

Electrochemistry of Proton Conducting Membrane Fuel Cells

Reviewed by Sarah C. Ball

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Work presented at the Fourth International Symposium on Proton Conducting Membrane Fuel Cells is reviewed here. For these fuel cells to become commercially successful there are a number of challenges to be met. For instance, the polymer electrolyte membrane fuel cell needs more active catalysts and cheaper, more durable, membranes. In addition, an improved understanding of the deterioration mechanisms of the membrane electrode assemblies is required. New work on all these aspects is described here. Work on direct methanol fuel cells is also reported, focusing on more effective anode catalysts and new proton conducting membrane materials with reduced permeability to methanol.

The 2004 Joint International Meeting combining the 206th Meeting of The Electrochemical Society with the 2004 Fall Meeting of The Electrochemical Society of Japan, was held in Honolulu, Hawaii, from 3rd to 8th October 2004. The programme consisted of over 1000 different lectures and 500 posters and was attended by a worldwide audience of around 2000 delegates. The meeting included the Fourth International Symposium on Proton Conducting Membrane Fuel Cells, which is the main subject of this review.

Improvements to the materials (cathodes, electrolyte and anodes) used in the polymer electrolyte membrane fuel cell (PEMFC) are required before they can be successful commercially, and new work on these, and new catalysts and membranes for the direct methanol fuel cell (DMFC) are described. Further, there is a need for better understanding of membrane electrode assembly (MEA) deterioration mechanisms.

The Background

Cathode Materials

A significant performance loss in the PEMFC is associated with the oxygen reduction reaction (ORR) at the cathode. While the best cathode catalysts are currently Pt-based, the drive to reduce metal loadings and costs and improve activity means that new materials, such as Pt alloys and metal carbides, are constantly being sought. The

conference featured many talks on the activity of new ORR catalysts and the use of combinatorial chemistry methods to speed up the search for improved ORR catalyst formulations.

Investigations into the durability of the platinum group metal catalyst materials themselves and the effects of long-term cycling and high potentials/temperatures (especially for cathode materials) showed that there is a loss of metal surface area and corrosion of the carbon support. These explain the loss in MEA performance over time and define the properties required for future materials.

Electrolyte Materials

In this area there is a need for solid polymer electrolyte membrane materials that are cheaper and more conductive than the current perfluoro-sulfonic acid (PFSA) materials, and which are also durable for up to 10,000 hours. In particular, membranes are needed for use at temperatures above 100°C where liquid water is no longer present for proton transport. For DMFCs, new membranes with reduced methanol permeability are required.

Membrane Electrode Assembly: Deterioration and Diagnostics

In order for PEMFCs to achieve the necessary durability for commercialisation (up to 10,000 hours), significant efforts have been directed

towards finding deterioration mechanisms and failure modes. Several studies on the effects of peroxide radicals, factors controlling their rate and place of formation in PEMFCs, and evidence of their attack on the membrane in PEMFCs were presented.

New Oxygen Reduction Reaction: Materials and Nanomaterials

New ORR materials for the PEMFC cathode based on PtX alloys ($X = \text{Ni, Co, Fe}$) were described by N. Wakabayashi and colleagues (University of Yamanashi, Japan) [Abs# W1-1856]. Their Pt alloys showed a higher onset oxidation potential for the ORR reaction, rationalised by the presence of a Pt skin overlaying the Pt alloy. V. Stamenkovic and colleagues (University of California at Berkeley, U.S.A.) [Abs# AD3-2308] also observed the formation of a Pt skin after annealing sputtered alloy surfaces of PtX ($X = \text{Ti, Fe, Co, Ni}$). They noted that activity for the ORR was increased for Pt₃Fe and Pt₃Co samples (with a Pt skin) due to reduced numbers of 'blocking species', such as OH⁻ and other anions, at the surface.

M. Teliska and D. E. Ramaker (The George Washington University, U.S.A.) and V. S. Murthi and S. Mukerjee (Northeastern University, U.S.A.) [Abs# W1-1919] used X-ray adsorption spectroscopy to observe the presence of anions, from HClO₄ and H₂SO₄ solutions, on the surface of Pt. They examined the anion effects on the absorption of H₂ and O₂. PtCo alloys, with and without Pt skins, were also investigated.

J. Zhang and coworkers (Brookhaven National Laboratory, U.S.A.) [Abs# W1-1920] deposited Pt monolayers onto Ru, Ir, Rh, Pd and Au, and by varying the metal substrates found that the ORR activity changed, in some cases producing a specific activity several times greater than that for Pt alone.

