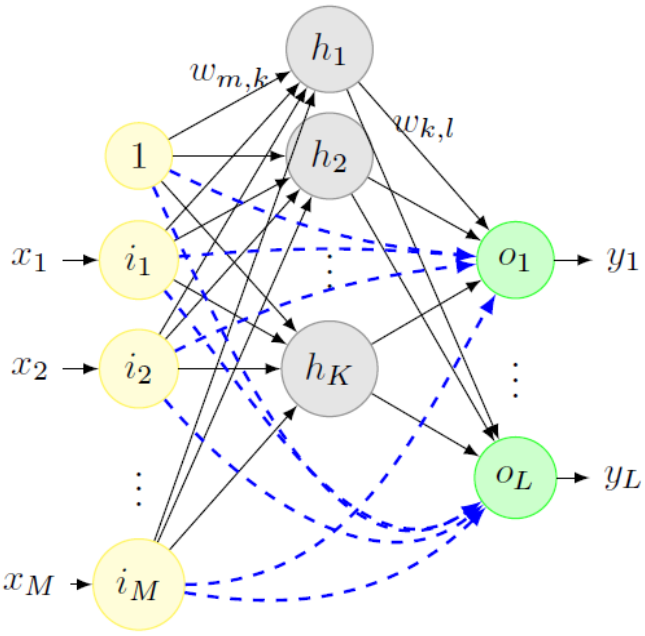
We adapt and apply a known algorithm for Distributed Moving Horizon Estimation (DMHE) to power systems. In this distributed approach, the power system is partitioned into several control areas. At each time step the state of the whole system is estimated locally in each area, by solving a local optimization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

Random Vector Functional Link Neural Network for Short-term Wind Power Ramp Forecasting

Ren, Y., P-N. Suganthan, N. Srikanth, G. Amaratunga. Presented to the International Conference on Soft Computing MENDEL, Brno, Czech Republic, June 2015.

Highlights

- A random vector functional link neural network (RVFLNN) is employed to forecast the wind power ramp and the ramp rate.
- The RVFLNN with classification approach has better performance than the three benchmark methods, including artificial neural network (ANN), random forests (RF) and support vector machine (SVM).
- The computational time required by RVFLNN is much less than that by ANN. RVFLNN is also faster than SVM.



Abstract

Wind is a clean and renewable energy source with huge potential in power generation. However, due to the intermittent nature of the wind, the power generated by wind farms is fluctuating and often has large ramps, which are harmful to the power grid. This paper presents algorithms to forecast the ramps in the wind power generation. The importance and challenges of accurate wind power ramp forecasting are addressed. Wind power ramp and power ramp rate are defined in this pa-

per. A random vector functional link neural network (RVFLNN) is employed to forecast the wind power ramp and the ramp rate. The RVFLNN applied to wind power forecasting based on regression has comparable performance as the benchmark methods: artificial neural network (ANN), random forests (RF) and support vector machine (SVM) but RVFLNN with classification approach has better performance than the other three benchmark methods. The computation time of training and testing is also in favour of RVFLNN. Possible future research directions are also identified.

3.4.4 Other achievements and news

IRP3 and 4 collaboration with REIDS project—Semaukau Island

IRP3 and 4 are currently working closely together to explore the possibility of a collaboration with ERI@N regarding the renewable energy integration demonstration microgrid (REIDS) at Semaukau Island using the tools and methodologies developed from the J-Park Simulator. A preliminary electrical diagram for REIDS has been developed and further research on the technical specifications of the equipment will be done in order to fully model and represent the entire electrical network.

Participation in CARES seminar series

A seminar on the work of IRP4 was given to the CREATE community on 13 August 2015, consisting of three short presentations:

* Jan Maciejowski (PI, Cambridge, IRP4): “Smart coordination of power generation and consumption”,
* Bhagyesh Patil (RF, NTU, IRP4): “Global optimization algorithms: design, implementation and application in process system engineering”,
* Joymala Moirangthem (RF, NUS, IRP4): “Selective harmonic optimization for flexible single-phase operation of cascaded H-bridge multilevel inverters”.

Technical Committee memberships

- Jan Maciejowski (PI, Cambridge, IRP4) is a Technical Committee member of the following conferences:
  * IFAC ‘Safeprocess’ Conference, Paris, France, September 2015,
  * IFAC Symposium on System Identification, Beijing, China, October 2015.
- Anthony Tran (SRF, NTU, IRP4) is a Technical Committee member of the following conferences:
  * ICCAIS'15 (International Conference on Control, Automation, and Information Science), Changshu, China, October 2015,
  * ISEE’15 (International Symposium on Electrical and Electronics Engineering), Saigon, Vietnam, October 2015.

Visits to Cambridge

Thuy Van Dang (PhD student, NTU, IRP4) visited Prof. Maciejowski’s group in Cambridge from 7 to 13 July 2015.

