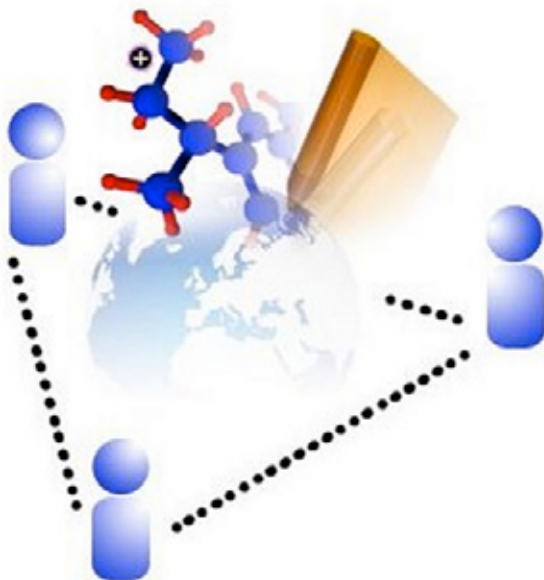


An international symposium

Anion-Exchange Membranes for Energy Generation Technologies

25 – 26 July 2013

Programme and Abstracts



Welcome

On behalf of the University of Surrey, I welcome you to Guildford. I hope you will have an enjoyable 2 days of high impact science and networking. If you need any assistance during your stay, please feel free to ask one of the organising committee!

The University of Surrey consistently has one of the best graduate employability track records in the UK with a world-renowned professional training scheme (with > 1000 industrial partners). It is in the process of a £213 million investment programme including the Ivy Arts Centre and Guildford School of Acting, Surrey Sports Park, a 5G Research Centre for the next generation of mobile communications; a new School of Veterinary Science; upgrades to the Manor Park student village; and a new Library & Learning Centre. It is also the home of Surrey Space Centre with its spin-out Surrey Satellite Technology Ltd. In 2012 it was awarded its 3rd Queen's Anniversary prize for its water research.

Prof John Varcoe
Symposium Chair

Co – Chair
Dr Simon Poynton

Local Organising Committee:

Dr Ai Lien Ong	Ms Lucy Howes
Dr Cathryn Hancock	Mr Sam Murphy
Ms Jessica Whitehead	Ms Sarah Mallinson



Introduction

The last decade has seen a significant increase in research activity looking at anion-exchange membrane in electrochemical energy technologies. Since 2003, the electrochemical energy materials team in the Department of Chemistry, University of Surrey has been world leading in the study of such membranes in solid alkaline fuel cells. To mark the 10th year of these efforts in Surrey, the University of Surrey is hosting a 2 day workshop to establish a consensus of the state-of-the-art regarding the use of anion-exchange membranes in various electrochemical devices such as fuel cells, redox flow batteries, electrolyzers and reverse electrodialysis cells. Select and renowned researchers from around the world [industrial and academic] have been invited to participate as have leading researchers in the UK. The workshop will also look at suitable next steps along with establishing new international collaborations in the field.

The organisers thank the UK's Engineering and Physical Sciences Research Council (Grants EP/I004882/1 and EP/H025340/1) and the University of Surrey Institute of Advanced Studies workshop grant scheme for funding. UK participants are funded with thanks to the Research Council UK's Energy Programme's Supergen Hydrogen and Fuel Cell Hub (Grant EP/J016454/1 led by Imperial College London). We also thank Prof Andrew Herring for assisting with the travel costs for some of the USA delegates as well as Caltest, Ametek, Alvatek and the Royal Society of Chemistry for sponsoring the workshop meal.



Day 1 Thursday 25 July

School of Management Building, Room 32MS01

- 09:00 Registration and coffee
- 10:00 **Welcome talk:** Prof John Varcoe
- 10:15 **Flash presentations (Part I)**
- 11:00 Coffee
- 11:10 **Flash presentations (Part II)**

Session 1 Chair: Dr Simon Poynton

- 11:50 **Prof John Varcoe**
1. Cationic head-group research at Surrey for alkaline-based systems
- 12:10 **Prof Tongwen Xu**
2. Development of novel anion-exchange membranes in USTC for fuel cells
- 12:30 Lunch and Posters I

Session 2 Chair: Ms Sarah Mallinson

- 13:20 **Prof Andrew Herring**
3. Anion transport in structured and non-structured di-block hydrocarbon polymers
- 13:40 **Prof Lin Zhuang**
4. Rational design of ionic channels in alkaline polymer electrolytes
- 14:00 **Prof Bryan Pivovar**
5. Influencing cation stability in base through substituent groups
- 14:20 **Prof Michael Hickner**
6. Ion mobility in anion-exchange membranes
- 14:40 **Dr Dan Brett**
7. Water sorption and interaction with CO₂ of alkaline membrane electrolytes using the quartz crystal microbalance
- 15:00 Coffee

