Effects of the thermal conductivity of the membrane and catalyst layer on the performance of PEM fuel cells

Knowing the local temperature distributions of the various components of the proton exchange membrane fuel cell is essential for the water and heat management. In this study, the effects of the thermal conductivity of the membrane and the catalyst layers have been investigated numerically using a three-dimensional (3-D) multiphase model developed in the Fluent® software. The results show that there are no significant differences in the power density of the fuel cells when the thermal conductivity of the membrane or the catalyst layer realistically changes. However, the local temperature gradients decrease when the thermal conductivity of the catalyst layer or the membrane increase due to the dissipation of the heat from the membrane electrode assembly, which results in a more uniform temperature distribution within the fuel cell components. Furthermore, increasing the thermal conductivity of the membrane or the catalyst layer increases the liquid water saturation as the temperatures decrease, leading to a slight improvement in the performance of the fuel cell.

NOTE: This abstract was submitted by Nahla Al-Hazmi, Leeds
Proton Exchange Membrane (PEM) fuel cells offer several advantages such as rapid start-up and shut-down, low temperature, high power density and fully solid state components. However, the high cost and low durability of the electrodes need to be addressed before commercialisation can be realised. It is well known that the activity of a catalyst depends on the particle size and dispersion pattern over the support structures. Therefore, catalyst support materials have a great influence on the cost, performance, and durability of PEM fuel cells. Carbon black is the most widely used catalyst support for state-of-the-art PEM fuel cells even though it is known to undergo carbon corrosion during operation. As carbon black corrodes, the metal nanoparticles detach and possibly agglomerate, resulting in electrochemical surface area loss, which consequently reduces the performance and durability of PEM fuel cells.

One strategy to reduce performance degradation due to carbon corrosion is to use a more robust carbon support. Recently, there has been great interest in nanostructured carbon nitride materials due to their unique properties such as extreme hardness, oxidation resistance, tunable band gap and morphology, and chemical inertness. The most exciting and stable material among them is graphitic carbon nitride (gCNM) which has great prospects in catalysis. A growing body of literature data suggests that the presence of nitrogen in carbon supports improves durability, as well as enhancing the intrinsic catalytic activity for both oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). The incorporation of nitrogen into carbon leads to a reduction in detrimental surface oxygen groups and thus provides enhanced tolerance towards corrosion.

The aim of this study is to investigate the potential application of the gCNM materials as catalyst support in PEFC. A rotating disk electrode (RDE) system is employed to characterize the activity and durability of the catalysed and non-catalysed gCNM materials using accelerated corrosion carbon corrosion protocol, and compared with that of commercial Vulcan XC-72R carbon. The start-stop and load cycling are performed by cycling the potential between 1.0 V to 1.5 V and between 0.6 V to 0.95 V respectively, in 0.1 M HClO₄ at 60°C. The stability of the support is evaluated by measuring the change in capacitance, whereas the stability of the catalysed support is evaluated by monitoring the change in electrochemical surface area (ECSA) and electrocatalytic activity.

References

From Catalyst to Device: Development of a Novel Low-Cost, High-Durable Electrode for use in Polymer Electrolyte Water Electrolysers

Ana Belen Jorge¹, Christopher Gibbs¹, Furio Corà², Paul Shearing¹, Paul F. McMillan², Daniel J. L. Brett¹

¹Roberts Building, Department of Chemical Engineering, University College London, Torrington Place, WC1E 7JE London, United Kingdom
²Christopher Ingold Building, Department of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ London, United Kingdom

Water electrolysers have gained traction recently as a storage solution for stabilising grid power with an increasing percentage of intermittent renewable generation. Generating hydrogen during periods of peak renewable electricity production and storing that hydrogen in the existing natural gas grid (power-to-gas programmes) not only provides a fast, effective method of stabilising the grid power supply but also decarbonises domestic heat – one of the trickiest sectors to decarbonise. Continental Europe, especially Germany and Netherlands, are leading this initiative by permitting significant hydrogen storage in the existing natural gas grid, and the UK is currently developing policy for such power-to-gas schemes.

Our goal is to develop a novel electrocatalyst and optimise the \textit{in situ} performance in water electrolysers for the production of hydrogen. Our catalyst is a low-cost alternative to platinum and platinum-alloys which has performed as well as, and in some regards better than, platinum in water electrolyser cathodes. We intend to study the \textit{in situ} performance of the new catalyst in single cells of water electrolysers, paying special attention to durability aspects, key for unlocking the full commercial potential of this catalyst. In addition, new catalyst supports will be introduced based on low-cost graphitic carbon nitrides (g-CN) which we have shown to be highly promising materials as catalyst substrates for use in fuel cells and electrolysers.

The innovation will enable the reduction of costs of technologies such as water electrolysers and fuel cells and increase their rate of market penetration, thus bringing forward and enhancing the impact on reducing anthropogenic climate change and the security of energy supply benefits using hydrogen as an energy vector.
Transient thermal and water balance of an evaporatively cooled fuel cell vehicle

Ashley Fly – Loughborough University

Hydrogen fuel cell vehicles are a promising alternative to internal combustion engines, however there are many challenges to be addressed to improve performance, one such challenge is how to reject the low grade heat (≈80°C) of Proton Exchange Membrane (PEM) fuel cells at high ambient temperatures (≈40°C). This project addresses that issue by using an evaporatively cooled fuel cell with a stored water supply, decoupling heat generation from stack temperature regulation. This allows peak thermal load to be averaged across a transient drive cycle.

