



In situ mapping of potential transients during start-up and shut-down of a polymer electrolyte membrane fuel cell



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HIGHLIGHTS

- A unique reference electrode array allows mapping of electrode potential in a PEMFC.
- Potential mapping and CO₂ measurement were used simultaneously for the first time.
- Drier conditions led to less corrosion; evidence links this to membrane resistivity.
- Most severe carbon loss located near outlet for start-up and inlet for shut-down.
- Results provide new insights into reverse current decay mechanism.

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ABSTRACT

Progression of a fuel/air front through the anode flow-field during start-up or shut-down of a polymer electrolyte membrane fuel cell is known to generate elevated cathode potentials, leading to corrosion of the carbon catalyst support. Here we present spatially resolved measurements of such potential transients in an operating fuel cell, using an innovative reference electrode array combined with quantification of carbon corrosion by measurement of CO₂ in the cathode outlet. A systematic study of the effect of relative humidity on start-up/shut-down potential transients and carbon corrosion rates was carried out at open circuit and with the application of a small external load. The results are discussed in the context of a schematic framework for the reverse current decay mechanism expressed in terms of local electrode potential. In all cases carbon corrosion was more severe during start-up than during shut-down, with the highest cathode potentials measured opposite the anode outlet during start-up and opposite the anode inlet during shut-down. The carbon corrosion rate was least severe under the driest conditions, which was attributed to the increased membrane resistivity. This new technique provides a powerful diagnostic tool for evaluation of start-up/shut-down tolerant catalyst layers and optimisation of fuel cell hardware design.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are a pivotal technology for a future hydrogen economy. However, widespread commercialisation is currently hindered by high cost and limited durability of components. One of the major PEMFC degradation modes occurs during start-up and shut-down (SU/SD), whereby high transient cathode potentials due to the presence of a hydrogen/air front in the anode flow-field lead to corrosion of the carbon-based catalyst support [1]. Repetitive SU/SD events can

result in dramatic loss of performance arising from a decrease in active catalyst area [1,2]. There has been a great deal of academic and commercial interest in this degradation mechanism in recent years, as it is a particularly important factor in automotive systems where many start/stop cycles can be expected, and where space and cost limitations prevent the use of a nitrogen purge or similar mitigation strategy. A recent review by Yu et al. [3] summarises much of the research that has been carried out in this area, and highlights the difficulty of measuring the potential transients in situ. Lamibrac et al. [4] used a specially designed segmented cell to measure the transient local current densities arising from the start-up process in order to estimate the amount of carbon corrosion from the charge exchanged. They found that the segments of the cell that were exposed to air for the longest were

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most degraded by carbon corrosion. Several researchers have made measurements of CO₂ in the cathode gas stream in order to quantify the extent of carbon corrosion. Linse et al. [5] used an infrared analyser to monitor the concentration of CO₂ in the cathode outlet with a known flow rate, which enabled them to calculate the amount of carbon corrosion occurring under a range of systematically controlled conditions. They showed that under open circuit conditions the carbon corrosion rate was proportional to the gas front residence time and that with an external load carbon corrosion was suppressed (more effectively for shut-down than for start-up). They also observed an approximately linear dependence of the rate of carbon corrosion on relative humidity (RH). However, they were unable to measure the local cathode potential in their experiments. Kreitmeier et al. [6] used mass spectrometry to measure CO₂ concentration, and constructed a cell comprising linear parallel channels with 11 gas extraction ports located along the length of the flow-field. They found that carbon loss from start/stop cycling was most severe towards the outlet, with regions in the middle of the flow-field being least affected. Comparison of rates of carbon corrosion during start-up and shut-down using such methods has revealed contradictory results, with some authors reporting that carbon corrosion is more severe during start-up than shut-down [6,7] and others the opposite [5]. This discrepancy has been attributed to the competing effects of Pt hydride/oxide redox reactions and the differing diffusion coefficients of H₂ and O₂/N₂ [6].

Whilst measurement of evolved CO₂ has proved extremely useful in elucidating the effects of SU/SD cycling on PEMFCs, there have been limited attempts to measure the cathode potential during start/stop events, mainly due to the practical limitations of using reference electrodes in PEMFCs. For example, Shen et al. [8] used a customised membrane electrode assembly (MEA) with a hydrogen reference electrode located on the membrane adjacent to the edge of the active area of the MEA to measure the electrode potentials, together with copper wires sandwiched between two membranes to measure the membrane potential. An interfacial potential difference between cathode and membrane as high as 1.6 V was indicated by the authors, although use of the copper reference electrodes was not subject to a rigorous calibration procedure.