Session 3 Chair: Prof John Varcoe

- 15:20 **Prof Adel O. Sharif**
8. Low-energy production of fresh water from the sea by forward osmosis
- 15:40 **Prof Kitty Nijmeijer**
9. Tailoring membranes for blue energy
- 16:00 **Prof Keith Scott**
10. Alkaline membranes for electrolyser and fuel cell applications
- 16:20 **Prof Yushan Yan**
11. Hydroxide-exchange membranes for fuel cells, electrolysers, solar hydrogen, and redox flow batteries
- 16:40 **Dr Richard Burkitt**
12. Application of anion-exchange membranes in microbial fuel cells
- 17:00 Symposium photograph
- 18:30 **Symposium meal** (Bel & The Dragon, Godalming)



Day 2 Friday 26 July

School of Management Building, Room 32MS01

09:00 Coffee

Session 4 Chair: Mr Sam Murphy

- 09:30 **Prof Neil McKeown**
13. Novel amine-based polymers for anion exchange membranes
- 09:50 **Dr Jochen Kerres**
14. AEM's consisting of BrPPO and DABCO and their application in alkaline DMFC
- 10:10 **Prof Steve Holdcroft**
15. Hydroxide-conducting polybenzimidazolium salts
- 10:30 Coffee

Session 5 Chair: Dr Ai-Lien Ong

- 10:50 **Dr Takenori Isomura**
16. AMFC materials development in Tokuyama Corp
- 11:10 **Dr Dario Dekel**
17. Alkaline membrane fuel cell - a reality
- 11:30 **Ms Corinna Harms**
18. Alkaline anion-exchange membranes for application in low temperature fuel cells
- 11:50 **Dr Bernd Bauer**
19. Anion-exchange membranes with improved stability for energy applications
- 12:10 **Dr Jonathan Samson**
20. AFC Energy: Powering Into the Future
- 12:30 Lunch and Posters II

Session 6 Chair: Dr Cathryn Hancock

- 13:20 **Prof William Mustain**
21. Room temperature electrochemical production of oxygenates from methane enabled by AEMs
- 13:40 **Prof Anthony Kucernak**
22. Cathode development for alkaline fuel cells based on a porous silver membrane
- 14:00 **Prof Peter Slater**
23. Doping studies of perovskite materials for potential applications as fuel cell cathodes
- 14:20 **Prof Plaman Atanasov**
24. Non-platinum group metal catalyst for anion-exchange membrane fuel cells
- 14:40 Coffee
- 15:00 **Final Discussion**
- 16:30 Symposium Closing Remarks
- 16:35 **Lab Tour**



Prof Plamen Atanasov

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Talk 24: Non-platinum group metal catalyst for anion exchange membrane fuel cells

This paper presents materials designed for direct non-carbon fuel (e.g. hydrogen, ammonia or hydrazine) anion exchange membrane fuel cell (AEMFC), consisting of NiZn bimetallic anode catalysts and Fe-nitrogen-carbon templated cathode catalyst. The synthesis, structural characterization and evaluation of the electrochemical performance of these two sets of catalyst will be demonstrated as well as their integration into AEMFC based on a membrane electrode assembly using a commercial anion exchange membrane and the corresponding ionomer for the catalysts inks. In the NiZn catalysts design the particular role of the alloying metal will be discussed as well as the mechanism of hydrazine bonding to yield the desired selectivity towards N_2 and H_2O as final oxidation products. The cathode catalyst design is based on templating silica particles by the sacrificial support method (SSM) for a synthetic carbon matrix that incorporates both nitrogen moieties along with the transition metal. Demonstration of the technology for automotive applications will be based on the Daihatsu Motor Co. vehicle prototype.

Dr Bernd Bauer

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Talk 19: Anion-Exchange Membranes with Improved Stability for Energy Applications

For more than 50 years, anion-exchange membranes are produced on industrial scale for different electro-membrane applications. As with anion-exchange resins, the applicability is sometimes limited by the chemical stability of the functional group. Most of the commercial anion-exchange materials are based on polystyrene resins and the benzyl-(tri-methyl) ammonium group. This functional group is sensitive to degradation in strong alkaline solutions due to a nucleophilic substitution followed by the formation of amines and alcohols. Other acrylic acid resins are less sensitive to substitution but may suffer from degradation via Hofmann elimination. Other functional groups, such as the sulphonium and the phosphonium cations were investigated in the 80's already. Their degradation products, however, are more toxic and thus these functional groups were ruled out initially.

The work at FUMATECH is focused on a functional group based on the ammonium cation. The strategy is to avoid Hofmann elimination by steric hindrance and to slow down substitution by electronic interaction. The first improvement in alkaline stability was found with a functional group based on 1-benzyl-1-azonia-4-aza-bicyclo[2.2.2]-octane in 1988 already (fumasep® FAA). The functional group could be in the main

chain or in the side chain. It turned out, that the stability of an anion-exchange group with a hydroxide counter ion in liquid water is very different to the stability of an anion-exchange group in strong alkaline solutions. The degradation mechanism and their kinetics are very different. In result, a membrane being stable in strong alkaline solutions will not necessarily be stable alkaline fuel cells (fumasep® FAA-3). In the mid 90's, the use of anion-exchange membranes in redox-flow batteries was shown successfully. In the field of batteries, chemical stability includes oxidation stability. At the meantime, membranes such as fumasep® FAP has shown stability of more than 7 years in the field.

