

# Report

## **NPL REPORT MAT 25**

**Reference electrodes for  
solid polymer fuel cells:  
a review**

**G. HINDS**

**NOT RESTRICTED**

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## **Reference electrodes for solid polymer fuel cells: a review**

G. Hinds

Industry and Innovation Division

### **ABSTRACT**

This report summarises the state of the art in reference electrodes for solid polymer fuel cells. The two most common reference electrodes used in such systems are the reversible hydrogen electrode and the dynamic hydrogen electrode. Uncertainty in the reliability of reference electrode measurements is mainly associated with the positioning of the reference electrode with respect to the fuel cell electrodes, the stability of the reference electrode and perturbation of fuel cell operation by the reference electrode. Reference electrodes may be positioned either internal or external to the fuel cell. Internal reference electrodes are typically constructed by sandwiching the electrode between two membranes, which may perturb fuel cell operation. External reference electrodes are usually connected to the fuel cell membrane by a salt bridge. The potential measured by an external reference electrode is dominated by edge effects caused by misalignment of the fuel cell electrodes, which are exacerbated by differences in electrode kinetics and mass transport between anode and cathode. There is a clear need for the development of reference electrode configurations that probe the local potential within the active layer without introducing such errors or affecting the performance of the cell.

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National Physical Laboratory  
Hampton Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of the Managing Director, NPL,  
by Dr M Cain, Knowledge Leader, Materials Team  
authorised by Director, Industry and Innovation Division

## CONTENTS

|                                               |           |
|-----------------------------------------------|-----------|
| <b>1. INTRODUCTION.....</b>                   | <b>1</b>  |
| <b>2. REFERENCE ELECTRODES.....</b>           | <b>1</b>  |
| <b>3. REVERSIBLE HYDROGEN ELECTRODE .....</b> | <b>3</b>  |
| <b>4. DYNAMIC HYDROGEN ELECTRODE .....</b>    | <b>9</b>  |
| <b>5. SUMMARY .....</b>                       | <b>14</b> |
| <b>6. RECOMMENDATIONS.....</b>                | <b>15</b> |
| <b>7. REFERENCES.....</b>                     | <b>16</b> |



## 1. INTRODUCTION

The solid polymer fuel cell (SPFC) is a potential replacement or hybrid partner for gas turbine, internal combustion engine and battery technologies. The three main types of SPFC are the polymer electrolyte membrane fuel cell (PEMFC), the direct methanol fuel cell (DMFC) and the alkaline exchange membrane fuel cell (AEMFC). The advantages of SPFCs are high efficiency, low emissions, silent operation and relatively fast start-up times but commercialisation of the technology is currently hampered by high material and processing costs, limited durability and the lack of a refuelling infrastructure. It is anticipated that improvements in efficiency and durability will be facilitated by system optimisation based on improved models of SPFC performance. In-situ measurement of critical parameters is required both for model validation and to develop further understanding of the physical processes taking place in the fuel cell. NPL's fuel cell research programme is focused on the development of measurement and modelling tools to support the UK fuel cell industry. An important aspect of this work is reliable measurement of electrode potential to facilitate model validation. This review was carried out to assess the state of the art in the use of reference electrodes in SPFCs and to make recommendations with regard to reference electrode development at NPL.

## 2. REFERENCE ELECTRODES

A reference electrode is an electrode whose potential is constant and can be related to a fundamental thermodynamic scale, e.g. the standard hydrogen electrode. Reference electrodes are widely used in electrochemistry as a standard against which to measure the potential of other electrodes. A list of the most common laboratory reference electrodes is given in Table 1.

**Table 1** Common laboratory reference electrodes.

| Electrode                  | Reaction                                                                                 | Potential<br>(vs SHE) |
|----------------------------|------------------------------------------------------------------------------------------|-----------------------|
| Standard hydrogen          | $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$                                   | 0 V                   |
| Saturated calomel          | $\text{Hg}_2^{2+} + 2\text{Cl}^- \leftrightarrow \text{Hg}_2\text{Cl}_2$                 | + 0.242 V             |
| Silver/silver chloride     | $\text{Ag} + \text{Cl}^- \leftrightarrow \text{AgCl} + \text{e}^-$                       | + 0.225 V *           |
| Copper/copper sulphate     | $\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$                                 | – 0.314 V *           |
| Mercury/mercurous oxide    | $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Hg} + 2\text{OH}^-$ | + 0.165 V *           |
| Mercury/mercurous sulphate | $\text{Hg}_2\text{SO}_4 + 2\text{e}^- \leftrightarrow 2\text{Hg} + \text{SO}_4^{2-}$     | + 0.680 V *           |
| Palladium/hydrogen         | $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$                                   | + 0.050 V             |

\* Indicative only – precise value depends on anion concentration.

The potential of the standard hydrogen electrode (SHE) is defined as zero. This electrode consists of a platinised platinum electrode dipped in a solution of 1 M acid (usually HCl) with hydrogen gas at a partial pressure of 1 atm bubbled along its surface (Figure 1).

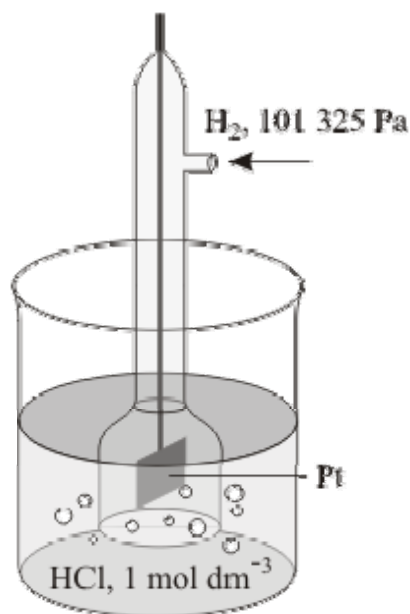


**Figure 1** Schematic of a standard hydrogen electrode.

The redox reaction of the SHE is:



and the electrode potential,  $E$ , is determined by the Nernst equation:

$$E = \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{[p_{\text{H}_2}/p_0]^{1/2}} \quad (2)$$

where  $R$  is the gas constant,  $T$  is temperature,  $F$  is Faraday's constant,  $a_{\text{H}^+}$  is the proton activity,  $p_{\text{H}_2}$  is the hydrogen partial pressure and  $p_0$  is standard atmospheric pressure. At unit activity and partial pressure of hydrogen,  $E = 0$  by definition. Maintaining these equilibrium concentrations is critical to the stability of the reference electrode potential. This requires uniform coverage of the electrode with adsorbed hydrogen gas and protons. In chloride reference electrodes, the chloride concentration is usually maintained constant by using a saturated solution with excess solute (saturated calomel electrode) or a high chloride concentration (silver/silver chloride electrode).