An evaporatively cooled fuel cell system model has been produced and experimentally validated; the model has been used to study the influence varying different operating parameters has on the ability of the system to obtain water balance. Initial results have shown that increasing stack pressure can significantly reduce required radiator size due to elevated operating temperatures. It has also been shown that for any set of operating parameters optimum operating currents exist for both instantaneous water balance and maximum net water gain.

Results obtained from the model are to be used in the development of a control algorithm which will be used to regulate water balance in an evaporatively cooled fuel cell system whilst minimising parasitic load.

Figure 1 - Evaporatively cooled fuel cell system
Transfer Function Analysis as a Novel Diagnostic Tool in Polymer Electrolyte Fuel Cells

Erik Engebretsen¹*, Tom Mason¹, James Robinson¹, Gareth Hinds², Paul Shearing¹, Dan Brett¹
¹Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE
²National Physical Laboratory, Teddington, Middlesex, UK, TW11 0LW

Fuel cells are a key technology in power production in the transition from a carbon-based economy to a sustainable, low carbon future. Polymer Electrolyte Membrane (PEM) fuel cells have a relatively high power density, low temperature operation, and produce no carbon emissions (depending on fuel source). However, there are limitations to the technology as PEM Fuel Cells have high catalyst costs, sensitivity to impurities and gaps in understanding of internal processes. In-situ diagnostic performance tests are essential to gain insight into the inner workings of an operational PEM fuel cell. This insight may lead to optimisation of durability and performance as well as more comprehensive models of fuel cell operation.

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool which can be used to identify various performance losses in a fuel cell. A small sinusoidal voltage is imposed on the fuel cell and the current response is measured. The phase shift and amplitude ratio between the voltage and current are dependent on the frequency of the imposed wave. These parameters, over a range of frequencies, can identify various resistances and capacitances in the system. In this work, similar cause-effect relationships are investigated to yield transfer functions which can infer other performance losses that are not accessible via EIS. The preliminary parameters for variation (causes) are:

- **Thermal** – varying temperatures will affect water management, reaction kinetics and can lead to mechanical failure
- **Chemical** – varying stoichiometry will affect reaction kinetics, catalyst degradation, and water management
- **Mechanical** – varying stress will affect water management, gas diffusion layer mass transport and membrane degradation
- **Electrical** – varying voltage and current will affect water management, temperature, and reaction kinetics
- **Pneumatic** – varying flow and pressure will affect mass transport properties
- **Photo** – varying light exposure to the catalyst may affect carbon monoxide poisoning processes.

The preliminary parameters for measurement (effects) are:

- **Thermal** – Sensible heat and radiation measurements using thermocouples and an infrared camera
- **Chemical** – Catalyst poisoning can be inferred from a CO sensor
- **Mechanical** – Strain can be measured using displacement sensors
- **Pneumatic** – Pressure and flow can be measured with pressure transducers and flow meters
- **Electrical** – Voltage and current can be measured with a potentiostat
- **Acoustic** – Acoustic emissions which show bubble rate can be measured with finely tuned hydrophones

The aim of these transfer function techniques is to develop a comprehensive set of diagnostic tools to identify faults, degradation mechanisms and general performance of operating systems.
Proton Exchange Membranes for Electro-chemical Hydrogen Compression

Martijn Mulder, Menno Koeman, Daniel Semerel, Wiebrand Kout, Peter Bouwman

Hydrogen Efficiency Technologies – HyET
Leemansweg 15
6827 BX, Arnhem / The Netherlands
Tel.: +31-26-36-23-944 Fax: +31-26-36-23-945
info@hyet.nl

Abstract

HyET has greatly extended the capabilities of Electro-chemical Hydrogen Compression and is presenting this novel technology as a solution for hydrogen processing steps like compression for storage, recirculation and purification.

Technical characteristics of this technology are:
- Exceptionally high, single stage compression up to 1000 bar ∆P
- Hydrogen stream purification or hydrogen extraction from gas mixture
- Accurate electrical bi-directional hydrogen flow rate control

The working principle of EHC is anodic oxidation of molecular hydrogen, subsequent proton migration through a proton-conducting polymer membrane and cathodic reduction of the protons back to molecular hydrogen by forcing an electrical current through an external circuit.

A key component is the membrane that provides gas separation, electrical insulation and good proton conduction between the high and low hydrogen pressure sides.

HyET’s adaptation of PEMFC membrane technology for EHC applications will be presented. It has resulted in a 1 Nm³/hr EHC prototype, ready for project-based field testing. Also EHC (and PEMFC) membrane challenges, like operation with dry feed gas will be discussed.

The company HyET focuses mainly on Research, Development and Production of EHC components like the membrane together with strategic partners targeting hydrogen processing markets.
ABSTRACT
A rigorous investigation has been conducted to study the effects of the addition of the microporous layers (MPL) on the through-plane gas permeability of the gas diffusion layer (GDL). In this investigation, using Darcy’s law, the gas permeability of some typical GDL samples has been experimentally estimated before depositing the MPLs. The permeability of these samples was found to be of the order of $10^{-11}$ m$^2$. The MPL blend was then applied to one side of the above GDL samples. Subsequently, the samples were heat-treated. The permeability of the coated sample was found to reduce by two orders of magnitude. Also, the effects of sintering and the composition of the MPL have been thoroughly investigated. Finally, with the assistance of scanning electron microscopy (SEM), the thickness of the added MPLs have been accurately estimated, leading to better estimation of the gas permeability of the MPLs.
PEMFC Modelling with CFD: Comparison of multiphase modelling approaches.

