In situ mapping of electrode potential in a polymer electrolyte fuel cell

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The polymer electrolyte fuel cell (PEFC) is a potential replacement or hybrid partner for gas turbine, internal combustion engine and battery technologies but commercialisation of the technology is currently hampered by high material and processing costs, lack of a refuelling infrastructure and limited durability [1]. In situ measurement of critical parameters is required both for model validation and to develop further understanding of the physical processes that govern fuel cell performance and durability.

Conventional fuel cell reference electrodes may be grouped into two categories: internal (or sandwich) type and external (or edge) type, as shown in Figure 1. Most conventional fuel cell reference electrodes are of the external type and are connected to the edge of the membrane via a salt bridge (usually a strip of Nafion membrane). The drawback with this type of reference electrode is that it is located relatively far from both electrodes and the measured potential is therefore subject to potential drop effects. In addition, the measured potential is often dominated by that of the edge of the nearer electrode due to any slight misalignment of the electrodes [2,3]. Internal reference electrodes are constructed by sandwiching a reference electrode between two membranes and hot-pressing. This approach has additional disadvantages in that both charge and water transport in the membrane are perturbed by the presence of the electrode and associated trailing wires [4]. However, the fundamental limitation of both types of reference electrode is that they do not account for the potential drop in the membrane.



Figure 1: Comparison of NPL configuration with that of conventional fuel cell reference electrodes.

An innovative PEFC reference electrode has been developed at NPL, comprising an external standard hydrogen electrode connected to the membrane electrode assembly by very fine Nafion tubing inserted through the end plates of the fuel cell (Figure 2). The ion conducting path through the gas diffusion layer is achieved by Nafion impregnation at the point of contact with the Nafion tubing. Our through-plate configuration overcomes the major limitations of conventional fuel cell reference electrodes in that ohmic drop, potential distribution and electrode edge effects in the membrane are negated. The use of an array of such electrodes makes possible for the first time accurate mapping of the variation in electrode potential across the active area of an operating PEFC.

The utility of the technique is demonstrated using a 3×3 array of NPL reference electrodes applied to both the anode and the cathode of an operating single cell PEFC. Polarisation measurements can be used to identify non-uniform catalyst utilisation across the active area of the cell and contrasting effects of humidification on anode and cathode performance. The reference electrode array may also be used to identify the location and severity of carbon support corrosion on the cathode during start-up and shut-down. Such information is particularly useful when combined with parallel measurement of evolved carbon dioxide at the cathode outlet.



Figure 2: Schematic diagram of NPL reference electrode. Inset: sealing method.

The fact that this configuration effectively provides a point measurement means that accurate spatial resolution of electrode potential across the active area of the fuel cell is now possible for the first time. This technique can be successfully applied to a wide range of fuel cell performance and durability issues, enhancing fundamental understanding of underlying mechanisms and facilitating significant improvements in fuel cell design.

Acknowledgements

This work was supported by the UK National Measurement System and an Industrial Group comprising Acal Energy, AFC Energy, C Tech Innovation, CMR Fuel Cells, Intelligent Energy and Johnson Matthey. The authors are grateful to Johnson Matthey for supply of fuel cell components.

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