



Localised electrochemical impedance measurements of a polymer electrolyte fuel cell using a reference electrode array to give cathode-specific measurements and examine membrane hydration dynamics

Erik Engebretsen^a, Gareth Hinds^{b,*}, Quentin Meyer^a, Tom Mason^a, Edward Brightman^b, Luis Castanheira^b, Paul R. Shearing^a, Daniel J.L. Brett^{a,**}

^a Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, UK

^b National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, UK

HIGHLIGHTS

- Localised measurements of impedance spectra of cathode measured for first time.
- Cathode-specific mass-transport limitation increases along channel.
- Spatial variations of high-frequency resistance give map of membrane hydration.
- Membrane resistance current step transients correlated with membrane swelling.

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ABSTRACT

Advances in bespoke diagnostic techniques for polymer electrolyte fuel cells continue to provide unique insight into the internal operation of these devices and lead to improved performance and durability. Localised measurements of current density have proven to be extremely useful in designing better fuel cells and identifying optimal operating strategies, with electrochemical impedance spectroscopy (EIS) now routinely used to deconvolute the various losses in fuel cells. Combining the two techniques provides another dimension of understanding, but until now each localised EIS has been based on 2-electrode measurements, composed of both the anode and cathode responses. This work shows that a reference electrode array can be used to give individual electrode-specific EIS responses, in this case the cathode is focused on to demonstrate the approach.

In addition, membrane hydration dynamics are studied under current load steps from open circuit voltage. A three-stage process is identified associated with an initial rapid reduction in membrane resistance after 10 s of applying a current step, followed by a slower ramp to approximately steady state, which was achieved after ~250 s. These results support previously published work that has looked at membrane swelling dynamics and reveal that membrane hydration/membrane resistance is highly heterogeneous.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have shown great promise as power sources in a wide range of applications due to their high efficiency and low-temperature operation and advanced diagnostics continue to inform more of their internal operation [1,2]. However, mass commercialisation of PEFCs has been hindered by a number of factors, including cost, performance and durability. One of the most effective ways to understand fuel cells and improve their design and

performance is to apply bespoke *in-situ* diagnostic techniques.

Many complex processes occur in PEFCs [3] which are further complicated by spatial variation due to changing conditions such as humidity and concentration, as gases flow through a system and reactants are consumed. Several methods have been proposed for measuring local currents in galvanic cells, such as incorporating mini-electrodes and Hall effect sensors [4–8]. Cleghorn et al. pioneered the most widely used design to measure local current densities: the segmented current collector [9]. Using a segmented printed circuit board

* Corresponding author.

** Corresponding author.

E-mail addresses: gareth.hinds@npl.co.uk (G. Hinds), d.brett@ucl.ac.uk (D.J.L. Brett).
URL: <http://www.ucl.ac.uk/eil> (G. Hinds).

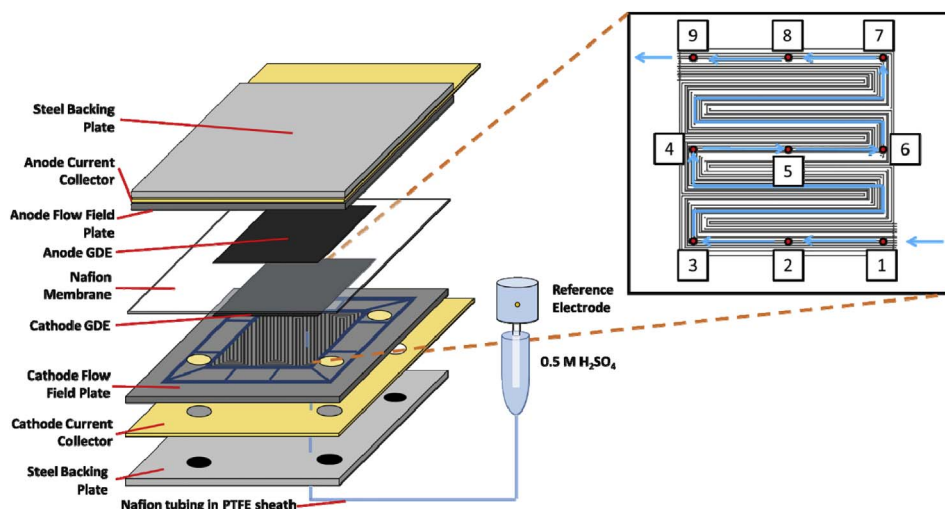


Fig. 1. Diagram of ionic connection between the catalyst layer and reference electrodes with schematic (inset) of the cathode flow-field with the direction of air flow shown in blue and placement of reference electrodes in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