A comparison of two different multiphase models is presented, namely the mixture model ($M^2$) and multi-fluid model (MFM), both implemented using commercially available CFD packages. Results for a full fuel cell with anisotropic properties influencing liquid water distribution show the differences between the models and crucially the level of saturation in the GDL under typical operating conditions. Performance is compared with a real fuel cell using polarization data obtained from an in-house fuel cell. Special attention is paid to the absolute and relative permeability for each phase in the GDL.

The level of saturation in the GDL is shown to vary depending on the relative permeability of the liquid water and the capillary pressure diffusivity in accordance with previous studies. In cases where convection occurs in the GDL results are shown to vary significantly depending on which model formulation is used as interfacial shear forces are treated differently. Results for a single straight channel with diffusion dominated vapour transport and a serpentine channel with both diffusion and convection is used to emphasise the magnitude of the modelling discrepancies.

Treatment of the GDL-Flow channel interface is varied using the MFM which allows the specification of a non-zero saturation value. Simple physical considerations are given to the forces that liquid water experiences at this boundary, namely critical mass for droplet detachment dependent on the velocity profile in the channel. This parameter is found to influence the saturation profile in the GDL and gives a more realistic representation of flooding when compared with the mixture model.

Tom Tranter
Postgraduate Research Student
Energy Technology and Innovation Initiative (ETII)
Faculty of Engineering
The University of Leeds
Leeds, LS2 9JT, UK
Tel: 07813 789586
Email: pmtgt@leeds.ac.uk
Advances in Fuel Cell Automation and Control

Amit M. Manthanwar∗†, Thiago Lopes‡, Stephen C. Atkins‡, Anthony R. Kucernak‡ and Stratos N. Pistikopoulos†

†Centre for Process Systems Engineering, Imperial College London
‡Department of Chemistry, Imperial College London

Abstract for H2FC SUPERGEN Researcher Conference

Fuel cells are sustainable energy conversion systems that can offer competitive advantage over other energy generation technologies, thus help realise goals of hydrogen economy. Barriers to fuel cell commercialisation are its cost, durability, and performance under varying operating conditions. Operational uncertainty is further compounded when fuel cells are integrated with remaining balance of plant components. Clearly, automation is a key to integrate fuel cell system efficiently and operate them reliably as well as cost effectively. Selection of instruments, choice of integration architecture and deployment of control software technology falls under the realm of automation. Automation hardware can help monitor operation of the complex phenomena taking place inside fuel cell while the control software can help achieve better heat, water and electricity management.

The goal of this research work is to achieve seamless integration of hardware and software platform that will allow efficient operation of fuel cells at multiple length and time scales for their application in a typical transport or stationary energy sector. In this presentation, we will highlight results of our fuel cell research carried out at micro, meso and macro scales as described in the following sequel. At micro scale, we are interested in understanding the complex phenomena taking place inside the fuel cell. We aim to achieve this goal by developing in situ functional map of temperature profiles for polymer electrolyte membrane unit cell. This function map can enable us to validate high fidelity mathematical models of the system. Resulting dynamic models can then be used for in silico analysis to investigate fuel cell’s degradation or study its behaviour at extreme operational scenarios. We will outline challenges encountered during in situ thermal monitoring and present the results of bespoke fuel cell unit cell integrated with in-house built highly precise data acquisition and monitoring platform. At meso scale, our goal is to study the dynamic behaviour of fuel cell stack appropriately interfaced with balance of plant components. Critical tool to achieve this goal is to built a fuel cell test platform. We have built a fully integrated fuel cell pilot plant with real-time control system architecture. The main features of this purpose built experimental test plant is its ability to benchmark various control strategies using our generic control framework for fuel cell stack integrated with balance of plant components. To demonstrate practicability of this framework to transport application, we have deployed our control framework on prototype mini fuel cell vehicle. Finally, we will present the objectives of our macro scale research on automation and control over smart grid by building a cyber physical platform for smart energy efficient buildings. Our proposed framework aims to seamlessly embed the local control loops into the microeconomics represented in the global control loop to jointly maximise each consumers utility as a trade-off function between home conditions and energy costs. This will achieve an optimal digital ecosystem enabling consumers to pursue the most efficient cost-to-comfort energy usage rather than simply the most economical solution alone.

Our automation and control technology is extremely flexible. It allows significant reduction in operational costs and improves overall performance of the system. We believe that the proposed automation architecture and embedded “model predictive control on a chip” strategy is the only available option for making smarter decisions in operating fuel cells reliability and improve their competitive edge.

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Polymer Electrolyte Fuel Cells (PEFCs) are a key technology to secure the future of the automotive sector. PEFCs are advantageous due to their low operating temperature (60-80 °C), quick start up times and responsiveness to load change. However, the requirement for expensive platinum, difficulty of water management and heat dissipation means that further improvements are required [1].

One of the ways PEFCs can be improved is by increasing their operating temperature (>100 °C) [2], commonly known as the Intermediate Temperature PEFC (IT-PEFC) (120 °C). This allows for the generation of high temperature heat, which allows more facile heat rejection, while simplifying water management as water will exist solely in the vapour phase. In order to optimise these IT-PEFCs, further improvement in the cell components is necessary.

Comsol Multiphysics was used to create a model of a single cell unit in order to assess the importance of Gas Diffusion Layer (GDL) properties within the electrode. Specifically, their porosity, permeability, electrical conductivity and thermal conductivity were investigated. Further to this, the modelling tool has been used to further improve the cell design by varying the cell materials and the cell configuration.

Results have shown that the GDL porosity is a key factor of influence on the PEFC electrode. The balance between the mass transport capabilities and the electrical conductivity is very important to the success of the electrode. It was found that the cell performance was most sensitive to the GDL porosity when the cell was in the “standard operating” range of 0.7-0.5 V. It was found that a porosity between 40-60 % was best.