A.1 Publications

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

A1.1 Joint IRP Publications

IRP1 and IRP3

- Amaniampong, Prince N., Quang Thang Trinh, Bo Wang, Armando Borgna, Yanhui Yang, and Samir H. Mushrif. 'Biomass Oxidation: Formyl C-H Bond Activation by the Surface Lattice Oxygen of Regenerative CuO Nanoleaves.' *Angewandte Chemie International Edition* 54, no. 31 (27 July 2015): 8928–33. doi:10.1002/anie.201503916.
- Azadi, Pooya, George Brownbridge, Immanuel Kemp, Sebastian Mosbach, John S. Dennis, and Markus Kraft. 'Microkinetic Modeling of the Fischer-Tropsch Synthesis over Cobalt Catalysts.' *ChemCatChem* 7, no. 1 (January 2015): 137–43. doi:10.1002/cctc.201402662.
- Li, Kaixin, Zhihong Yang, Jun Zhao, Junxi Lei, Xinli Jia, Samir H. Mushrif, and Yanhui Yang. 'Mechanistic and Kinetic Studies on Biodiesel Production Catalyzed by an Efficient Pyridinium Based Ionic Liquid.' *Green Chem.* 17, no. 8 (2015): 4271–80. doi:10.1039/C5GC00976F.

IRP3 and IRP4

- Chen, Tengpeng, Dexiang Zhou, Tri Tran, Catharine A. Kastner, K-J Tseng Ling, and Jan M. Maciejowski. 'Distributed Moving Horizon Estimation for Power Systems.' In *Proceedings of 2015 IEEE Power and Energy Society General Meeting (PES GM'15)*. Denver, Colorado, 2015.

A.1.1 IRP1— MUSCAT

- Dai, Yihu, Ye Wang, Bin Liu, and Yanhui Yang. 'Metallic Nanocatalysis: An Accelerating Seamless Integration with Nanotechnology.' *Small* 11, no. 3 (January 2015): 268–89. doi:10.1002/smll.201400847.
- He, Chao, Ke Wang, Apostolos Giannis, Yanhui Yang, and Jing-Yuan Wang. 'Products Evolution during Hydrothermal Conversion of Dewatered Sewage Sludge in Sub- and near-Critical Water: Effects of Reaction Conditions and Calcium Oxide Additive.' *International Journal of Hydrogen Energy* 40, no. 17 (May 2015): 5776–87. doi:10.1016/j.ijhydene.2015.03.006.
- He, Chao, Ke Wang, Yanhui Yang, Prince Nana Amaniampong, and Jing-Yuan Wang. 'Effective Nitrogen Removal and Recovery from Dewatered Sewage Sludge Using a Novel Integrated System of Accelerated Hydrothermal Deamination and Air Stripping.' *Environmental Science & Technology* 49, no. 11 (2 June 2015): 6872–80. doi:10.1021/acs.est.5b00652.
- Liu, Wen, Mohammad Ismail, Matthew T. Dunstan, Wenting Hu, Zili Zhang, Paul S. Fennell, Stuart A. Scott, and J. S. Dennis. 'Inhibiting the Interaction between FeO and Al_2O_3 during Chemical Looping Production of Hydrogen'. *RSC Adv.* 5, no. 3 (2015): 1759–71. doi:10.1039/C4RA11891J.
- Sheng, Yuan, and Hua Chun Zeng. 'Monodisperse Aluminosilicate Spheres with Tunable Al/Si Ratio and Hierarchical Macro-Meso-Microporous Structure.' *ACS Applied Materials & Interfaces* 7, no. 24 (24 June 2015): 13578–89. doi:10.1021/acsami.5b03011.
- ———. 'Structured Assemblages of Single-Walled 3d Transition Metal Silicate Nanotubes as Precursors for Composition-Tailorable Catalysts.' *Chemistry of Materials* 27, no. 3 (10 Febru-

ary 2015): 658–67. doi:10.1021/cm502691s.

- Yang, Shiliang, Ke Zhang, and Jia Wei Chew. 'Computational Study of Spout Collapse and Impact of Partition Plate in a Double Slot-Rectangular Spouted Bed.' *AIChE Journal*, August 2015, n/a – n/a. doi:10.1002/aic.14973.
- Yan, Yibo, Jianwei Miao, Zhihong Yang, Fang-Xing Xiao, Hong Bin Yang, Bin Liu, and Yanhui Yang. 'Carbon Nanotube Catalysts: Recent Advances in Synthesis, Characterization and Applications.' *Chem. Soc. Rev.* 44, no. 10 (2015): 3295–3346. doi:10.1039/C4CS00492B.
- Zhan, Guowu, Christopher C. Yec, and Hua Chun Zeng. 'Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts.' *Chemistry - A European Journal* 21, no. 5 (26 January 2015): 1882–87. doi:10.1002/chem.201405697.
- Zhao, Jun, Chunmei Zhou, Chao He, Yihu Dai, Xinli Jia, and Yanhui Yang. 'Efficient Dehydration of Fructose to 5-Hydroxymethylfurfural over Sulfonated Carbon Sphere Solid Acid Catalysts.' *Catalysis Today*, August 2015. doi:10.1016/j.cattod.2015.07.005.

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Cover figure: Figure a) FESEM, b) and c) TEM images of 3D Pt_3Co NWA. (Reference paper: DOI: 10.1002/ange.201411544) Figure d) FESEM image of FeO(OH) NWs/rGO; e) and f) FESEM image and TEM image of FeP NWs/rGO, respectively. (Reference paper: DOI: 10.1002/advs.201500120). Image credit: Dr Yan Ya (RF, NTU, IRP2)

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