The  $\text{H}_2/\text{H}^+$  redox reaction on platinum is extremely fast and reversible, making it eminently suitable as a thermodynamic standard. In addition, the mechanism of the reaction is well understood and both chemical species are stable over a wide range of conditions. However, the standard hydrogen electrode is inconvenient for general laboratory use so its primary function is as a calibration standard for the other reference electrodes listed in Table 1.

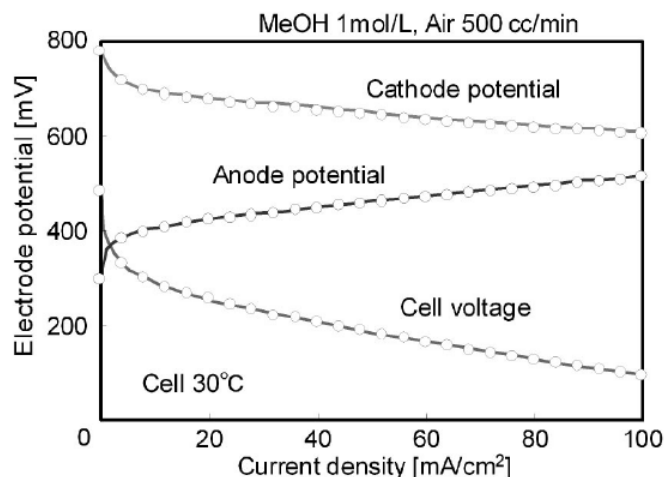


**Figure 2** Example of separate measurements of anode and cathode polarisation using a reference electrode, in this case for a direct methanol fuel cell (after Kunimatsu et al<sup>1</sup>). The cell voltage is the difference of the two.

In fuel cell applications, the anode is often considered as a pseudo-reference electrode since it behaves much like a reversible hydrogen electrode when pure hydrogen is used as the fuel. However, when other fuels such as reformat or methanol are used the anode polarisation becomes significant. Even with pure hydrogen, at high current densities the anode is unable to maintain its equilibrium reactant concentration due to mass transport losses. In these cases a separate reference electrode is required to discriminate between the respective losses in the anode and the cathode. The cell voltage is the difference between the two, as exemplified in Figure 2. The two most commonly used reference electrodes in PEMFC research are the reversible hydrogen electrode (RHE) and the dynamic hydrogen electrode (DHE). The pros and cons of these two types of electrode are discussed below. Very little work is reported on other reference electrode systems.

In liquid electrolyte systems, measurement of the potential of the working electrode with respect to the reference electrode is usually achieved by placing a Luggin capillary in the current flow path close to the working electrode. If the current and electrolyte resistance is known, this allows correction of the measured potential to account for the IR drop in solution. In thin solid electrolytes such as those employed in a typical membrane electrode assembly (MEA), positioning of the reference electrode is less straightforward due to geometric constraints. Internal reference electrodes may be constructed by sandwiching the electrode between two membranes but this usually perturbs the normal operation of the fuel cell. Most reference electrodes are of the external type and are connected to the electrolyte via a salt bridge.

### 3. REVERSIBLE HYDROGEN ELECTRODE

The RHE used in fuel cell applications is essentially a standard hydrogen electrode with a solid electrolyte (typically Nafion) instead of 1 M HCl. In many cases, the

anode of the fuel cell itself is used as a reference electrode (or the cathode fed with  $H_2$ ) but the assumption that these electrodes behave as RHEs is not always justified.

Springer et al<sup>2</sup> used a RHE to resolve the anode and cathode losses in a PEMFC of active area  $5\text{ cm}^2$ . The RHE consisted of a 3 mm diameter Nafion-impregnated disk of a commercially available electrode, which was hot-pressed onto the membrane above the anode. The RHE was exposed to the  $H_2$  gas stream but electrically isolated from the anode. Effective hydration was achieved by locating the RHE close to the humidified gas inlet. Good agreement was obtained in the potential differences between anode and cathode and between RHE and cathode. The authors concluded that as long as the anode humidification was maintained high, the anode losses were negligible in their fuel cells.

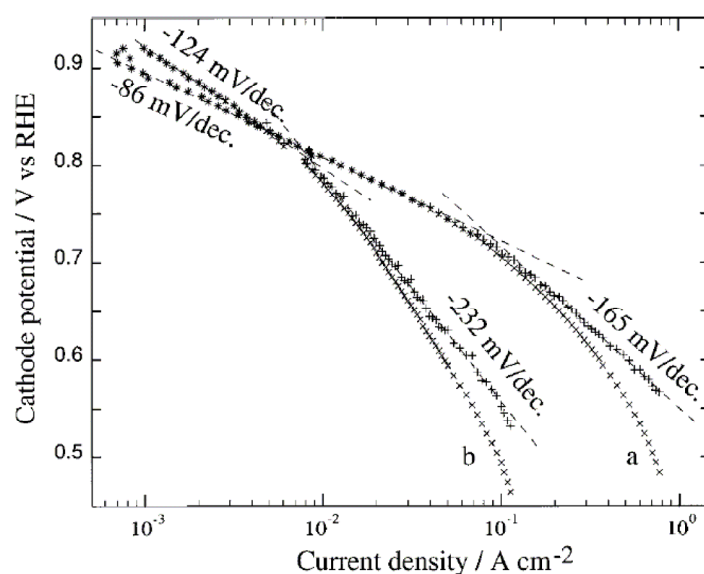


**Figure 3** Cathode polarisation curves for a single cell PEMFC using a RHE: uncorrected (x) and IR-corrected (+), (a) 40 °C and (b) 70 °C (after Ihonen et al<sup>3</sup>).

