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Short Communication

In operando investigation of anode overpotential dynamics in direct methanol fuel cells

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ABSTRACT

This work illustrates the application to direct methanol fuel cell technology of an innovative reference electrode setup with a through-plate configuration, which enables localised measurement of electrode potential in an operating cell. The utility of the technique is demonstrated by monitoring the evolution of anode overpotential at two different locations in the cell over different time scales, ranging from minutes to hundreds of hours. The measurements provide valuable insight into critical degradation phenomena, identifying localised hydrogen evolution on the anode during short term operation and highlighting the contribution of anode temporary degradation to the overall performance decay during long term operation. This novel approach can be used as a diagnostic tool to improve operational protocols, such as refresh cycles, for direct methanol fuel cells.

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Introduction

Direct methanol fuel cell (DMFC) technology has several advantages over traditional hydrogen-fed fuel cells, which make it particularly suitable for portable applications: methanol is a liquid with a high energy density that is more easily transported and stored and is stable under a wide range of conditions. However, together with the relatively sluggish methanol oxidation reaction, one of the main drawbacks of DMFC technology is that it tends to suffer from more severe degradation than hydrogen-fed fuel cells because, even though most of the observed degradation mechanisms are similar, they are complicated and enhanced by the presence

of methanol crossover, more significant water transport rates and a higher cathode potential, resulting from the lower current density due to the considerable anode overpotential [1,2]. Moreover, strongly heterogeneous degradation over the membrane electrode assembly (MEA) has been reported in Ref. [2], which was attributed by the authors to local inhomogeneous operation of anode and cathode electrodes.

Anode degradation has been widely investigated by performing *in situ* electrolytic characterisation of methanol oxidation, with hydrogen supplied to the cathode acting as a pseudo-reference electrode. This diagnostic technique has been useful particularly for demonstrating the presence of anode temporary degradation and quantifying its magnitude compared to permanent degradation [3], mainly attributed to

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Ru dissolution and crossover mechanisms [1,4,5]. However, the usefulness of such analysis is hindered by the unknown and complex interaction between anode and cathode electrode degradation in galvanostatic operation, which has not yet been investigated in the literature. To our knowledge no studies have been conducted to measure the evolution of anode overpotential *in operando*, especially during long term tests, which requires a suitable reference electrode.

Due to significant temporary degradation, DMFCs are rarely operated continuously for long periods; instead *refresh* cycles, comprising a combination of operation interruption and air bleed periods [2], are typically performed at regular intervals. The refresh cycle is designed to recover performance primarily by reducing the Pt oxides formed during operation, by decreasing the cathode potential below 0.5 V [6]. The influence of such a cycle on the local anode overpotential has never been investigated due to the lack of an appropriate *in situ* technique.

Reference electrodes have been widely applied to DMFCs to separate anode and cathode contributions to the cell voltage [7–10], primarily using an edge-type configuration whereby the reference electrode is connected to the edge of the membrane, either directly or via a salt bridge [11]. However, the drawback with this type of reference electrode is that it is located far from both electrodes and the measured potential is therefore subject to potential drop effects [12]. 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 [13,14]. An innovative reference electrode configuration for hydrogen-fed fuel cells has been developed at the National Physical Laboratory (NPL), whereby a Nafion® salt bridge connects an external reference electrode to the catalyst layer through holes in the end plates of the cell [15]. Use of an array of such electrodes 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.

This paper presents the application of such investigations using a locally-resolved reference electrode approach for the first time to DMFCs and demonstrates its suitability for the characterisation of anode overpotential evolution at different time scales, ranging from minutes to hundreds of hours.

Experimental

Commercial DMFC MEAs of active area 25 cm², manufactured by IRD Fuel Cells A/S, were used in this work. The membrane was Nafion® 115, anode catalyst loading was 1.8 mg cm⁻² (PtRu alloy) and cathode catalyst loading was 1.2 mg cm⁻² (Pt); both anode and cathode diffusion layers were Sigracet® SGL35DC (with microporous layer (MPL), overall thickness 325 µm, 20% PTFE content).

Nominal current density and cell operating temperature were respectively 0.25 A cm⁻² and 75 °C; anode and cathode were fed respectively with 1.0 M methanol solution, and air saturated with water at ambient temperature (stoichiometries equal to 6 and 3 respectively at 0.25 A cm⁻²) in a counter-flow configuration. These operating conditions follow the recommendations of the MEA manufacturer and are consistent with

[2,3,6], where the experimental setup utilised in this work is explained in detail.

The local reference electrode measurement setup is thoroughly explained in Ref. [15]. It is based on a Nafion® tube salt bridge, fully water-saturated, which directly connects the surface of the anode GDL with an electrolyte solution in which a Gaskatel HydroFlex® reversible hydrogen electrode (RHE) is immersed. Within the anode GDL, the required proton conductive path to the catalyst layer is achieved by impregnation with a small amount (about 2 µL) of Nafion® polymer solution. In order to achieve an insight into the local evolution of anode overpotential, two measurement points were employed, close to the inlet and outlet of the cell as shown in Fig. 1.

This study initially investigates the short term dynamics of anode potential during the refresh cycle. Then a 200-h degradation test, adopting refresh cycles, is reported and discussed, in order to demonstrate the reliability of the proposed setup and study the evolution of anode performance during long term operation. A *full refresh* procedure, including a suitable 16-h shut down [2], was adopted every 100 h during the long term tests, before performing diagnostics to check complete recovery of performance from temporary decay.

Results and discussion

In order to evaluate any influence of the presence of the reference electrodes on the cell operation, polarisation curves with and without the reference electrodes were compared. No noticeable effects were observed over the current density range from 0 to 0.4 A cm⁻². The uncertainty in the potential measured by the reference electrodes is estimated to be ±5 mV.

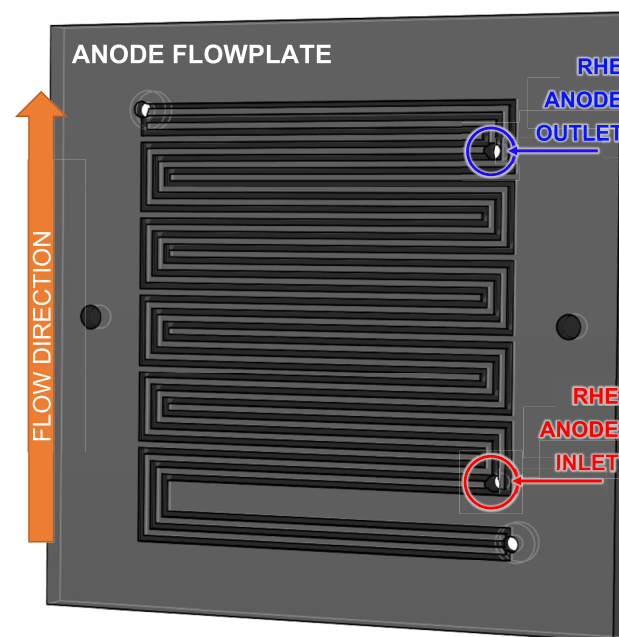


Fig. 1 – Schematic diagram of DMFC flow-plates (showing RHE locations).

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