It was also found that by replacing some of the conventional cell materials with novel component composite materials, the heat removal from the stack could be increased significantly as well as the electrical conductivity of the material. This could lead to a reduction in the requirement for the high gas flow rates specifically for cooling of the cell and therefore an increase in the air utilisation which lowers the parasitic losses from the system.

In conclusion, the GDL is a very integral component of the PEFC, however, the effect of its properties on the MEA performance is not sufficiently understood. In the work presented, it is shown that the MEA performance is sensitive to changes in the GDL porosity and therefore electrical conductivity. It was also found that the materials used in the MEA and therefore the stack can influence the heat transfer properties of the stack and so the cost of novel materials to improve heat transfer must be carefully considered against the lifetime of the stack. Future work will involve the continuation of the study to gain a better understanding of the GDL permeability and the effect it has on the cell performance.

Abstract

Developing catalysts with high activity and high resistance to surface poisoning still remains a challenge in direct formic acid fuel cells (DFAFCs) research. Although, considerable progress has been made in developing DFAFCs electrode materials, the catalytic property and improved stability of the electrode are still pending for all low-temperature fuel cells. Hence, the need for further advancement of DFAFC technological development of efficient anode catalyst for formic acid electrooxidation. The anode catalyst selection is pivotal in directing formic acid oxidation to proceed via the dehydrogenation reaction, thus the need for more research to exclusively promote direct dehydrogenation reaction. The Pd-based catalyst was synthesized using modified sodium borohydride reduction method. The catalyst was characterised by using X-ray diffraction (XRD) and High Resolution Transmission Electron Microscopy (HRTEM). HRTEM showed that Pd particles were homogeneously distributed on the surface of the carbon support. These particles exhibit much higher formic acid oxidation activities than that on pure Pd nanoparticles, and they are much more resistant to the surface poisoning. Cyclic voltammetry indicated that a much greater enhancement in catalytic activity was observed when compared with the improvement in electrochemical surface area (ECSA) and Pd % utilization.
Carbon support corrosion under pseudo fuel cell operating conditions

Christos Kalyvas*a, Anthony Kucernak*a

*aDepartment of Chemistry, Imperial College London, London, UK, SW7 2AY, UK

One of the major reasons for the degradation of cathode electrodes in polymer electrolyte fuel cells (PEFCs) is carbon support corrosion. The rate of carbon corrosion is slow under normal cell conditions when the potential is between 0.4-0.7 V. However, under some circumstances where the electrode is exposed to increased electrochemical potentials, the corrosion reaction is noticeably accelerated. One of the states of high-electrode potentials is characterised by local fuel starvation caused either by flow maldistribution or blockages in the fuel channel or during the startup/shutdown of the cell.

A new insitu diagnostic approach has been developed for the study of the electrochemical oxidation of carbon black supports in PEFCs during transient events and under critical operating conditions. In the present work, a series of polarisation experiments in MEA samples were conducted under high potential holds and sweeps. By monitoring CO₂ evolution at the cathode exhaust via online mass spectrometry, the carbon corrosion was evaluated. The catalytic effect of platinum on the corrosion of carbon was also studied. Compared to Pt-free carbon support material, the presence of catalyst can substantially increase the corrosion rate. The tests also revealed that the exposure of cathode electrode to different potential modes resulted in different oxidative processes. It was concluded that the nature of potential exposure may change the mechanism of electrochemical oxidation of carbon support.
In most developed countries the new laws are pushing the car industry to reduce the CO\textsubscript{2} emissions and fuel cells are one of the most viable options to achieve this without considerably sacrificing the range. However, the use of PEMFCs in the transport sector requires lower weights, sizes and significant cost reductions. The present carbon/carbon-composite BPP (bipolar plates) are one of the major contributors to cost and weight of the PEMFCs. The use of stainless steel (SS) BPPs is currently the most effective way to bring down the costs as well as reduce the weight of PEMFCs. This, however, also has its drawbacks such as increased interfacial contact resistance (ICR) between the stainless steel and the GDLs leading to ohmic inefficiencies. Moreover, the ICR increases continuously during the life cycle due to the passivation of the steel in the acidic media. Currently, this problem can be overcome by using expensive protective coatings such as gold platings and PVD coatings. PANI (Polyaniline), a conductive polymer, is a more economical alternative that can be easily coated electrochemically and is very stable in acidic environment.

In the present work, 0.1 mm SS coupons were coated with different PANI coatings using cyclic voltammetry. Ex-situ corrosion revealed that a PANI layer allows a shift in the inversion potential of SS from -0.1 V\textsubscript{SHE} to +0.28 V\textsubscript{SHE} and corrosion current decreases to less than half. Its morphological structure and homogeneity studied by optical microscopy and SEM, showed that increasing the coating thickness leads to a higher degree of porosity leading to poor adhesion. In addition, ICR of the coated samples also increases with thicker PANI coatings. Hence, it is important to control the thickness. In conclusion, it is possible to affirm that electropolymerised PANI coatings display better corrosion resistance to stainless steel and can be considered as a promising protective layer for metallic BPP.
Effect of small molecules architecture containing cationic groups on the performance of fuel cell grade catalyst for oxygen reduction reaction in aqueous KOH (1 mol dm\(^{-3}\))