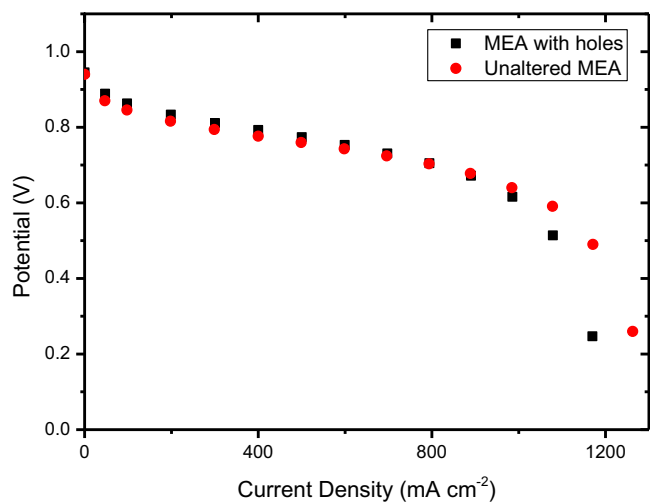


Fig. 2. Polarisation curves of unaltered MEA and MEA with nine holes in the cathode GDL at reference electrode points. Humidified hydrogen and air (90% RH) were supplied at two times stoichiometry, 80 °C and 204 kPa back pressure.

(PCB) design, this approach allowed the effects of varying humidity and stoichiometric flow rate of air to be determined spatially across the extent of a cell. The segmented flow-field and current collector approach has been applied in further studies to measure the local effects on current density when altering cell temperature, clamping pressure, polarisation, dynamic drive cycles, gas humidity, effects on cold start, and introducing trace amounts of poisoning gases into the feed streams [10–28]. Segmented sensing plates have also been used to study localised thermal and electrical effects [29,30].

A crude measure of local current does not allow the various losses that constitute performance to be determined. However, electrochemical impedance spectroscopy (EIS) is a powerful non-destructive diagnostic tool that can infer these various performance losses [31].

Localised impedance measurements have been made in previous studies using the segmented flow-field configurations where one or both of the flow-fields were segmented. Although Cleghorn et al. [9] recorded the spatial effects of membrane hydration at steady state by measuring the high-frequency resistance (HFR), Brett et al. presented the first work of localised impedance spectroscopy on a PEFC [20]. Using ten segmented measurements with independent loads, this work demonstrated how reactant consumption strongly influenced the mass transport impedance along a flow channel. Schneider et al. [21]

investigated the effects of humidity and stoichiometry of the feed gas on localised impedance; demonstrating that the overall cell impedance spectrum can be misleading. Hakenjos and Hebling [32] then coupled impedance data with thermal performance by developing a diagnostic system which could perform thermal imaging through an IR transparent flow-field simultaneously with EIS on 16 individual segments. A number of studies demonstrated the spatial variations of a ten segment single cell PEFC with Hall effect sensors to measure local currents under varying conditions, such as CO poisoning of the anode gas [15,16,33], acetonitrile [13] and acetylene poisoning [14] of the cathode gas, as well as studies varying the flow field geometry [17] and back pressure [18].

Bender et al. also demonstrated the spatial dependence of HFR with polarisation. The critical commonality in all the aforementioned studies is that the designs of the flow-fields have been altered to perform local measurements and EIS was performed in a two-electrode configuration, meaning that the cathode performance cannot be unequivocally separated from that of the anode.

Reference electrode placement in PEFCs is difficult due to geometrical constraints. Conventional reference electrodes are either internal (sandwich) or external (edge) type. The internal type is fabricated by placing a thin reference electrode between two membranes and hot pressing. This has effects on both the ionic and water transport across the membrane [34]. The external type reference electrodes are connected to the edge of the membrane with a salt bridge. This type of reference electrode suffers from potential drops due to the distance to the reference electrode and edge effects caused by misalignment between the electrodes [35,36]. Several computational studies have been conducted applying EIS to a three-electrode configuration [37–41] to determine the impedance through the cathode catalyst layer. Cruz-Manzo et al. [37–39] showed agreement between computational models and experimental results using an edge-type reference electrode, but were unable to provide spatially-resolved impedance spectra of a single cell.

Piela et al. [42] and Hinds and Brightman [43,44] developed reference electrode designs which overcome the limitations of sandwich and edge-type reference electrodes by approaching the electrode through the flow-field plate. Although this configuration adds complexity to the design of the fuel cell system, it allows for multiple reference electrode measurements to be made with local resolution of potential, and most importantly, the measurement is free from iR potential drop in the membrane.

In this work, localised EIS was applied using a reference electrode array to determine, for the first time, spatially-resolved impedance

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