Dr Dan Brett

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Talk 7: Water sorption and interaction with CO_2 of alkaline membrane electrolytes using the quartz crystal microbalance

Water management in membrane electrolytes for fuel cells is important in determining performance and longevity. For alkaline membranes the interaction with CO_2 also plays a critical role. The quartz crystal microbalance allows the dynamic interaction of alkaline ionomer thin films with water vapour and CO_2 to be studied with high mass sensitivity. Comparison is made with Nafion and the implications for operation in fuel cells discussed.

Dr Richard Burkitt

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Talk 12: Application of anion exchange membranes in microbial fuel cells

Microbial fuel cell (MFC) combining wastewater treatment and energy generation is a technology that originated more than a century ago and has become a rapidly growing research area in the past decade. The material aspect is a critical factor affecting further application and commercialisation of the technology. Low cost electrode materials, oxygen catalysts, and membrane separators are under investigation to obtain cost-effective MFCs. Low cost quaternary 1,4-diazabicyclo-[2.2.2]-octane (DABCO) polysulfone (QDPSU) anion exchange ionomer was synthesised and applied to Microbial Fuel Cells (MFCs). Both electrochemical half-cell experiments and MFC power output were enhanced with QDPSU compared to applying Nafion, mainly due to the improvement in cathode performance and increased rate of OH⁻ transfer produced by the oxygen reduction reaction. Different membrane separators including commercial cation exchange membranes (CEMs) and anion exchange membranes (AEMs), as well as microporous polyethylene battery separator were tested in MFCs in phosphate buffered artificial wastewater. The power output obtained for MFCs was in the order of AEMs > Polyethylene Battery separator > CEMs.

The main reason for the higher performance from AEMs is the improvement on the cathode, which confirmed the study with QDPSU. Various commercial CEMs and AEMs synthesised in house were tested in different electrolytes, including $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, Cl^- and $\text{HCO}_3^-/\text{CO}_3^{2-}$ electrolytes. Electrochemical impedance spectroscopy (EIS) was used to probe ion conductivities and high frequency Warburg diffusion co-efficient which were examined as a function of applied potential for each membrane. The interaction between ion exchange groups with transferring ions was investigated.

Dr Dario R Dekel

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Talk 17: Alkaline membrane fuel cell - a reality

Alkaline membrane fuel cell technology is now blooming. Numbers of studies on this field has significantly increased in past years. New membranes are being developed, with more stable chemistries already tested. First studies on non-Pt catalysts for this technology are now emerging. First alkaline membrane fuel cell stack was also developed, and first tests on 1kW level were demonstrated. Although power densities achieved are enough for first commercial application, performance stability is still a concern. Current challenges in the development of anion conducting polymers as well as of electrocatalysts for alkaline membrane fuel cells with improved stability will be discussed.

Ms Corinna Harms

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Talk 18: Alkaline anion exchange membranes for application in low temperature fuel cells

Proton exchange membrane fuel cells (PEMFC) have been under investigation for the production of clean and efficient power for a long time. PEMFCs are promising candidates for several applications like automotive applications, stationary power systems and portable devices but there are issues on performance, durability and costs [1]. The use of alkaline anion exchange membranes (AAEM) instead of proton exchange membranes has several advantages [2]. One of the most important one is the possibility of avoiding platinum as electrocatalyst and using low cost non precious metals instead [3]. Other advantages are the use of low cost metal bipolar plates due to decreased corrosion at high pH and faster oxygen reduction reaction on the cathode side [4]. Challenges for the use of AAEMs are the increase of their durability by decreasing the membrane degradation caused by the cleavage of cationic groups in alkaline media and the need for higher anion conductivity for an enhanced fuel cell performance.

Alkaline anion exchange membranes were produced using a functionalized PBI polymer with a covalently bound cationic group and a mobile anionic counter ion. Membranes were prepared using a doctor blade technique from a DMSO solution. Afterwards they were characterized regarding chemical stability, thermal properties using TGA coupled to GC-MS and functional properties like ionic conductivity. Additional information about MEA structure based on alkaline anion exchange membranes were gained by μ -CT measurements. [1] J. Wu, X. Z. Yuan, J. J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, J. Power Sources 184 (2008) 104–119. [2] G. Merle, M. Wessling, K. Nijmeijer, Journal of Membrane Science 377 (2011) 1–35. [3] C. G. Arges, V. Ramani, and P. N. Pintauro, The Electrochemical Society Interface Summer 2010. [4] J. R. Varcoe, R. C. T. Slade, Fuel Cells, Special Issue: Polymer Membranes I, 5, Issue 2, (2005) 187–200.