Ai Lien Ong,* Daniel K. Whelligan, Sam Murphy, and John R. Varcoe

* Corresponding author; Tel.: +44 (0) 1483 682616; E-mail: a.ong@surrey.ac.uk

This work studies the effect of 1 mmol dm\(^{-3}\) concentrations of a selection of small cationic molecules on the performance of a fuel cell grade oxygen reduction reaction (ORR) catalyst (Johnson Matthey HiSPEC 3000, 20 wt. % platinum on carbon) in aqueous KOH (1 mol dm\(^{-3}\)). The cationic molecules studied include ammonium—(i.e. TMA, BTMA, MBTMA and BOTHMA), DABCO—(i.e. BAABCO and MBAABCO), imidazolium—(i.e. BMI), quinuclidinium—(i.e. MBABCO) and phosphonium-based (i.e. MDTTMPP) examples as shown in Scheme 1, which model the head-groups proposed for used in alkaline anion exchange membranes (AAEM) for alkaline polymer electrolyte fuel cells (APEFCs).

Both cyclic and hydrodynamic linear sweep techniques were used. The resulting voltammograms, derived estimates of apparent electrochemically active surface areas, Tafel slopes (Figure 1), apparent exchange-current densities and number of electrons transferred (per O\(_2\) molecule) were compared. The results show that the ability to successfully utilise imidazolium (modelled here using BMI) and phosphonium head-groups (modelled here using MBTTMPP) in the AAEMs and alkaline ionomers APEFCs is still to be proven.

**Scheme 1** The molecular structures of the model molecules bearing cationic head-groups: TMA = tetramethylammonium, BTMA = benzyltrimethylammonium, MBTMA = 1-{4-methylbenzyl}trimethylammonium, BMI = 1-benzyl-3-methylimidazolium, BAABCO = 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane, MBAABCO = 1-(4-methylbenzyl)-4-aza-1-azoniabicyclo[2.2.2]octane, MBABCO = 1-(4-methylbenzyl)-1-azoniabicyclo[2.2.2]octane, BOTMHA = 6-(benzyloxy)-N,N,N-trimethylhexan-1-aminium and MBTTMPP = (4-methylbenzyl)tris(2,4,6-trimethoxyphenyl)phosphonium. Cl\(^-\) counter anions were used throughout.

**Figure 1** The Tafel plots at 25 °C of HiSPEC 3000-coated RDE in the O\(_2\)-saturated aqueous KOH (1 mol dm\(^{-3}\)) electrolytes with and without addition of 1 mmol dm\(^{-3}\) of each of the additives. Derived from hydrodynamic linear sweep voltammetry recorded at scan rate of 5 mV s\(^{-1}\) and RDE rotation rate range 400 - 2000 rpm.
The Effects of Wettability on Liquid Water Transport in Gas Diffusion Layers using Lattice Boltzmann Method

F. Jinuntuya\textsuperscript{a}, R. Chen\textsuperscript{a}, H. Ostadi\textsuperscript{b}, K. Jiang\textsuperscript{c}, Y. Gao\textsuperscript{d}, X. Zhang\textsuperscript{d}

\textsuperscript{a} Department of Aeronautical and Automotive Engineering, Loughborough University, Leicestershire LE11 3TU, UK
\textsuperscript{b} Intelligent Energy Ltd., Charnwood Building, Holywell Park, Ashby Road, Loughborough, Leicestershire LE11 3GB, UK
\textsuperscript{c} Centre for Bio-medical and Micro Engineering, School of Mechanical Engineering, University of Birmingham, Birmingham B15 2TT, UK
\textsuperscript{d} Department of Engineering, University of Liverpool, Liverpool L69 3GH, UK

The gas diffusion layer (GDL) plays a crucial role in the overall performance of a polymer electrolyte fuel cell (PEFC) by providing pathways for reactant gases to be transported from the gas supply channel to the catalyst layers (CL) and product water to be removed from the CL to the gas channel. The excessive presence of liquid water in the GDL hinders the access of reactant gases to the active sites of the CL leading to the performance reduction. The GDL is a carbon fibre based porous material typically made of woven carbon cloth or non-woven carbon paper which has a hydrophilic nature. Therefore, the GDL is commonly treated with a hydrophobic agent such as PTFE to render the fibres more hydrophobic in order to facilitate liquid water removal and gas transport. In order to improve the performance of a PEFC through the effective water removal, a profound understanding of liquid water transport in the GDL under varying wettability is necessary. The lattice Boltzmann (LB) method is a particle-based numerical model that can unveil the fluid transport processes in the GDL at a pore-scale level. The LB method has the capability to incorporate complex boundaries and wettability property of the GDL. In this study, the influence of GDL wettability on liquid water transport in the x-ray reconstructed 3D model of the GDL sample was examined using the two-phase 3D LB model. The results showed the significant effect of wettability on liquid water invasion pattern. For the hydrophobic GDL, the capillary fingering characteristics of water transport were observed. Liquid water selectively invaded the larger pores of the GDL suggesting the availability of smaller pores for gas transport. On the other hand, the stable displacement characteristics were observed in the hydrophilic GDL indicating the flooding of liquid water in the GDL. The results also indicated the substantial decrease in water saturation in the GDL as the wetting characteristic of the GDL change from hydrophilic to hydrophobic.

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The development and characterisation of silver electrodes for alkaline membrane fuel cells

Graham Smith and Anthony Kucernak
Chemistry Department, Imperial College London
South Kensington, London, UK. SW7 2AZ

Alkaline membrane fuel cells (AMFC) offer an interesting route to reduce the material cost of low temperature fuel cells. In contrast to traditional proton exchange membrane fuel cells (PEMFC) hydroxide ions rather than protons carry charge [1]. Critically, unlike alkaline fuel cells AMFC are resistant to metal carbonate precipitation and can purge themselves of carbonate anions during operation [2]. The resulting rise in pH increases the stability and possibly reactivity of some oxygen reduction reaction (ORR) catalysts such as Ag and Ni [3].