Ihonen et al<sup>3</sup> used a RHE to investigate the kinetics and mass transport limitations of the oxygen reduction reaction in a PEMFC. The RHE was deposited as a Pt/C slurry on the anode side of the membrane, 5 mm from the edge of the active layer and 2 mm – 3 mm in size. It was then covered with a small piece of backing material attached to a Pt wire. Polarisation curves corrected for IR drop using the current interrupt technique revealed two distinct Tafel slopes; a kinetic Tafel slope at low current density and a second Tafel slope at higher current density with a value about twice that at low current density (Figure 3). In both regions the current density was proportional to the cathode thickness and to the oxygen partial pressure, implying mass transport limitation by oxygen diffusion in the agglomerates. This is a good example of the use of reference electrodes to identify rate-limiting steps in fuel cell reactions.

He and Nguyen<sup>4</sup> demonstrated that edge effects are critical for reference electrode measurements in PEMFCs. A schematic of a typical RHE configuration is shown in Figure 4, where  $\delta$  is the electrolyte thickness,  $d$  is the misalignment of anode and cathode and  $L$  is the distance between the RHE and the edge of the nearest electrode.

The authors define a misalignment factor,  $d/\delta$ , which arises due to the limited precision of the MEA fabrication process. Here the relationship between the electrolyte potential at the surface of the working electrode and the electrolyte potential at the surface of the RHE is complex because the potential distribution outside the main current path is complicated and non-linear.

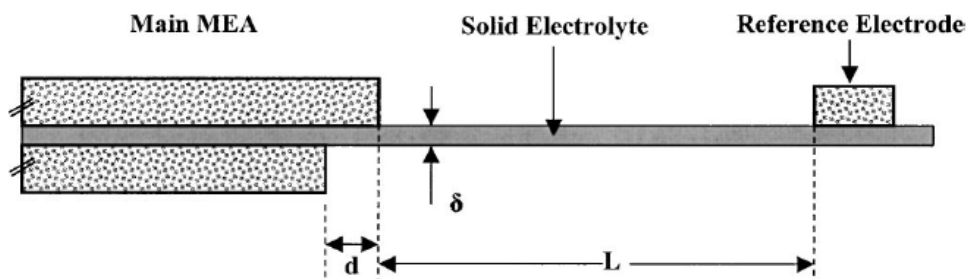


**Figure 4** Schematic of typical RHE arrangement in a SPFC highlighting the misalignment factor  $d/\delta$  (after He and Nguyen<sup>4</sup>).

The RHE used to test the effect of electrode misalignment was catalysed carbon paper (Toray TGPH-060) hot-pressed onto a strip of Nafion, which could be attached to the edge of the fuel cell membrane. The catalyst ink was 20% Pt on XC-72 carbon and 5 wt% Nafion solution. The Nafion strip was kept hydrated by a wicking technique and stable operation of the RHE was demonstrated up to 70 °C. By testing MEAs with electrodes of different sizes and alignments, it was shown that even with slight misalignment ( $d/\delta > 1$ ) the potential measured by the RHE is dominated by that of the protruding electrode.

Modelling is an essential tool in the analysis of reference electrode measurements in such geometries. In general, the current and potential distributions can be divided into three categories:

1. Primary distribution – ohmic (kinetic and mass transport losses negligible).
2. Secondary distribution – ohmic/kinetic (mass transport losses negligible).
3. Tertiary distribution – ohmic/kinetic/mass transport.

He and Nguyen<sup>4</sup> used finite element modelling to simulate the potential distribution for a range of cell configurations. The secondary potential distribution for a cell with  $d/\delta = 4$  is compared to one with perfectly aligned electrodes in Figure 5. Even with perfect alignment ( $d/\delta = 0$ ), the potential distribution is not symmetrical between the electrodes due to differences in kinetics at anode and cathode. With a misalignment factor  $d/\delta = 4$ , the potential that would be measured by a RHE on the right hand side is dominated by the upper (protruding) electrode. The authors also used modelling of the tertiary distribution to demonstrate that the reference electrode can be used as a qualitative tool to detect flooding at the cathode.

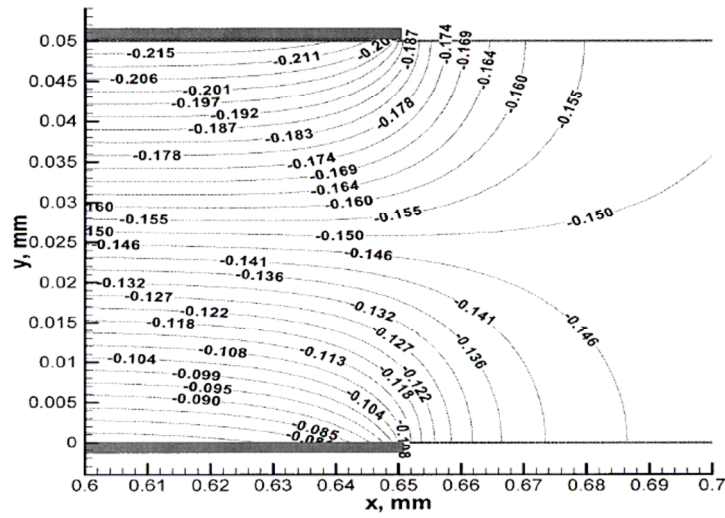
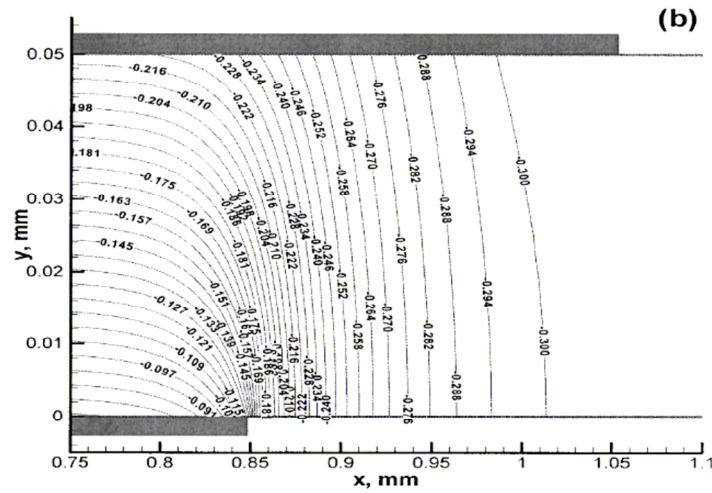
(a)  $d/\delta = 0$ (b)  $d/\delta = 4$ 