Prof Andy Herring

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Talk 3: Anion transport in structured and non-structured di-block hydrocarbon polymers Proposal Discipline: Polymer Science

We are developing a large number of di-block co-polymers consisting of a cationic block and a ethylene or isoprene block. These materials may be structured as lamella or amorphous materials. Using a wide range of analytical tools we are characterizing the ionic transport and morphology of the materials. Transport is studied using PFGSE NMR, electrochemical impedance spectroscopy, and broadband electric spectroscopy. Morphology is characterized using SAXS, SANS and HR-TEM. All the measurements are made under environmental and temperature control. Water uptake is quantified using dynamic vapor sorption. Further understanding of the systems is made through the use of modeling, where initial theoretical/experimental validation uses fluoride anions, which have the advantage of being non-reactive and easily handled by classical molecular dynamics. For promising systems we study the materials in their hydroxide form where rigorous exclusion of CO_2 is required and a reactive model is used for the simulation of hydroxide transport. In one model lamella system we see that the polymer pores are occupied with polymer brushes. Simple solvation of the polymer brushes is insufficient to promote anionic conductivity, which is only achieved when sufficient water enters the system to promote an aqueous channel in the pore center.

Prof Michael Hickner

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Talk 6: Ion mobility in anion exchange membranes

One of the key barriers to widespread anion exchange membrane deployment is the low ion conductivity of readily-available materials. There have been a few examples of high conductivity anion exchange membranes, but the fundamental polymer structure, conductivity, and hydration relationships in these materials that can lead to detailed design rules for high conductivity membranes are still being uncovered. We have explored the mobility of several different anionic species in anion exchange membranes containing either polymer-tethered quaternary ammonium or bis(terpyridine)ruthenium(II) cations. The intrinsic conductive properties of the materials as a function of hydration were expressed as dilute solution normalized diffusion coefficients of the mobile species versus hydration number. We found that the ion mobility in the membranes approached the dilute solution mobility only at high hydration numbers. For the quaternary ammonium-based AEMs, the maximum ion mobilities for hydroxide, bicarbonate, and chloride anions approached their dilute solution mobilities at hydration numbers greater than 10. For materials with bis(terpyridine)ruthenium(II) cations, higher hydration numbers, on the order of 50 or higher, were required for high intrinsic anion mobility. The differences between quaternary ammonium and bis(terpyridine)ruthenium(II) cations can likely be explained by their different size and charge density. By exploring crosslinking and block copolymer motifs, we have examined several systematic series of materials with a wide range of ion contents and hydration numbers. Our progress on understanding the intrinsic ion mobility in anion exchange membranes will be reported.

Mr Tobias Hoefner

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Poster: Assessment of AEMs for the alkaline anion exchange membrane water electrolysis

Water electrolysis provides a sustainable solution for the production of hydrogen when coupled to renewable power sources such as wind and solar energy. Despite alkaline electrolysis being a mature technology, breakthrough improvements could be still obtained by coupling the positive aspects of both alkaline electrolysis and polymer electrolyte membrane (PEM) electrolysis. This could be achieved by using anion exchange membranes (AEMs), curtailing the drawbacks provided by liquid electrolytes and diaphragms on conventional alkaline electrolysis. In this study we assess different commercial AEMs in

order to develop membrane electrode assemblies (MEAs) for water electrolysis. In order to evaluate the specific conductivity of the samples, electrochemical impedance spectroscopy (EIS) was applied together with a potentiometric titration to measure the ionic exchange capacity (IEC). Thermo mechanical analysis was applied to investigate the tensile strength together with Young's modulus and elongation at break. In order to determine the hydrogen crossover through the membrane, a three electrode cell setup coupled to the MEA was designed in order to measure the crossover rates for the different membrane materials. Based on these results, we demonstrate, together with the company FuMa-Tech GmbH, AEMs with promising activities for alkaline electrolysis, aiming to create a new generation of alkaline water electrolyzers.

Prof Steven Holdcroft

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Talk 15: Hydroxide-conducting polybenzimidazolium salts

A stable hydroxide-conducting membrane based on polybenzimidazolium hydroxide will be described. The molecular and polymeric analogues possess hydroxide stability in neutral and KOH solutions as the soluble benzimidazolium salt - made possible by steric crowding around the C2-benzimidazolium position. The polymers were cast and insolubilized by blending with neutral polybenzimidazole followed by KOH-activated electrostatic interactions.

Ms Lucy Howes

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Poster: The application of anion-exchange membranes in microbial electrochemical systems

Microbial fuel cells are emerging as an important area of investigation in the field of renewable energy and wastewater treatment. The research into microbial fuel cells at The University of Surrey is currently focused on several different areas. Anion-exchange membranes (AEMs) have been extensively researched for application in low temperature fuel cells at Surrey but have the potential for use in microbial fuel cells. These membranes potentially possess characteristics desirable in a microbial fuel cell setup such as low oxygen permeability and low resistance. The Surrey-made AEMs have been compared to Surrey CEMs and Nafion (the current industry standard) both in-situ and ex-situ. Stability testing has been carried out on Surrey AEMs and CEMs ex-situ to determine whether the various components of solutions used in the cells have any measurable effect on their performance. Tests include ion exchange capacity, conductivity and gravimetric water uptake measurements and analytical methods such as Raman spectroscopy.

Dr Takenori Isomura

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Talk 16: AMFC materials development in Tokuyama Corp.