As well as having exceptional conductivity silver has been shown to have an ORR price activity (£/mA) similar to the archetypal PEM catalyst platinum when in contact with alkaline membranes [4]. It is an outstanding material for both transport layers and cathode catalysts in AMFC. Unlike platinum, it is not possible to measure the specific surface area of a silver catalyst using hydrogen adsorption or oxide formation.

We will discuss specific surface area measurements on silver nanoparticles down to 10nm in size, using the well-known technique of lead under potential deposition (UPD) [5]. We will also show the use of UPD in characterising and optimising ORR activity in novel silver electrodes.

We will present the development of an AMFC electrode based on a transport layer made of commercially available silver filtration papers treated with an amorphous fluoropolymer [6]. Our results have shown that these transport layers can catalyse the ORR to provide current densities in excess of 100 mA cm⁻² @ 0.65V without the addition of any extra catalyst.

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Petri-net analysis of polymer electrolyte membrane fuel cells to ascertain lifetime and degradation forecasts

Michael WHITELEY, Dr Sarah DUNNETT, Dr Lisa JACKSON

Department of Aeronautical and Automotive Engineering
Risk and Reliability Research Group
Loughborough University
Leicestershire
LE11 3TU
UK

Abstract:

With the recent increase in interest in environmental issues and climate change concerns, the scientific community have been tasked with developing low carbon technologies to mitigate against climate change. One of the most promising technologies is the hydrogen fuel cell, particularly when integrated into an automobile. Hydrogen Fuel Cells are an electro-chemical, zero-emission energy conversion and power generation device. Their only output products are heat, electrical energy, and water vapour.

There are three main hurdles to the commercial uptake of this technology; Infrastructure, Cost and Reliability. An understanding of the reliability of fuel cells can be obtained through in-depth reliability analysis including techniques such as Failure Mode and Effect Analysis (FMEA) and Fault Tree analysis (FTA) amongst others. As hydrogen fuel cells are a relatively new technology this in-depth analysis is still in its infancy, and needs development. It was found through the FMEA and FTA that due to the inherent complexity of PEMFC systems, the failure modes are seldom independent in nature, which makes the use of FTA as a reliability analysis technique inappropriate.

In this work the issues with using basic FMEA and FTA for a Polymer Electrolyte Membrane Fuel Cell (PEMFC), such as dependencies between failure modes, and disparities between failure mode operating principles are considered. The development of Petri-Net analysis, which can take into account dependencies and degraded states, is explored in order to realistically model the reliability of a fuel cell.

The ability to accurately model fuel cell reliability will help fuel cell manufacturers concentrate on key areas for improvement, so the fuel cells can operate to acceptable lifetimes of around 5000 hours of operation or 150,000 miles (for automotive applications).

Mosab Alrahmani, Rui Chen, Salah Ibrahim

Department of Aeronautical and Automotive Engineering, Loughborough University, Loughborough, LE11 3TU, UK

Fuel cells are an environmentally friendly power source candidate aim to replace conventional combustion engines. Proton exchange membranes (PEM) fuel cells are one among many types of fuel cells that are favourable to be used for their low operation temperature and compactness. Water management is a serious issue that affect the performance and durability of PEM fuel cells by a great deal. Surface wettability has proven its influence on water behaviour and fuel cell performance through various experimental investigations. Experimental results lead researchers to examine the liquid water behaviour in gas channels numerically. Volume-of-fluid method has been used in a wide range for its advantage of showing the multi-phase interface in a CFD simulation. Many studies treated the gas diffusion layer (GDL) as a solid surface with a different quality than the wall; however, flow diffusion into the GDL was not included. In the current study, flow diffusion into the GDL was included to determine its effect on liquid droplet behaviour in a small section of the gas channel. Percentage of flow diffusion, GDL wettability, pore size, and water inlet velocity will be changed to investigate its impact on liquid water behaviour. Liquid water behaviour will be studied via pressure drop, water occupancy of the channel, and water coverage of the GDL.
Advanced diagnostic techniques applied to a printed circuit board polymer electrolyte fuel cell.

O. Obeisun1*, F. A. Daniels, C. W. Gibbs1, A. Kucernak2, D. J. L. Brett1

1Electrochemical Innovation Lab, University College London, Torrington Place, London WC1E 7JE, UK
2Department of Chemistry, Imperial College London, South Kensington London SW7 2AZ, UK
* Email: oluwanmayowa.oboisun.11@ucl.ac.uk

Fuel cells are currently being considered as promising alternatives for portable power applications (1-100 W) due to their good energy conversion efficiency, flat geometry, high power and the energy density of their fuel sources, making them advantageous over batteries [1]. The increasing importance of compact design for portable devices necessitates miniaturization of fuel cell stack components in order to maximize power density and for easy system integration [1]. In this study, an air breathing fuel cell has been developed using printed circuit board (PCB) technology. The uses of PCBs afford cost-effective prototypes and design flexibility, which can help to reduce the cost of developing fuel cell stacks.

In an air breathing fuel cell, supply of oxygen to the cathode is achieved through free or natural convection of air-flow. The output power densities of these type of fuel cells are typically low when compared with forced convection fuel cells [2]. However, they are still considered attractive options for portable application due to other key advantages over forced convection designs, such as simplicity of natural convection air delivery, lower cost, less noise and no pumps required. The cathode performance is usually the major source of voltage loss as a result of natural convection of air which can lead to mass transport limitations and inadequate water removal.