**Figure 5** Comparison of secondary potential distribution for cells with (a) perfectly aligned electrodes ( $d/\delta = 0$ ) and (b) misaligned electrodes ( $d/\delta = 4$ ) at a cell voltage of 0.5 V (after He and Nguyen<sup>4</sup>).

Parallel work by Liu et al<sup>5</sup> also highlighted the importance of reference electrode positioning and ohmic compensation. The authors compared primary and secondary potential distributions for perfectly aligned and misaligned electrodes. A misalignment factor,  $r$  (equivalent to  $d/\delta$  in the work by He and Nguyen<sup>4</sup>), was used. The primary potential distribution for a range of values of  $r$  is shown in Figure 6. In Figure 6a the potential distribution is linear between the perfectly aligned electrodes but becomes highly non-linear close to the edges. Beyond a distance of about  $1.5b$ , where  $b$  is the membrane thickness, the potential becomes uniform at all points across the membrane. This is referred to as the region of constant potential (RCP).

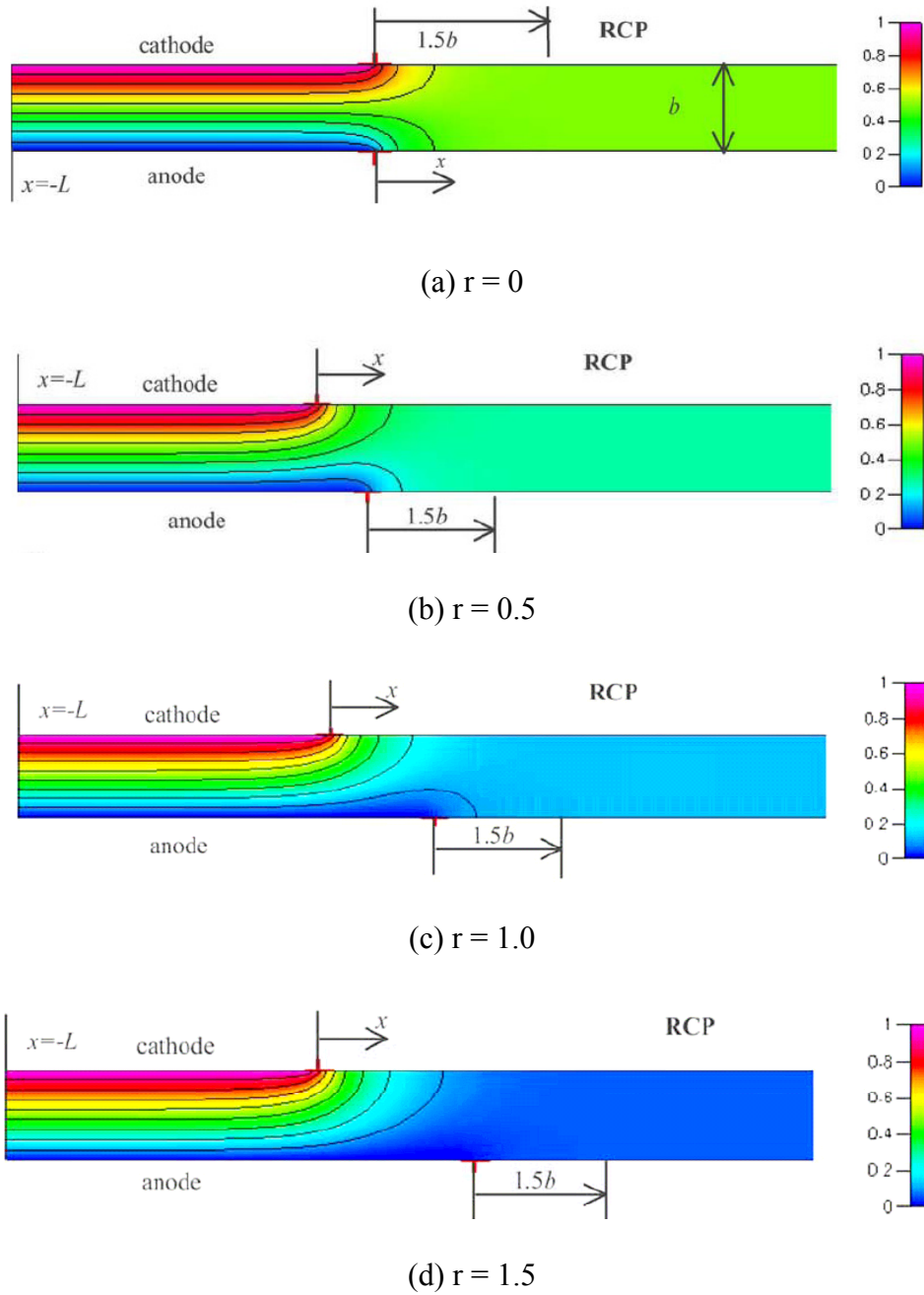
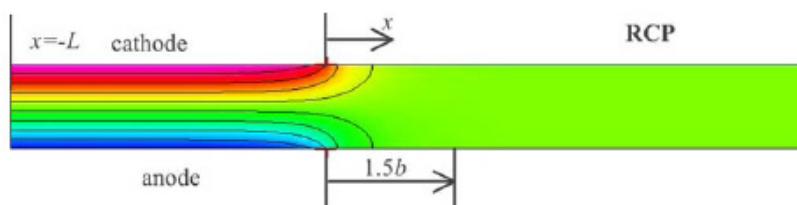