A novel fuel cell reference electrode has been developed at the National Physical Laboratory (NPL) that overcomes the limitations of conventional fuel cell electrodes by making contact with the working electrode through the back of the gas diffusion layer (GDL) [9]. Very small diameter Nafion tubing is inserted through the end plates of the fuel cell to act as a salt bridge, and the ionic pathway is extended through the GDL to the electrode by impregnating the GDL with Nafion at the point of contact. This innovative configuration ensures that potential drop effects in the membrane and electrode edge effects are avoided, and by using an array of such electrodes the spatial distribution of electrode potential can be measured. The reference electrode is relatively straightforward to implement on a technical-scale cell and can therefore provide in situ measurements on a commercial prototype with minimal perturbation of the system.

In the present study, the NPL reference electrode array has been applied to a generic research cell, in parallel with measurement of CO₂ in the cathode outlet stream, to investigate the effect of relative humidity on the potential transient and concomitant carbon oxidation under SU/SD cycling, with spatial resolution of the potential transient and quantification of the total carbon oxidation. SU/SD cycles were carried out under open circuit conditions and in the presence of an external fixed load on the cell, which is a commonly used mitigation strategy. An alternative mitigation strategy, whereby Nafion tubing was used in an attempt to enhance

the lateral proton conductivity between affected regions at the cathode, was also investigated.

2. Reverse current decay mechanism

The reverse current decay mechanism first proposed by researchers at UTC Fuel Cells [1] is generally accepted to be responsible for the loss of performance observed as a result of SU/SD cycling. Although the general basis of the mechanism appears sound, discussion in the literature is not ideal, focusing on parameters such as electrolyte potential that cannot physically be measured. In our opinion, electrode potential is a more appropriate basis for construction of a SU/SD scheme as it can be verified by measurement. Division of the active area of the PEMFC into four regions during SU/SD is shown schematically in Fig. 1. Before start-up of a PEMFC, both anode and cathode compartments are filled with air, either due to an air purge or via gradual leakage from the atmosphere through the anode seal or across the membrane from the cathode. During start-up (Fig. 1a), hydrogen entering the anode flow-field leads to generation of excess protons and electrons close to the anode inlet (Region 1) with an electrode potential close to that of the reversible hydrogen electrode (~0 V). In Region 2, the electrode potential remains close to the open circuit potential for oxygen/water on Pt (~1 V). If the anode is considered in isolation, under these conditions a mixed potential will be established between Region 1 and Region 2, depending on the polarisation of each reaction (in this case the oxygen reduction reaction will show greater polarisation) and the ionic conductivity of the electrolyte phase. Although there is high electronic conductivity throughout the anode (between Region 1 and Region 2) the lateral proton conductivity is relatively low. Therefore the electrode potential in each region will be polarised only slightly towards that of the other region due to the large ohmic drop in the ionic phase. Representative values based on those observed in this work are given in Fig. 1.

Prior to start-up, the electrode potential at the cathode is at the open circuit potential for oxygen/water on Pt (~1 V), which is a mixed potential determined by the balance between the water oxidation/oxygen reduction redox reaction and the platinum hydride/oxide reactions. When hydrogen enters the anode compartment, excess protons and electrons are generated in the anode catalyst layer (Region 1). Normally, these protons can only cross the membrane to Region 3 to be consumed in the oxygen reduction reaction if there is an electronically conducting path to simultaneously supply the electrons from Region 1, a condition that is not satisfied at open circuit. Similarly, although the electrons generated in Region 1 can readily move to Region 2, the low lateral proton conductivity in the electrolyte phase limits the oxygen reduction reaction in Region 2. The simultaneous demand for electrons in Region 3 and protons in Region 2 provides the driving force for an oxidation reaction to occur in Region 4. Oxidation of water, carbon or platinum is possible, which provides a complete circuit consisting of lateral electronic current in each electrode and through-plane proton current in the membrane. As a result the cathode potential in Region 4 is shifted to more positive potentials (typically > 1.4 V) to generate the required protons and electrons. The cathode potential in Region 3 and the anode potential in Region 2 are both shifted to more negative potentials to support the oxygen reduction reaction, which is the rate limiting step of the process due to its relatively slow kinetics compared to hydrogen oxidation.

The reverse process occurs during shut-down, the main difference being that air is displacing hydrogen rather than vice versa. In this case the potential map of the active area is a mirror image of that during start-up and it is the cathode potential in Region 3 that

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