This work explores the use of advanced diagnostic techniques to understand the internal working of air breathing polymer electrolyte fuel cells. This includes the use of a thermal imaging camera to observe the production and distribution of heat (Fig 1). The effect of cell orientation and temperature on performance will be studied using polarization data and electrochemical impedance spectroscopy and direct visualization of open channels to observe water formation.

![Fig 1: Temperature distribution in the air breathing fuel cell at 150 mA cm⁻² (Left) and 500 mA cm⁻² (Right).](image)

References


Cutting edge method for the preparation of catalysts for Polymer Electrolyte Fuel Cells, Alkaline Fuel Cells and Direct Alcohol Fuel Cells

Dr. Paramaconi Rodriguez
School of Chemistry, University of Birmingham B15 2TT, UK. E-mail: p.b.rodriguez@bham.ac.uk

In the last few decades, remarkable advances have been achieved in the preparation of highly dispersed, homogeneously small nanoparticles for fuel cell application. A fundamental component of all these known synthetic methods is the addition of extra chemical stabilizers which limit the size or control the shape of the nanoparticle. However, these stabilizers, surfactants or capping materials are big organic molecules that block the active sites of the catalyst and adversely affect its performance in catalysis. Here, I will report a radically different, simple, cheap, quick and scalable method of nanoparticle synthesis, opening a new route for producing nanomaterials with improved catalytic properties. The method is based on extreme cathodic polarization of a metal, leading to the formation of metal anions, which then act as precursors to the formation of nanoparticles.

In contrast to the methods based on cation metal reduction, our method allows unique control of the chemical composition, size and shape of the nanoparticles, and it does not require any additional synthesis steps such as annealing/reducing at high temperatures nor the removal of organic reagents employed in chemical routes with colloids or micelles. Because of the high level of cleanliness, the nanoparticles present improved catalytic activity in comparison with the state-of-the-art Pt nanoparticles on carbon supports (Figure 1A).

I will demonstrate that by using the cathodic corrosion method we can control the particle size, the composition of alloy nanoparticles and the surface orientation (Figure 1B-D). It will be shown that the catalytic activity of these nanoparticles towards the oxygen reduction reaction (Figure E) and towards alcohol oxidation is substantially improved. I will also present cathodic corrosion as a unique single-step method to prepare size-controlled metal nanoparticles directly dispersed on conductive oxide supports (Figure 1F).

Figure 1. Voltammetric profiles of the (A) CO oxidation and (C) methanol oxidation on different Pt and Pt alloy nanoparticles as indicated in the figure. (E) Tafel plot of the ORR on different Pt and Pt alloy nanoparticles. TEM images of (B) 2nm Pt nanoparticles, (D) Pt(100) nanoparticles and (F) Pt nanoparticles supported on conductive TiO₂.

Advanced Diagnosis on Dead Ended Anode operations for Proton Exchange Membrane Fuel Cell Stacks

Quentin Meyer\textsuperscript{a}, Sean Ashton\textsuperscript{b}, Oliver Curnick\textsuperscript{b}, Tobias Reisch\textsuperscript{b}, Dan Brett\textsuperscript{a}

\textsuperscript{a) University College London, Department of Chemical Engineering, London, WC1 6BT, UK.}

\textsuperscript{b) Intelligent Energy Ltd, Ashby Road, Loughborough, LE11 3GB, United Kingdom}

Quentin.meyer.11@ucl.ac.uk

Proton Exchange Membrane Fuel Cells (PEMFCs) offer the possibility of zero-emission electricity generation. The technology has shown tremendous advances in terms of performance and durability and wide-scale commercialisation in a range of applications is imminent. In order to make further improvements to the key performance metrics, it is important that we know as much as possible about the way the fuel cell is working in space and time. Electrochemical impedance spectroscopy (EIS) is a powerful in situ diagnostic technique for monitoring fuel cell performance; however, its use has been mainly limited to single cells using costly potentiostat hardware. Here we present a low-cost multichannel impedance analyser developed using a commercial data acquisition hardware and LabVIEW software\textsuperscript{1}. This novel diagnostic system is applied to a commercial Intelligent Energy air-cooled open-cathode 5-cell PEMFC stack.

This system was used to characterise and distinguish the causes of the voltage loss in dead ended anode conditions. A novel reconstructive impedance strategy was proposed. The same frequency of interest was measured every 20 seconds in through-flow and dead-ended conditions. The events were repeated, but changing the frequency of interest (1 kHz to 1 Hz) at each repeat. Using this technique, it was found possible to associate Nyquist plots with different stages of the voltage loss over time (Fig 1 a). These results (Figure 1 b) highlight a significant increase of the resistance in the low frequency region, which is an indication of flooding.

High frequency impedance, along with thermal imaging, was used to characterise the hydration level of the cells. Finally, off-gas analysis enabled to quantify the amount of nitrogen accumulating in the anodic compartment diffusing from the air through the Nafion membrane.

A hybrid electric canal boat using a metal hydride store and a PEM fuel cell.

Sal Adrwish, Rex Harris, Alex Bevan, Etienne Picard, David Book and Andreas Zuttel*
School of Metallurgy and Materials, University of Birmingham, UK.
*EMPA, Zurich, Switzerland.