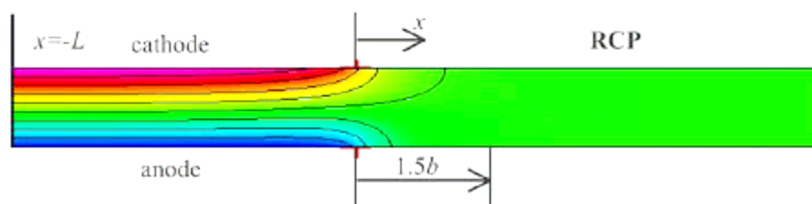
**Figure 6** Comparison of primary potential distribution for cells with (a) perfectly aligned electrodes ( $r = 0$ ) and misaligned electrodes (b)  $r = 0.5$  (c)  $r = 1.0$  (d)  $r = 1.5$  (after Liu et al<sup>5</sup>). RCP is the region of constant potential.

In the case of a primary current distribution with perfectly aligned electrodes (Fig 6a), the potential in the RCP is exactly equal to half that of the potential drop between the electrodes. When a RHE is positioned in the RCP, it is straightforward to subtract half the IR drop (as measured by ac impedance or current interrupt techniques) to correct for the electrode potential. However, when the electrodes are not perfectly aligned (Fig 6b-d) or when the kinetics and mass transport processes are not equivalent at each electrode (as is generally the case) large errors can be introduced. The authors demonstrated the effect of different rates of electrode kinetics at anode and cathode by introducing the Wagner number,  $W_a$ , which is the ratio of the kinetic resistance of the

electrode to the ohmic resistance. The secondary potential distribution for electrodes with equal Wagner numbers in a cell with perfectly aligned electrodes is symmetrical, as shown in Figure 7a. However, when the anode has a lower kinetic resistance (as is the case in a PEMFC), the secondary potential distribution is asymmetrical and the potential in the RCP is closer to that of the anode. Now the ohmic correction for each electrode poses a problem. When misalignment, kinetics and mass transport effects are all combined, the ohmic correction becomes extremely difficult to determine.



(a)  $W_a(\text{cathode})/W_a(\text{anode}) = 1$



(b)  $W_a(\text{cathode})/W_a(\text{anode}) = 1000$

**Figure 7** Secondary potential distribution for a cell with perfectly aligned electrodes and (a) equal kinetic resistance on anode and cathode (b) higher kinetic resistance at the cathode (after Liu et al<sup>5</sup>).

The problem of electrode misalignment was addressed by Eccarius et al<sup>6</sup>, who introduced a post-processing laser ablation step to smooth the edges of the MEA and achieve more precise alignment of the electrodes. The authors identified additional sources of error arising from different flowfield resistances, inhomogeneous pressure distributions in the gas diffusion layer and low cathode flow rates.

A microtubular reference electrode with potential applications in fuel cell research was designed by Kunimatsu et al<sup>1</sup>. The electrode consisted of a Pt wire inside a Flemion tube of outer diameter 0.6 mm. Catalyst paste (Pt black powder and 5 wt% Nafion solution) was injected into the polymer electrolyte tube, dried at room temperature and then heat treated at 135 °C for 3 min. The microtubular electrode has the advantages of small, size, zero hysteresis and the ability to function as a counter electrode in a two-electrode configuration. However, it cannot be used in electrolytes containing cations other than  $H^+$ , although this is not a problem for most SPFC applications. The authors successfully demonstrated its use in a DMFC, where its potential differed from that of both the anode and cathode fed with  $H_2$  by  $\pm 0.2$  mV.

RHEs have been used to evaluate the performance of DMFC catalysts<sup>7</sup>, to interpret the polarisation curves of DMFCs<sup>8</sup>, to study CO oxidation on PtRu/C in PEMFCs<sup>9</sup>, to

investigate carbon corrosion in PEMFC cathodes<sup>10</sup> to study water management in DMFCs<sup>11</sup> and to characterise hydrogen starvation in PEMFCs<sup>12</sup>. An increasing number of papers have also been published on the use of RHEs in impedance spectroscopy<sup>13,14</sup>.

#### 4. DYNAMIC HYDROGEN ELECTRODE

The DHE, shown schematically in Figure 8, is a two-electrode system first proposed by Giner<sup>15</sup> in 1964. Electrode A is polarised cathodically with respect to Electrode B so that hydrogen is evolved on its surface. If adequate current is applied, the potential of Electrode A differs from that of the RHE by a constant correction term, e.g. 20 mV – 40 mV at 1 mA/cm<sup>2</sup>. Electrode B is positioned above Electrode A to minimise interference from the oxygen evolved at that electrode. The DHE has the advantage that no hydrogen supply is required and contamination of the fuel cell is minimised.

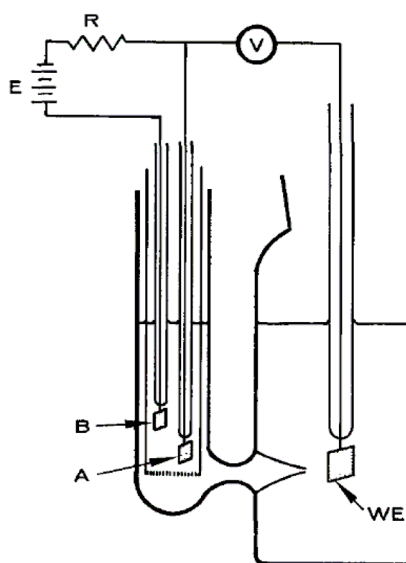


**Figure 8** Schematic diagram of dynamic hydrogen electrode (after Giner<sup>15</sup>).

Significant sources of error can arise when using the DHE in neutral or unbuffered solutions due to pH changes close to the surface of Electrode A. In addition, if the electrolyte contains species that can be reduced at potentials more noble than the potential for hydrogen evolution, the DHE will cease to function as a hydrogen-evolving electrode. In PEMFCs, the electrolyte is strongly acidic and ideally at least contains no such impurities so the use of the DHE is usually acceptable.