Alkaline Membrane Fuel Cell (AMFC) is one of the promising applications for anion-exchange polymeric materials. Because of its possible use of non-precious metal group catalysts, it has been studied extensively as one of the alternatives for PEMFC. Tokuyama Corp., Japan, has been developing anion-exchange materials for AMFC. Our goal is to supply high performance AMFC materials with good durability into market. In our development, one of the biggest challenges is to improve material durability. Although it had been confirmed that AMFC could operate over 2,000 hours in our study, at the same time, we observed its degradation phenomena with some methods. The recent results on AMFC degradation and Tokuyama's state of material development will be shown and discussed.

Mr Rhodri Jervis

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Poster: Catalyst development for the alkaline fuel cell

With the high cost and limited availability of platinum, much effort has gone into the reduction of catalyst loadings in fuel cell electrodes. Platinum is the most effective catalyst for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) in acidic polymer electrolyte fuel cells (PEM), but the vastly improved kinetics of the ORR in an alkaline medium opens up the possibility of utilizing cheaper catalysts for alkaline anion exchange membrane fuel cells (AAEM). Rotating disk electrode (RDE) studies, along with in-situ fuel cell testing, have shown a novel, high-efficiency low cost catalyst to have activation properties matching that of Pt, when used in alkaline conditions. The performance of the low cost catalyst in an AAEM is also similar to that of an AAEM made using commercially available Pt electrodes, suggesting a potential route for future reduction of cost and precious metal use in fuel cell electrodes.

Dr Jochen Kerres

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Talk 14: AEM's consisting of BrPPO and DABCO and their application in alkaline DMFC

Poly(1,5-dimethylphenyleneoxide) was brominated with N-bromosuccinimide (NBS) up to a substitution degree of 80%. The brominated polyphenylene oxide (BrPPO) was cross-linked with 1,4-diazabicyclo(2,2,2)octane (DABCO) to yield a covalently cross-linked membrane. Additionally Polyvinylidene fluoride (PVDF) as stabilizing matrix polymer was used. The "mesh width" of the network was widened up by using diiodobutane (DIB) as an additional cross-linker. It could be determined that the ion conductivity (Cl⁻) with additional DIB increases from 2.3 mS/cm to 5.4 mS/cm despite a higher hydrophobicity of the DIB membranes. An IEC of around 1 meq/g was reached and the methanol uptake was lower than 20%. The alkaline stability was investigated at 90°C in 1 M KOH, yielding the result that all membranes showed a constantly stable behaviour. The direct methanol fuel cell application of the membranes led to an excellent performance of 132 mW/cm² when using a non-precious FeCo/C catalyst at the cathode.

Prof Anthony Kucernak

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Talk 22: Cathode development for alkaline fuel cells based on a porous silver membrane

Porous silver membranes were investigated as potential substrates for alkaline fuel cell cathodes by the means of polarisation curves and electrochemical impedance spectroscopy measurements. The silver membranes provide both electrocatalytic function, mechanical support and a means of current collection. Improved performance, compare to a previous design, was obtained by increasing gas accessibility (using Teflon AF instead of PTFE suspension) and by adding a catalyst (MnO₂, Ag or Pt) in the membrane structure to increase the cathode activity. This new cathode design performed significantly better (~ 55 mA cm⁻² at 0.8 V, ~295 mA cm⁻² at 0.6 V and ~630 mA cm⁻² at 0.4 V) than the previous design (~ 30 mA cm⁻² at 0.8 V, ~250 mA cm⁻² at 0.6 V and ~500 mA cm⁻² at 0.4 V) in the presence of 6.9 M KOH and oxygen at room temperature. The hydrophobisation technique of the porous structure and the addition of an extra catalyst appeared to be critical and necessary to obtain high performance. A passive air-breathing hydrogen-air fuel cell constructed from the membranes achieves a peak power density of 65 mW cm⁻² at 0.40 V cell potential when operating at 25°C showing a 15 mW cm⁻² improvement compare to the previous design.

Ms Sarah Mallinson

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Poster: Redox flow battery strategies: making renewable energy viable

With the increasing cost and lack of supply of non-renewable energy supplies, research has focused on alternative renewable energy. The intermittency of renewable energy sources is a major issue. Energy storage provides a solution by allowing excess energy (produced during optimum conditions) to be stored until it is required. The area of large scale energy storage in redox flow batteries (RFBs) is recently new at The University of Surrey. The following areas are under investigation: The synthesis of novel ion-exchange membranes to alleviate potential problems associated with vanadium ion crossover, the additional development of the electrolyte via the use of additives and modification of the electrodes. Each of these will potentially improve overall cell efficiency. Currently, our all-vanadium RFBs involves 0.5 – 3.0 mol dm⁻³ vanadium salts dissolved in 1.0 – 5.0 mol dm⁻³ aqueous sulphuric acid, using Nafion and other candidate separator membranes. Radiation-grafted anion exchange membranes (AEMs) have been extensively researched for application in low temperature fuel cells at Surrey, but have the potential for use in flow batteries, primarily to aid the reduction of vanadium cation permeability. Two AEMs were selected from the fuel cell research group based on trimethylamine (TMA) and 1,4-diazabicyclo(2,2,2)octane (DABCO) chemistries. These AEMs were compared to commercial anion- and cation-exchange membranes in comprehensive testing including stability, conductivity and permeability.