W. S. Baker, P. J. Bouwman and K. E. Swider-Lyons (Naval Research Laboratory, U.S.A.) and W. Domowski (University of Knoxville, U.S.A.) [Abs# W1-1915] used Pt, Au and Pd deposited onto metal oxides, such as SnO_x and TiO_x, as ORR PEMFC catalysts, exploiting the strong metal sup-

port interaction (SMSI). These catalysts showed good resistance to SO₂ poisoning and had enhanced activity.

In general, workers preparing and testing PtX alloys (where X is a base metal such as Co, Fe, V) found problems with base metal corrosion from the catalysts in acid media.

A Pt-V₂O₅ ORR catalyst was produced by Y. Suzuki and colleagues (Yokohama National University, Japan) [Abs# W1-1911] by sputtering thin metal oxide layers (Sn, W, V, Cr oxides) onto a glassy carbon electrode, with Pt particles then deposited on top. The catalyst had higher specific activity but lower mass activity than Pt/C. A. Ishihara (Japan Science and Technology Agency (JST), Japan) and K. Lee and colleagues (Yokohama National University, Japan) [Abs# W1-1859] demonstrated that Ta oxynitride (TaON) had some activity for the ORR reaction, but the catalyst was significantly less active than Pt. Poor results were thought to be partly due to difficulties with electrode preparation and poor sample conductivity of the powdered oxides.

Nanoparticle catalysts, described by C. L. Hui, X. Li and I.-M. Hsing (Hong Kong University of Science and Technology, Hong Kong) [Abs# W1-1861], were prepared using surfactant SB12 ((dodecyldimethyl 3-sulfopropyl) ammonium hydroxide) as stabiliser. Preparations at higher pH (> pH 8) gave greater Pt surface area, and higher molar ratios of the surfactant to metal were found to prevent agglomeration.

The difficult process of depositing Pt onto carbon nanofibres via colloidal and conventional routes was discussed by K. Sasaki and colleagues (Kyushu University, Japan) [Abs# W1-1912]. Of the different types of nanofibres studied, the highest Pt surface areas were achieved from Pt deposition onto platelet nanofibres, followed by herringbone, with tubular nanofibres allowing only the smallest Pt areas.

Metals Loading Targets/Ideal Performance

B. Sompalli and H. Gasteiger (General Motors, U.S.A.) [Abs# W1-1867] stated that 0.2 g Pt kW⁻¹ at 0.6 V was an ideal PEMFC performance target.

Rotating disc electrode (RDE) measurements in HClO_4 of mass and specific activity for catalysts 40%Pt/C (Tanaka KK) and 20%Pt/Vulcan (E-TEK) demonstrated the superior performance of the Tanaka KK material. Tests on RDE and MEA at 900 mV gave agreement for mass and specific activity, but differences in the Tafel slopes were observed.

In the drive towards lower metal loadings and enhanced activity, F. A. Uribe, T. Rockward and J. A. Valerio (Los Alamos National Laboratory, U.S.A.) and R. R. Adzic (Brookhaven National Laboratory, U.S.A.) [Abs# W1-1857] described the use of electroless deposition for the production of monolayer electrodes of Pt on Pd nanoparticles (cathode loadings of 40 and 77 $\mu\text{g Pt cm}^{-2}$) and Pt on Ru nanoparticles (anode loadings of 18 $\mu\text{g Pt cm}^{-2}$). Anode durability was assessed at 50 ppm CO/H₂ and 4% air bleed, and a 50 mV decay was observed over 1000 hours of MEA testing. Uribe also showed polar curves for low loaded PtPd cathodes that met a 0.6 g Pt kW⁻¹ target.

High Temperature Membranes for PEMFCs

A prototype portable high-temperature PEMFC set-up, having a MeOH-fuelled steam reformer operating at 280°C and a polybenzimidazole-based (PBI) MEA operating at 150°C, was described by R. Koripella and coworkers (Motorola, U.S.A.) [Abs# W1-1870]. This system produced 0.51 W at steady state. The entire system was encased in a thermally insulating ceramic holder of size 2" × 2" × 0.25" to maintain an outside temperature at 45°C during operation. The system has a start-up time of 30 minutes but this is expected to be reduced by miniaturisation.