The first detailed evaluation of the use of a DHE in an operational solid polymer electrolyte fuel cell was published by Kuver et al<sup>16</sup> in 1994. Two 11 mm diameter platinised Pd-Au grids were inserted on either side of a DMFC membrane (d in Figure 9). A separate RHE was attached to the membrane via a salt bridge for comparison. Prior to fuel cell operation, a charging current of 3 mA – 10 mA was applied to the DHE to pre-charge with hydrogen. Thereafter a constant charging current in the range 0.01 mA – 0.04 mA was applied to the DHE. At the maximum charging current used, the potential of the DHE was 40 mV more negative than the RHE and a constant correction factor could be applied. At high current densities (up

to  $500 \text{ mA/cm}^2$ ), a drift of order  $50 \text{ mV}$  was observed in the potential of the DHE, which was ascribed to changes in the activity of  $\text{H}^+$  in the vicinity of the electrode.

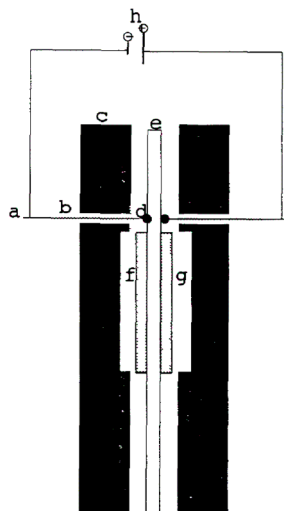


**Figure 9** DHE applied to a DMFC (after Kuver et al<sup>16</sup>).

Ren et al<sup>17</sup> used a similar configuration (shown in Figure 10) to resolve the performance of anode and cathode in a DMFC. Here the electrodes were two Pt-ink coated carbon cloths (h and i in Figure 10). The current applied to the DHE was 150 times greater than that used by Kuver et al. The authors reported enhanced stability of their DHE due to greater separation between the DHE and the MEA (4 mm) and improved hydration of the membrane adjacent to the DHE. Current interrupt measurements were used to subtract the IR drop across the membrane from the polarisation curves obtained for each electrode. The DHE was used to identify a significant anode polarisation at current densities above  $200 \text{ mA/cm}^2$  with  $1 \text{ M}$  methanol feed, which was attributed to mass transport losses in the gas diffusion layer.

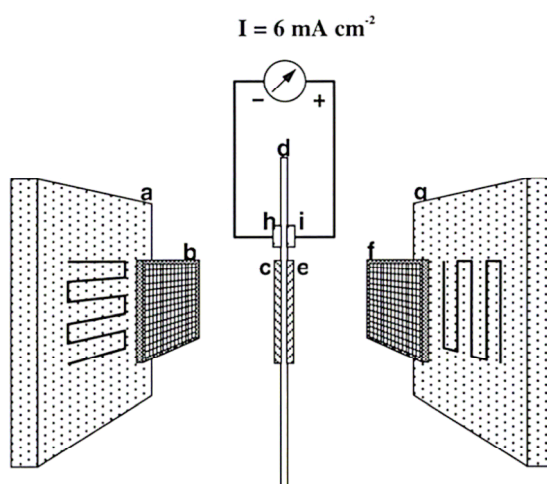
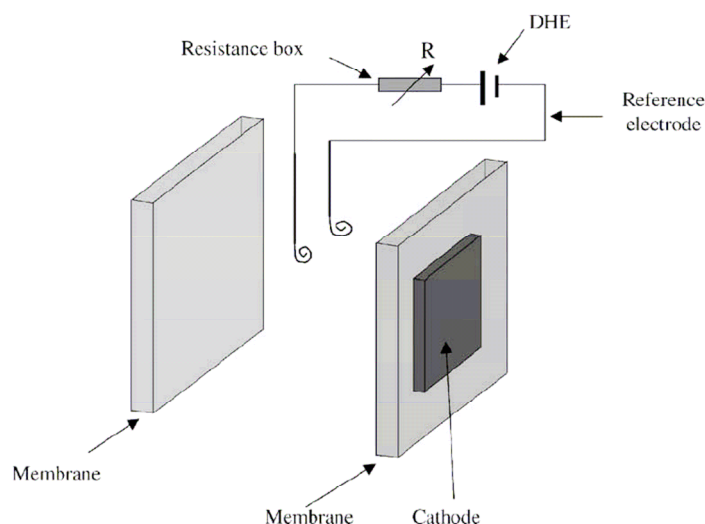
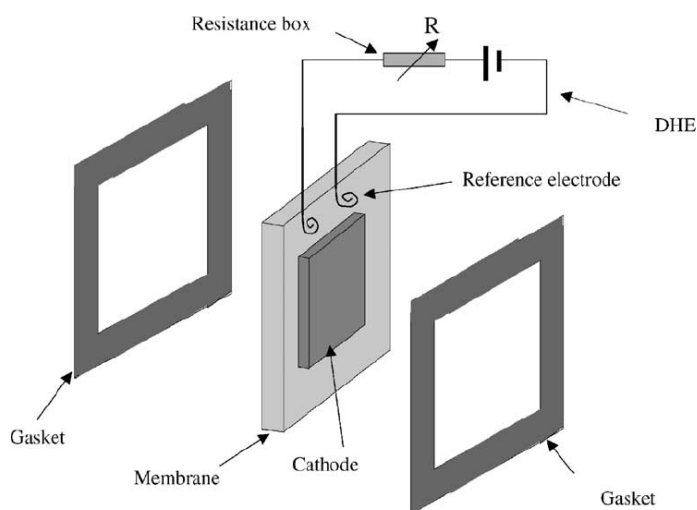