Email: S.M.A.Adrwish@bham.ac.uk, saladrwish@yahoo.com

Throughout the world, many investigations are underway as part of a huge effort to develop an effective, solid state, reversible, light weight hydrogen store for road transport applications. It should be pointed out however, that there are a number of much less demanding transport applications which could employ metal hydride-based storage units. Development of these systems would allow solid state storage technologies to gain a “toe-hold” and thus provide valuable operating experience. With this in mind, we have been developing a hybrid electric canal boat called the Ross Barlow. A conventional, diesel-powered canal boat has been modified to produce an electrically powered craft using a combination of a NdFeB-type permanent magnet electric motor, a lead acid battery stack and a PEM fuel cell supplied by a (Ti,V)(Fe,Mn)2 hydride store. This project is part of an Anglo-Swiss collaborative research and development programme. The interface activities with the general public and with schools are funded by the Royal Academy of Engineering as part of their Ingenious programme.

In this contribution, we describe the main features of the canal boat together with some of the performance figures relating to the charge and discharge of the hydride store and to the operation of the fuel cell and electric motor. Possible future developments are reviewed, particularly with regard to the provision of “green hydrogen” which could ensure the long term viability of the project and would allow for a realistic economic appraisal.
A New Oxygen Partial Pressure Imaging Method Based on Chemiluminescence: Application to Polymer Electrolyte Fuel Cells

Thiago Lopes and Anthony Kucernak

Department of Chemistry, Imperial College London, London – UK

A great breakthrough in PEFC science was attained in the 1990s at the Los Alamos National Laboratory, where researchers drastically diminished the amount of platinum applied on a PEFC,\(^1\) bringing this technology closer to commercial viability. Since then, the challenge left is a breakthrough at the cathode electrode, e.g. (i) cost competitive ORR catalysts with high enough activity and durability; and (ii) cathode electrodes (gas diffusion layers (GDLs), catalyst layer etc) and flow field designs for managing the delicate mass transport phenomena. These key factors play a crucial role in reducing the amount of platinum required by a PEFC and in augmenting the partial pressure of oxygen at the catalyst layer region, respectively. The later is related to the first-order dependence of the kinetics of the ORR in the oxygen partial pressure on actual PEFC catalysts.\(^2\)

The goal of flow field design is to maximize the partial pressure of oxygen at the catalyst layer interface whilst preventing deleterious effects (large pressure drops, flooding etc) and thus optimising overall PEFC system performance and efficiency. Modelling has played a crucial role in such developmental work. However, there are few experimental methods available for confirming such modelling results.\(^3\) This lack of experimental verification hampers further theoretical and PEFC system developments.

The work presented in this talk utilises a new gas-phase approach to allow imaging of oxygen transport through fuel cell electrodes and flow fields. This new indirect oxygen partial pressure imaging technique is based on a chemiluminescence reaction between a reactive gas and dye molecules, The light produced by this reaction is related to the ease with which gas molecules can penetrate the electrode structure, and so represents a method of directly measuring local gas transport properties at high spatial (100 \(\mu\)m in the current implementation, but in principal down to a 1 \(\mu\)m) and time (20 ms in the current implementation, but 1 ms is possible) resolution. An example of such imaging is provided in Figure 1, where the gas transport through a serpentine flow field and gas diffusion layer is imaged as a function of flow rate through the flow-field.

Figure 01: Example of the indirect oxygen partial pressure imaging technique. The top diagram shows a cross-section of the serpentine flow field and how reactant generates light when it has traversed across the gas diffusion layer. The bottom two images show experimental images of light generation, highlighting those regions in which reactant permeation through the gas transport layer is enhanced. Turbulent flow near flow field corners enhances light generation. Air flow rates as specified on Figure.

Temperature-controlled growth of Pt nanowires for high performance catalyst electrodes in polymer electrolyte fuel cells

Yaxiang Lu*, Shangfeng Du, Robert Steinberger-Wilckens
School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
Tel.: +44-121-414-5283
yxl210@bham.ac.uk

One dimensional Pt nanowires (Pt NWs), benefiting from the inherent structural characteristics like anisotropy and preferential exposure of highly active crystal facets, exhibit improved catalytic activity and durability in polymer electrolyte fuel cells (PEFCs) [1]. In our previous research, integrated gas diffusion electrodes (GDEs) with Pt NW catalyst layers have been developed by directly growing Pt NWs on gas diffusion layers (GDLs) [2]. To further improve the GDE performance, a well-controlled growth of the Pt nanowires is very important. For example, they should possess a suitable length to enable self-support, an ultra-thin size to obtain a high electrochemical surface area, or an optimal distribution in the catalyst layer for a low charge and mass transfer resistance during the electrochemical reaction. As we know, in the synthesis process of nanostructures, reaction temperature has been regarded as an important controlled factor, as it is a good tool to tune the phase formation kinetics and adjust the driving force for the mass transfer, thus changing the morphology and property of the product [3].

In this work, Pt-NW GDEs with Pt nanowires grown at different temperatures from 5 to 50 °C were fabricated and tested in a 16 cm² hydrogen-air single-cell fuel cell. Polarization and electrochemical impedance spectroscopy (EIS) measurements were performed to check the GDE performance. SEM analysis was conducted to investigate the relationship between morphologies and properties of the as-prepared electrodes. The results showed that temperature played a vital role in the growth of Pt NWs thus influencing their properties. The GDE prepared at an optimal temperature of 40 °C showed a better performance than the state-of-the-art TKK Pt/C catalyst. It reached a maximum power density of 0.865 W cm⁻² at 70 °C with a Pt NW loading of 0.4 mg cm⁻². The durability of the GDE with optimized Pt nanowires was also checked by accelerated durability test, which was undertaken by cycling voltage scans between 0.6 V and OCV for 3000 cycles, and a degradation rate of only 1.85% was found to the power density.

References