Prof Neil McKeown

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Talk 13: Novel amine-based polymers for anion exchange membranes

We report a new class of polymer based on the formation of the bridged bicyclic amine Troger's base (TB). Depending on the aromatic diamine monomer used for polymerisation the microporosity of the resulting polymer can be tuned. For example, the polymer derived from diaminoethanoanthracene (PIM-EA-TB) displays good processability for film formation and an apparent surface area of 1000 m² g⁻¹. This polymer has exceptional promise for gas separation membranes [1]. Others TB polymers are non-porous. The amines within the TB unit are readily quaternized to provide a positively charged polymer, which may have application as anion-exchange membranes.

[1] Carta et al. Science, 2013, 339, 303.

Mr Sam Murphy

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Poster: Degradation study of alkaline anion exchange membrane head groups

The positively charged groups of anion exchange membranes (AEMs) will degrade over time in an alkaline environment at different rates. Using adaptable methods to synthesise AEMs and model compounds, the screening of different positively charged nitrogen groups for long term stability at raised temperatures in aqueous alkaline environments can be studied spectroscopically. Several different AEMs and compounds have been synthesised, and shown to possess variable stability under test conditions.

Prof William Mustain

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Talk 21: Room temperature electrochemical production of oxygenates from methane enabled by AEMs

Over the past several years, a significant effort has been put forth by several groups to develop high conductivity, high stability anion exchange membranes (AEMs). The advantage of AEMs in electrochemical applications is their tolerance to the presence of CO₂ and/or production of carbonates in the system; which are poisonous to traditional alkaline cells. What this means is that, for the first time, carbonate anions - which are efficient oxygen donors, even at room temperature - can be leveraged to facilitate new catalytic pathways. This talk will focus on new chemistries enabled by AEMs with a particular focus on the electrochemical partial oxidation of methane to oxygenates (i.e. methanol and formaldehyde) at room temperature. This process has potential advantages over the typical methane steam reforming that requires a considerable amount of high quality heat (~ 200 kJ/mol at T > 800°C) to first oxidize methane to syngas, then reduce the syngas back to the oxygenate of interest including a reduction in energy requirements, a reduction in the number of processing steps, and lessening the size of balance of plant components.

Prof Kitty Nijmeijer

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Talk 9: Tailoring membranes for blue energy

Blue energy or reverse electrodialysis (RED) is a non-polluting, sustainable technology to generate power from the mixing of solutions with different salinity, i.e. sea and river water. Ion exchange membranes are the key components in RED. The currently commercially available ion exchange membranes are not optimized for RED and new molecular membrane designs and geometries especially tuned for RED are essential to increase the power output obtainable per membrane area. In this work we synthesize anion exchange membranes (AEMs) using a methodology to prepare such membranes in a safe, environmental-friendly way. Halogenated polyethers such as polyepichlorohydrin (PECH) [1] are used as starting material. 1,4-diazabicyclo-[2,2,2]-octane (DABCO) is used as a tertiary diamine to introduce the quaternary ammonium functionality required for ion exchange and crosslinking simultaneously. Polyacrylonitrile (PAN) is added as an inert supporting polymer. Prepared blend PECH membranes exhibit a resistance of only 2.05 $\Omega\cdot\text{cm}^2$ and a permselectivity of 91.9 %, which is the highest value reported. For the first time we show the performance of these tailor-made membranes in RED. Increasing blend ratio, i.e. increase in the amount of active polymer PECH, provides a membrane with lower resistance giving a higher power density. Decreasing the thickness of the membranes decreases the membrane resistance further, resulting in a power density as high as 1.3 W/m². Traditionally, the ion exchange membranes are separated by non-conductive spacers, which reduce the active membrane area available for ion exchange. Here we introduce the use of microstructured ion conductive membranes, which integrate the spacer and membrane functionality. The geometry of the structures determines the flow profile in the channels and introduces mixing, while the structures, made from ion conductive material, create conductive pathways for ions and thus improve the power output [2].

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Talk 5: Influencing cation stability in base through substituent groups

Benzyl trimethylammonium has been the primary cation used in the development of anion exchange materials and membranes. For the purposes of electrochemical devices from anion exchange membranes, base stability is a critical issue. We have investigated a series of controlled substitutions on the benzene ring for benzyl trimethylammonium to study the impact of electron donating and withdrawing groups on base stability.

Our experiments combine NMR measured degradation rates with those obtained by gas chromatography-mass spectrometry performed on head gas samples. This approach has allowed us to study degradation products in the liquid and gas phase. Computational studies of these materials have also been performed and in general show good agreement with experimental studies. Substitution of electron withdrawing groups on the benzene ring has been shown to have a significant impact on reducing the base stability of benzyl trimethylammonium; however, the introduction of electron donating groups was not found to have a significant impact on improving base stability. These results suggest that only modest gains in durability would be likely through simple substitutions onto benzyl trimethylammonium groups.