A. B. Borcarsly and colleagues (Princeton University, U.S.A.) [Abs# W1-1976] demonstrated excellent PEMFC performance using an Aciplex[®] perfluorosulfonic acid SiO₂ composite membrane at 130°C. The enhanced performance at low relative humidity was thought to be due to a change in ionomer morphology, rather than increased water uptake. A good performance on 500 ppm CO/H₂ at 130°C for a TiO₂-doped membrane demonstrated the benefits of higher temperature

operation for CO tolerance. Using titania, from different manufacturers, produced different performance enhancements when incorporated into the membrane, and anatase, rather than rutile, was identified as contributing most performance enhancement. This was due to the presence of unsaturated Ti(IV) on the surface, which allowed interaction with the sulfonic acid groups in the ionomers used.

Catalyst and Membrane Stability

N. Miyake and coworkers (Asahi Kasei Corporation, Japan) [Abs# W-1880] presented a durability study on the membrane material Aciplex[®] S1002 at different temperatures, using dry conditions to accelerate degradation. H₂ crossovers from anode to cathode were compared at different times to quantify membrane integrity. Experiments performed included replacing cathode and anode electrodes in turn, with ELAT[®] carbon cloth (no Pt), and using N₂ instead of air. They concluded that Pt and O₂ (air) at the cathode had the greatest impact on membrane degradation rates; this was thought to be due to combustion of H₂ (from crossover) and accompanying exotherms rather than to peroxide formation. Greater relative humidity restrains degradation, as H₂O disperses both the heat and peroxide radicals. Samples did not fail consistently in the same manner: some failed by pinholing and others by thinning.

S. Mukerjee, V. S. Murthi, L. Zhang (Northeastern University, U.S.A.) [Abs# W1-1882] described durability measurements on non-fluorinated ionomers and membranes using an accelerated fuel cell test. They showed that the cathode was the main point of peroxide attack.

In contrast, M. Murthy and D. Moore (W. L. Gore and Associates, U.S.A.) [Abs# W1-1886] and W. Lui and D. Zuckerbrod (W. L. Gore and Associates, U.S.A.) [Abs# W1-1894] presented data indicating that peroxide was mainly generated at the fuel cell anode. Murthy described how H₂ and O₂ (from air bleed) at the anode generate a higher proportion of peroxide radicals when the MEA anode is poisoned by CO, as Pt sites poisoned with CO cannot oxidise H₂O₂ to water. Therefore, the maximum membrane degradation

(in a 500 hour test) was observed for an example of 500 ppm CO/H₂ + 10% air bleed (300 μV h⁻¹), while 500 ppm CO/H₂ with no air bleed, or H₂ + air bleed with no CO, produced minimal degradation < 10 μV h⁻¹ (degradation rates defined in terms of non-recoverable losses). W. Lui and D. Zuckerbrod (W. L. Gore and Associates, U.S.A.) [Abs# W1-1894] presented data on peroxide formation within the MEA using *in situ* Pt wire probes, 2 per MEA, at varying distances from the cathode and anode. A strong correlation was observed between decreasing membrane thickness and increasing H₂O₂ concentrations. O₂ crossover strongly correlates with membrane thickness while H₂ crossover does not, so the H₂O₂ formation was thought to be due to O₂ crossover to the anode.

V. Stanic (Teledyne Energy Systems, U.S.A.) and M. Hoberecht (NASA Glenn Research Center, U.S.A.) [Abs# W1-1891] presented a matrix of PEMFC experiments with relative humidities of 20 and 100% and temperatures of 50 and 60°C, to investigate the mechanism for membrane pinhole formation. Mechanisms for failure were tearing and pinhole formation due to mechanical creep and chemical contamination with metal ions (resulting in blister formation). Membrane cracking under dry conditions was also observed.

W. Inaba and coworkers (Doshisha University, Japan) and T. Kinumoto and Z. Ogumi (Kyoto University, Japan) [Abs# W1-1885] demonstrated the effect of impurity ions (Fe²⁺, Cu²⁺) on peroxide formation and membrane degradation, and used a rotating ring disc electrode (RRDE) to look at ORR and H₂O₂ formation at different Pt loadings of a 20% Pt/C catalyst. The amount of peroxide formed increased towards anode potentials and for higher dispersed Pt/C materials with greater Pt surface area.

By contrast, results from A. S. Agarwal and colleagues (Case Western Reserve University, U.S.A.) [Abs# W1-1896] implied that the amount of H₂O₂ produced decreased with increasing Pt area. They demonstrated that on agglomerated Pt particles, larger amounts of end-on O₂ bonding produced high amounts of peroxide, while higher Pt surface area enhanced rates of peroxide decomposition.

T. Jarvi (UTC Fuel Cells, U.S.A.) [Abs# W1-

1887] described electrochemical measurements of carbon corrosion at 950 mV, for Vulcan XC-72R carbon with and without Pt. The results indicated that CO₂ was produced when Pt was present, implying that Pt facilitates carbon oxidation.