**Figure 10** DHE applied to a DMFC (after Ren et al<sup>17</sup>).



(a) Sandwich-type DHE



(b) Edge-type DHE

**Figure 11** Comparison of two different DHE configurations for SPFCs (after Li and Pickup<sup>18</sup>).

Li and Pickup<sup>18</sup> compared two types of DHE – the sandwich type and the edge-type shown in Figure 11 – for both PEMFC and DMFC. In all cases the DHE electrodes were 0.1 mm diameter Pt wires, which were encased in polyvinyl chloride (except for the ends) and between which a current of 6  $\mu\text{A}$  was passed. No drift of the reference electrode potential was observed for either configuration. Comparison of polarisation curves for a PEMFC in each configuration revealed that, while the anode polarisation curves were similar, there was a significant difference between the cathode polarisation curves. The performance of the cell with the sandwich-type DHE was severely perturbed by the presence of the DHE, leading the authors to conclude that the edge-type configuration was preferable. Using this configuration it was demonstrated that the measured potential was relatively insensitive to the position of the DHE.

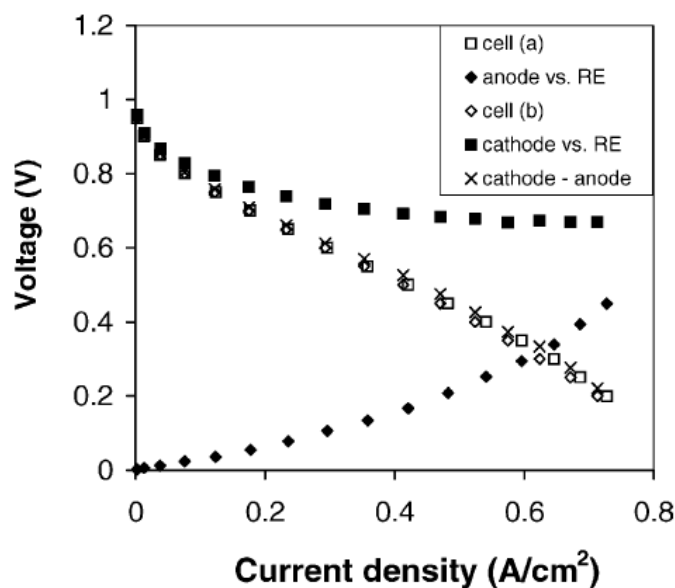


**Figure 12** Polarisation curves for a 1 cm<sup>2</sup> single cell H<sub>2</sub>/O<sub>2</sub> PEMFC at 60 °C using an edge-type DHE (after Li and Pickup<sup>18</sup>).

An example of a polarisation curve obtained for a 1 cm<sup>2</sup> single cell H<sub>2</sub>/O<sub>2</sub> PEMFC at 60 °C using the edge-type DHE is shown in Figure 12. A striking feature is the unexpectedly large anode polarisation, particularly at high current densities. The anode overpotential was found to be strongly dependent on the level of humidification, suggesting that dehydration of the anode was the source of the high anode overpotentials. This dehydration is caused by electro-osmotic drag of water from anode to cathode and increases with increasing current density.

Siroma et al<sup>19</sup> combined these two approaches to produce a sandwich-type DHE that could be attached to the edge of an MEA, as shown in Figure 13. The ends of two PTFE-coated Pt wires separated by 1 mm were exposed and covered with a Pt catalyst ink. The wires were then sandwiched between two small strips of Nafion 112 membrane (2 mm × 5 mm) and hot-pressed at 20 MPa for 1 min at 140 °C. The DHE unit could then be hot-pressed onto the anode side of the MEA. By testing the DHE in deaerated aqueous solution, an optimum current of 50 µA was identified for potential stability. When oxygenated solution was used, a much higher current was required to consume the oxygen diffusing through the membrane, which led to significant polarisation of the DHE, implying that this electrode is suitable for use on the anode side of a PEMFC. Some fluctuation in the potential of the DHE was observed (of the order of 5 mV). The authors attributed this to the instability of the partial pressure of hydrogen gas in contact with the electrode and suggested increasing the gas permeability of the DHE membranes to counteract this.

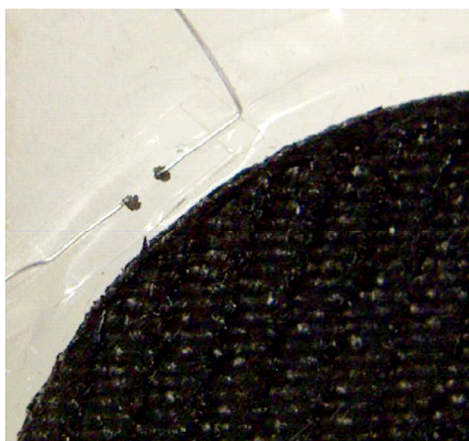


**Figure 13** Photograph of MEA with DHE attached close to the edge of the gas diffusion layer (after Siroma et al<sup>19</sup>).

Using the edge-type DHE described above, Li and Pickup<sup>20</sup> demonstrated that potentials measured by external reference electrodes are essentially local values dominated by the nearest edge of the fuel cell electrode. They compared measurements from two separate DHEs located at the top and bottom of a PEMFC. With the cell in steady state at a constant potential of 0.7 V, an aliquot of CO in N<sub>2</sub> was injected into the H<sub>2</sub> inlet (at the top of the cell). The quantity of CO injected was sufficient to poison only a fraction of the total anode Pt surface area. The current density and the anode potential relative to each DHE are shown in Figure 14. While the anode polarisation relative to the top DHE was significantly affected, that relative to the bottom DHE was relatively unchanged, indicating that little CO reached the bottom of the anode. In a separate experiment, a similar but less marked difference between the potential measured by each DHE was observed by deliberately introducing a water gradient through the cell.