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Talk 20: AFC Energy: Powering Into the Future

The commercial focus of AFC Energy Plc is the development and commercialisation of its unique low-cost alkaline fuel cell technology. The fuel cell and commercial development work is centred at AFC Energy's state-of-the-art facility in Surrey, where they have also recently established a fully operational production facility. AFC Energy's flagship system is of a modular design which features multiple '10 kW cartridges'. Uniquely, these cartridges can be 'hot swapped' during system operation, whereupon the electrode and stack components can be recycled or reused at their end of life. AFC Energy's initial target field of commercialisation is the Chlor-Alkali industry, where the equivalent of >£300 m of electricity per annum is potentially available. To this end, AFC Energy has been collaborating with AkzoNobel at their plant in Bitterfeld, Germany in the deployment and operation of its fuel cell systems. Since AFC Energy was established in 2006, other markets have become of interest to AFC Energy. This includes the waste-to-energy sector, where multiple 1000's MW of electricity generating potential is available.

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Talk 10: Alkaline membranes for electrolyser and fuel cell applications

The performance data obtained with a range of alkaline ion exchange membranes for applications in fuel cells, electrolyzers and reversible fuel cells is described. This includes membranes based on methylated melamine grafted poly vinyl benzyl chloride (mm-qPVBz/Cl⁻) and radiation grafted polymers. Conductivity and cell performance data is described for these different materials. For example the aminated poly (LDPE-g-VBC), poly (HDPE-g-VBC) and poly (ETFE-g-VBC) membranes were produced from different base polymer film properties and grafting technique used. In plane conductivities increased with degree of grafting and membranes with the highest degree of swelling showed the highest through plane conductivity of 0.07-0.11 S cm⁻¹. The membrane specific resistance (per MEA cm²) of most of the produced membranes was in the range of 0.09-0.18 ohm cm². In fuel cells high peak power densities were obtained, at a high potential of 500 mV: 823 mW cm⁻² at 60 °C, 718 mW cm⁻² at 50 °C and 648 mW cm⁻² at 20 °C under oxygen (atm). Peak power densities with air were also high; 424, 451 and 471 mW cm⁻² at cell potential of 0.6 V at 40, 50 and 60 °C, respectively.

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Talk 8: Low-energy production of fresh water from the sea by forward osmosis

Water is not just the essential ingredient for life, but also a fundamental factor in the economy and security of any country. Coupled with increased population and climate change effect, the availability of food, water, and energy are the biggest challenges that the world faces. Over the next two decades water demand will exceed water supply by about 40% according to many scientific studies and reports. Food and energy shortages have also been described by the UK Government's Chief Scientific Advisor, Prof. Sir John Beddington, to create the "perfect storm" by 2030.

The provision of drinkable supplies through desalination could offer a sustainable solution to the drinking water problem but also presents a technical challenge too.

Seawater and brackish water are desalinated by thermal distillation and membrane methods such as reverse osmosis (RO) and electrodialysis. All these methods involve high operating and investment costs.

RO is the most widely used desalination techniques, while thermal methods are mainly used in the Gulf countries. However, the high operating cost of RO is due to essential pre-treatment, scaling, bio-fouling and the high-energy consumption.

A novel manipulated/forward osmosis (MFO) desalination and water purification process has been invented and developed at the Centre for Osmosis Research and Applications at the University of Surrey in collaboration with Modern Water plc. In the MFO process seawater is converted into an osmotic agent's solution by taking advantage of the natural osmosis process. Pure water is then recovered from the osmotic agent's solution using a membrane process, where the agent is reused.

The technical obstacles being overcome in this process are the avoidance of all scaling, bio-fouling, high operating pressures, and necessity for pre-treatments and the associated chemical wastes, which result in direct and indirect reduction of cost.

The pilot plant and Modern Water's commercial plants data in Oman and Gibraltar that follow from the MFO process route offers up to 30% saving in the specific energy consumption over a conventional RO process. The MFO process also offers an increase in fresh water recovery rate coupled with minimal membrane fouling propensity and brine disposal. Additionally, the process can be incorporated into existing RO and thermal plants with reasonable modifications. New plant based on the MFO principle should also have lower capital costs and smaller footprint.

The new technology can be used to obtain clean water from any available water source irrespective of its purity, such as waste streams, seawater, brackish water, river water, etc.

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Talk 23: Doping studies of perovskite materials for potential applications as fuel cell cathodes

The development of highly conducting alkaline polymer electrolyte membranes has led to a resurgence of world-wide interest in alkaline polymer electrolyte membrane fuel cells (APEMFCs). The use of alkaline membranes rather than traditional acidic membranes confers a number of significant advantages. In particular, such alkaline membranes offer the potential for replacing precious metal (Pt, Pt/Ru) catalysts conventionally used with acidic membranes, with cheaper alternatives. In this work, we have been examining the preparation of doped perovskite- and K₂NiF₄-type phases for potential applications as fuel cell electrodes for both solid oxide and alkaline polymer electrolyte membrane fuel cells. Work will be presented highlighting novel doping strategies in perovskite systems, along with preliminary results from electrode testing.