In situ MEA carbon corrosion measurements from R. Makharia and coworkers (General Motors, U.S.A.) [Abs# W1-1888] showed that a 3% loss in carbon could have dramatic effects on PEMFC performance, due to mass transport problems. Measurements of corrosion rates *ex situ* showed enhanced corrosion for 50%Pt/Vulcan XC-72R compared to Vulcan XC-72R alone. Cycling experiments showed a slower fall-off in electrochemical area for Pt supported on graphitised Vulcan XC-72R carbon.

H. Colon-Mercado, H. Kim and B. Popov (University of South Carolina, U.S.A.) [Abs# W1-1922] looked at the stability of ORR PtX alloys (X = Ni, Co) using an accelerated durability test, where catalyst layers on gas diffusion layers (ELAT from E-TEK) were immersed in 0.3 M H₂SO₄ and held potentiostatically at 0.8 and 0.9 V for up to 250 hours, with periodic electrolyte sampling. The ORR current was observed to fall as leaching of X progressed. TEM showed increased metal particle size on comparing fresh and aged samples, but there was greater sintering for Pt than for PtCo.

Data from H. Gasteiger, R. Makharia and M. Mathias (General Motors, U.S.A.) [Abs# W1-1927] indicated that Pt alloy cathode catalysts were able to meet the 2 × Pt activity target, but further improvements would be necessary if these catalysts were to find commercial use in automotive fuel cells. Extrapolated data (based around Pourbaix diagrams and values from the literature) implied that PEMFC operation at 100–120°C would result in rapid Pt dissolution and loss of area. This indicated that new ORR catalysts which retain high activity, and which are more stable at elevated temperatures than the currently available carbon-supported Pt catalysts, must be found.

Combinatorial Techniques

Combinatorial techniques are increasingly being used to identify new PEMFC and DMFC catalyst formulations. Combinatorial co-sputtering onto a

glass substrate was used by J. F. Whitacre and S. R. Narayanan (Jet Propulsion Laboratory/California Institute of Technology, U.S.A.) [Abs# W1-1898] to find new DMFC catalysts based around PtRuNiZr formulations. Initial results on PtRu alone were used to validate the method, and a ratio of 82:18 for Pt:Ru was found to be the optimum composition. Tests were carried out without annealing the sample, but sputtering gave a well-controlled surface.

High throughput screening was used by Y.-G. Shul and colleagues (Yonsei University, South Korea) [Abs# W1-1899] to investigate PtRu/AuTiO₂ materials for DMFC and CO-tolerant PEMFC anode applications.

D. A. Stevens and colleagues (Dalhousie University, Canada) [Abs# W1-1900] described a combinatorial technique in which a mask is used to deposit an 8×8 catalyst array onto 3M nanostructured film. Up to 5 different elements were deposited by magnetron scattering, building up a series of submonolayer wedges to generate a true alloy. Samples were transferred onto Nafion[®] membrane and tested against a continuous anode in a 64-channel fuel cell set-up. The catalyst dots are much smaller than the gas diffusion media to avoid mass transport and diffusion issues. For PtNi, optimum ORR performance occurred with Pt_{0.6}Ni_{0.4}.

E. S. Smotkin (NuVant Systems, U.S.A.) [Abs# W1-1901] used a 5×5 array of GDEs (gas diffusion electrodes) on Nafion[®] 117 with a single anode counter electrode, for combinatorial studies in a fuel cell set-up. This allowed evaluation of catalyst ink preparation/application methods and different GDE types, as well as investigation of different catalysts.

Electronic impedance spectroscopy (EIS), real time gas analysis and micro thermocouples were utilised by Q. Dong and M. M. Mench (Pennsylvania State University, U.S.A.) [Abs# W1-1902]. They sampled MEA performance in different regions of the MEA, using a segmented single pass flow field and low humidity conditions. They concluded that a dry cathode responds rapidly to changes in voltage and there is a reversal point along the flow field/MEA at which the

dominant process changes from electro-osmotic drag to back diffusion.

Data obtained from a 100-segmented PEMFC cell by Z. Siroma and K. Yasuda (National Institute of Advanced Industrial Science and Technology (AIST), Japan) and A. Nishikawa, R. Kitayama and S. Koge (Shindaiwa Kogyo Co. Ltd., Japan) [Abs# W1-1904] produced a map of temperature and current variations with time. Unexpectedly, no clear relationship was observed between changes in current and temperature. This was explained by assuming there are localised changes in water production in the PEMFC as current and heat vary.