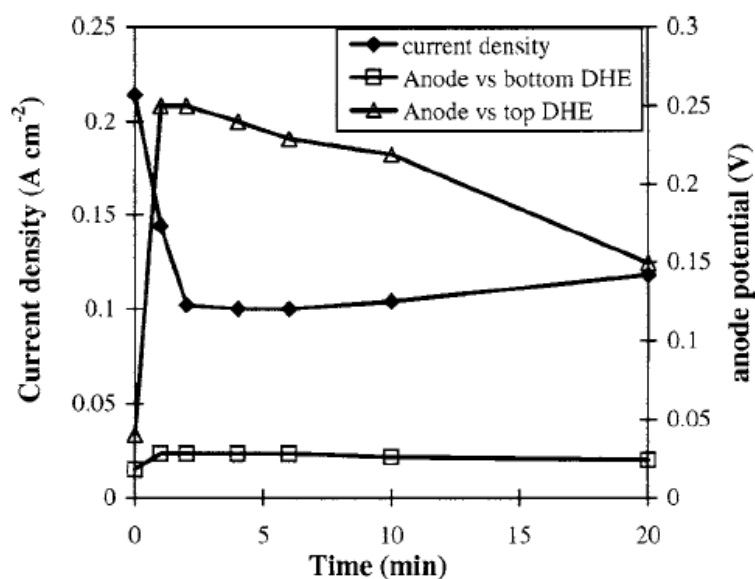


**Figure 14** Current density and anode overpotential vs top and bottom DHEs following injection of an aliquot of CO into the top of the cell (after Li and Pickup<sup>20</sup>).

## 5. SUMMARY

- The two most common reference electrodes used in solid polymer fuel cell research are the reversible hydrogen electrode and the dynamic hydrogen electrode. Very little work is reported on other reference electrode systems.
- Uncertainty in the reliability of reference electrode measurements is mainly associated with the positioning of the reference electrode with respect to the fuel cell electrodes, the stability of the reference electrode and poisoning of the fuel cell by chemical species from the reference electrode.
- The major concern with the use of internal reference electrodes is that they can significantly perturb the operation of the fuel cell.
- The potential measured by an external reference electrode is dominated by edge effects caused by misalignment of the fuel cell electrodes. This is exacerbated by differences in rates of electrode kinetics and mass transport between anode and cathode.
- Finite element modelling of the potential distribution in the electrolyte membrane provides useful insight into sources of error in reference electrode measurements.

## 6. RECOMMENDATIONS

It is clear that the positioning of the reference electrode is a critical factor in solid polymer fuel cell measurements. The use of multiple external electrodes is one way around the electrode positioning issue but does not really address the issue of the potential distribution close to the electrode and within the active area. A measurement system that facilitates spatial resolution of the electrolyte potential close to the electrode would be beneficial. This could be achieved by feeding an array of miniature salt bridges through the back of the fuel cell to various locations across the active layer. It would also avoid the problem of the asymmetrical potential distribution in the membrane.

The following recommendations are made with regard to reference electrode development under the NPL fuel cell research programme:

1. Develop salt bridge technique from the active layer through the bipolar plate and gas diffusion layer, focusing initially on Nafion.
2. Investigate the use of reference electrode systems other than  $H^+/H_2$ .
3. Add finite element modelling of potential distribution in membrane to current fuel cell modelling capability.
4. Consider adding DMFC test capability to fuel cell laboratory, as these systems have a significantly greater need for reference electrode measurements.

## 7. REFERENCES

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- <sup>1</sup> M. Kunimatsu, H. Qiao, T. Okada, J. Electrochem. Soc. **152**, E161 (2005).
- <sup>2</sup> T.E. Springer, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. **140**, 3513 (1993).
- <sup>3</sup> J. Ihonen, F. Jaouen, G. Lindbergh, A. Lundblad, G. Sundholm, J. Electrochem. Soc. **149**, A448 (2002).
- <sup>4</sup> W. He, T. Nguyen, J. Electrochem. Soc. **151**, A185 (2004).
- <sup>5</sup> Z. Liu, J.S. Wainwright, W. Huang, R.F. Savinell, Electrochim. Acta **49**, 923 (2004).
- <sup>6</sup> S. Eccarius, T. Manurung, C. Ziegler, J. Electrochem. Soc. **154**, B852 (2007).
- <sup>7</sup> B. Gurau, R. Viswanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Smotkin, E. Reddington, A. Sapienza, B.C. Chan, T.E. Mallouk, S. Sarangapani, J. Phys. Chem. B **102**, 9997 (1998).
- <sup>8</sup> Y.J. Kim, W.H. Hong, S.I. Woo, H.K. Lee, J. Power Sources **159**, 491 (2006).
- <sup>9</sup> S. Enback, G. Lindbergh, J. Electrochem. Soc. **152**, A23 (2005).
- <sup>10</sup> R. Dross, B. Maynard, ECS Transactions 11, 1059 (2007).
- <sup>11</sup> S. Eccarius, F. Krause, K. Beard, C. Agert, J. Power Sources **182**, 565 (2008).
- <sup>12</sup> W.R. Baumgartner, P. Parz, S.D. Fraser, E. Wallnofer, V. Hacker, J. Power Sources **182**, 413 (2008).
- <sup>13</sup> H. Kuhn, B. Andreaus, A. Wokaun, G.G. Scherer, Electrochim. Acta **51**, 1622 (2006).
- <sup>14</sup> K. Wiezell, P. Gode, G. Lindbergh, J. Electrochem. Soc. **153**, A759 (2006).
- <sup>15</sup> J. Giner, J. Electrochem. Soc. **111**, 376 (1964).
- <sup>16</sup> A. Kuver, I. Vogel, W. Vielstich, J. Power Sources **52**, 77 (1994).
- <sup>17</sup> X. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. **147**, 92 (2000).
- <sup>18</sup> G. Li, P.G. Pickup, Electrochim. Acta **49**, 4119 (2004).
- <sup>19</sup> Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S.-I. Yamazaki, K. Yasuda, J. Power Sources **156**, 284 (2006).
- <sup>20</sup> G. Li, P.G. Pickup, Electrochem. Solid State Lett. **156**, A249 (2006).