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Talk 1: Cationic head-group research at Surrey for alkaline-based systems

This presentation will provide a summary and highlight some of the recent research conducted at the University of Surrey on ion-exchange membranes for energy systems and CO₂ capture. This includes studies on: (1) alkaline stabilities of various anion-exchange [cationic] head-groups; (2) rotating disk studies on the effect of these head-groups on the fuel cell reactions at high pH; (3) the application of ion-exchange membranes in energy systems such as fuel cells and reverse electrodialysis; and (4) ionic-liquid “inspired” polymers for CO₂ capture.

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Poster: Solvent-free synthesis of alkaline anion exchange membranes proposal

As a critical component of an alkaline anion exchange membranes fuel cells (AAEMFCs), the alkaline anion exchange membrane (AAEM) acts as a barrier between electrodes and simultaneously transport hydroxyl ions due to the bounded cationic sites. This study presents a solvent-free strategy for AAEMs by in-situ polymerization. Different from conventional methods, this non-solvent strategy was performed by dissolving polymer electrolytes (cardo polyetherketone, brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO)) in liquid monomers mixture of vinylbenzyl chloride (VBC) and divinylbenzene (DVB), then in-situ polymerizing to incorporate BPPO into the network of poly(VBC-DVB). After quaternization, translucent and flexible AAEMs are obtained. These AAEMs exhibit excellent mechanical strength (8-12 MPa), favourable water uptakes (17.6-34.2%) and hydroxide conductivity (0.019-0.04 S cm⁻¹). The favourable performances suggest that this method holds promise as an environmental friendly strategy to develop AAEMs for AAEMFCs.

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Talk 2: Development of novel anion exchange membranes in USTC for fuel cells

The alkaline fuel cell (AFC) is considered to be a promising energy conversion device for stationary and mobile applications. However, one of their key components—anion exchange membranes (AEMs) are not favourable for practical application due to poor ionic conduction and alkaline stability. Recently, AEMs with elegant properties are developed in USTC for fuel cells. Firstly, bromomethylated poly(phenylene oxide) (BPPO) is functionalized with 1-methylimidazole, benzimidazole, 1,2-dimethylimidazolium, 1,1,2,3,3-pentamethylguanidine, and tris(2,4,6-trimethoxyphenyl phosphine). Compared with AEMs containing quaternary ammonium cationic functional groups, the above-mentioned membranes exhibit appealing alkaline stabilities and high hydroxide conductivities. Secondly, novel aromatic anion exchange polyelectrolytes featured with pendent long spacer (i.e., $-\text{O}-(\text{CH}_2)_4-$) instead of conventional benzyl-type spacer (i.e., $-\text{CH}_2-$) are successfully synthesized via straightforward polyacylation of pre-quaternized monomers. The resultant membranes display a promising peak power density of 120 mW/cm² on a preliminary H₂/O₂ single cell at 50 °C. Thirdly, comb-shaped copolymers of bromomethylated poly(phenylene oxide)-g-quaternary 4-vinylbenzyl chloride (BPPO-g-QVBC) are synthesized by atom transfer radical polymerization (ATRP) graft from BPPO macroinitiator with hydrophilic monomers-QVBC. The obtained membranes with nanometre-sized ionic clusters imbedded in the hydrophobic BPPO matrix offer considerably high conductivities up to 0.1 S/cm at 80 °C. Lastly, a solvent-free strategy for AEMs synthesis by in situ polymerization was explored. It starts from the dissolution of polymer with monomers (e.g., 4-vinylbenzyl), not solvent, followed by in situ polymerization and quaternization. This is a simple, rapid, environmental friendly route for production of AEMs. In summary, our studies focus on the fabrication of AEMs for fuel cell applications with enhanced stabilities and ionic conductivities via feasible means.

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Talk 11: Hydroxide exchange membranes for fuel cells, electrolyzers, solar hydrogen, and redox flow batteries

Energy has been fundamental to human civilization. The availability of cheap and abundant fossil energy has been primarily responsible for the fastest ever human progress for the past 100 years. With the depletion of fossil energy, the increase of world population, the improvement of living standard in large population centers, and the concern of the air quality and climate change, one of the grand challenges facing humanity today is to develop an alternative energy system that is clean, safe, and sustainable and where combustion of fossil fuels no longer dominates. Fuel cells coupled with solar hydrogen represent a safe, clean and sustainable energy system that can help significantly alleviate or eliminate the energy supply and CO₂ problem. In this presentation, I will focus on our recent work on hydroxide exchange membrane fuel cells (HEMFCs), where the platinum catalysts to be replaced by non-platinum-group-metals, thus drastically reducing the cost of fuel cells and making them potentially economically viable. I will also discuss our new concepts of using HEMs in electrolyzers or flow batteries for large scale solar/wind electricity storage and for solar hydrogen generation.

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Talk 4: Rational design of ionic channels in alkaline polymer electrolytes

A combined computational and experimental study on the rational design of ionic channels in alkaline polymer electrolytes (APEs) is reported. The resulting APE exhibits a clear hydrophobic/hydrophilic microstructure and a hydroxide-ion conduction as efficient as the proton conduction in Nafion (greater than 0.1 S/cm at 80 °C under moderate ion-exchange capacity of 1.0 mmol/g).

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