PEMFC Anode Materials

A. Weickowski and colleagues (University of Illinois, U.S.A.) [Abs# W1-1858] used ¹⁹⁵Pt NMR to study PtRu alloys, including Johnson Matthey (JM) materials. Results indicated that the catalyst surface was enriched in Pt (Pt 65:Ru 35) for JM materials, and that Pt migrated to the surface as a result of heat treatment.

In a novel approach to enhancing anode CO tolerance, W. L. Gellet and J. Leddy (University of Iowa, U.S.A.) and K. Bahram-ahi and S. D. Minteer (Saint Louis University, U.S.A.) [Abs# AD3-2303] added magnetic particles of NdFeB and Sm₂Co₇ to Pt anode catalysts. This resulted in negative shifts in the CO oxidation feature of up to 600 mV in cyclic voltammetry experiments (when compared to Pt alone) due to the magnetic field enhancing the low potential diffusion-controlled CO oxidation. The application of an external magnetic field had some benefit, but including magnetic particles on a single crystal or catalyst layer was far more effective at enhancing the low potential CO oxidation. A Pt anode that contained magnetic particles produced PEMFC polar curves showing significantly better performance when using a 100 ppm CO reformat.

S. Ball, B. Theobald and D. Thompsett (Johnson Matthey Technology Centre, U.K.) [Abs# W1-1916] demonstrated how PtMo/C anode materials were tolerant to high levels of CO. PEMFC data using 5000 ppm CO reformat at the PtMo/C anode produced enhanced performance

over conventional PtRu anode materials. PtMo was also shown to be active for conversion of percentage levels of CO₂ to ppm of CO, explaining the origin of the 'extra' CO₂ poisoning observed for PtMo (compared to PtRu materials), when running on real reformat.

Catalysts prepared by deposition of Pt or Pd on to SnO₂ nanoparticles absorb little CO, so were investigated as CO-tolerant anodes by Y. Anzai, T. Tageguchi and W. Ueda (Hokkaido University, Japan) and R. Kikuchi and K. Eguchi (Kyoto University, Japan) [Abs# W1-1921]. Temperature programmed reduction (TPR) data showed that Sn was present as oxide (unreduced form), and so was suitable for use in the PEMFC anode. Reduced Sn is unstable under acid conditions. Optimum performance in an MEA was observed using a Pd/C/SnO₂ anode at 500 ppm CO/H₂.

DMFC Anode Materials

K. Miyazaki and colleagues (Kyoto University, Japan) [Abs# Q1-1515] looked at nano gold particles on PtMoO_x/C. These were found to have greater activity for MeOH oxidation below 550 mV and reduced CO coverage, compared to conventional DMFC catalysts.

DMFC lifetime tests characterising catalysts and membranes, were carried out by X. Cheng and colleagues (Xiamen University, China) and Q. Fan (Gas Technology Institute, U.S.A.) [Abs# W1-1926]. There is significant degradation after 200 hours, and a further degradation at 1000 hours. The catalysts tested were JM 30%PtRu/C and Pt black and the membrane used was Nafion[®] 117. End-of-life XRD and high resolution transmission electron microscopy (HRTEM) on the catalysts used showed particle agglomeration and growth had occurred, and there was Ru loss from the PtRu particles, which may have been converted to Ru oxides.

Conclusions

The work reported at this conference shows that commercial use of proton conducting membrane fuel cells is not so far away, and that there are many organisations with dedicated scientists working to achieve this. Meetings of The

Electrochemical Society are held every six months, whilst Fuel Cell Symposia are held every year, and details of future venues are available on the ECU website at <http://www.electrochem.org>.

Much of the work presented here was exciting, in particular the new combinatorial methods, which will greatly assist the search for new cathode catalyst formulations. The new high temperature membrane materials will open up possibilities of greater efficiency and enhanced reformat tolerance, and will bring the commercialisation of PEMFCs closer, especially for automotive applications. At this symposium a greater focus than usual on MEA stability and enhanced diagnostics resulted in an improved understanding of MEA degradation processes.

The proceedings for the Fourth International Symposium on Proton Conducting Membrane Fuel Cells is currently being compiled by The Electrochemical Society (<http://www.electrochem.org>) and will contain more information on the presentations described in this review.



The Reviewer

Sarah Ball is a Research Scientist in the Electrotechnology/Catalyst Preparation Group at the Johnson Matthey Technology Centre in the U.K. She is interested in anode catalysis for reformat-tolerant applications, and novel cathode materials and alloys for PEMFCs.