



## Short communication

## Paradox phenomena of proton exchange membrane fuel cells operating under dead-end anode mode

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## H I G H L I G H T S

- $R_{hf}$ ,  $V_a$ ,  $V_c$  concomitantly shift during the cell voltage drop of PEMFC in DEA mode.
- $H_2$  depletion tests reveal  $H_2O$  may accumulate at the catalyst/ionomer interface.
- Ultrathin PFSA film is key to understand the water transport in the catalyst layer.

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## A B S T R A C T

By using two spatially separated reference electrodes in a single cell proton-exchange membrane fuel cell (PEMFC), the individual potentials of the anode and cathode are recorded under realistic operating conditions. The PEMFC is operated under dead-end anode (DEA) mode, without any humidification, to mitigate water accumulation at the anode. Although  $N_2$  crossover from cathode to anode may play an important role in PEMFCs operating under DEA mode, our results unexpectedly show that the over-potentials of both the anode and cathode concomitantly increased or decreased at the same time. The increases of over-potentials correlate to the increase of the high frequency resistance of the cell ( $R_{hf}$ ) imply that the water content in the membrane electrode assemblies is critical. However, the subsequent  $H_2$  depletion tests suggest that water may accumulate at the interface between the surface of the catalyst and the ultrathin perfluorosulfonic acid (PFSA) ionomer film and this contradicts the above (the increase in  $R_{hf}$  implies the drying out of the MEAs). This study highlights the need for further research into understanding the water transport properties of the ultrathin PFSA ionomer film (<60 nm): it is clear that these exhibit completely different properties to that of bulk proton-exchange membranes (PEM).

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## 1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) represent a promising clean energy generation technology that is at the beginning of commercial application. The cost of the PEMFCs has been reduced by >80% since 2002. The cost of the Fuel Cell system for the vehicle has been reduced to \$49  $kW^{-1}$  (in 2011) [1]. Although it is still \$19  $kW^{-1}$  higher than the DOE 2015/2017 target, fuel cell vehicles are being introduced into the market (starting in Japan). However, the cost still needs to be reduced further for wide acceptance of fuel cell cars to be realized.

Fuel cells operating under dead-end anode (DEA) mode is of increasing interest [2–13] as control systems can be significantly simplified. However, water accumulation and the  $N_2$  crossover (cathode → anode) are issues of concern [2–10]. However, the primary factors that are causing the significant drops in cell performance remain the subject of debate. By using neutron image technology, Siegel et al. [3] observed that accumulation of liquid water in the anode channels was followed by a significant drop in voltage when the air supply was fully humidified. Others argue that  $N_2$  crossover from the cathode to the anode, when the fuel cell is operated under DEA mode, leads to a high concentration of  $N_2$  and subsequent fuel depletion in the anode [6–8]: this will also cause the performance drop of the cell. In support of the latter, the performance of a DEA-mode fuel cell yielded a constant cell performance for  $3 \times$  longer periods of time when supplied with pure  $H_2$  and  $O_2$  compared to when  $H_2$  and air supplies were used [8]. Meyer

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et al. [13] claimed that 50 ppm  $N_2$  in the grade of  $H_2$  used (BOC zero grade  $H_2$  – likely to be widely used in such research work) leads to accumulation of  $N_2$  at levels up to 2.3% in the anode of DEA PEMFCs (i.e. contributes to most of the  $N_2$  observed in the anode). They also observed that the  $N_2$  contents at the anode increased from 0.25% to 3% when the fuel cell was switched from flow mode to DEA mode. This highlights that the impurities in the  $H_2$  supply need to be considered when discussing the effect of  $N_2$  crossover from the cathode to the anode. However, the results presented in this study imply that the water content of the membrane electrode assemblies (MEA) is the critical factor that is responsible for the significant performance drops in cell performance. It is hypothesized that water accumulation at the interface between the catalyst surface and the ionomer plays an important role and that this needs to be subject to more detailed research.

## 2. Experimental details

A single cell with an active area of  $19\text{ cm}^2$  was employed in this study. Carbon paper electrodes, each containing a catalyst layer (Pt loading =  $0.95\text{ mg}_{Pt}\text{ cm}^{-2}$ ) coated onto a micro-porous carbon layer, were hot-pressed onto  $50\text{ }\mu\text{m}$  Nafion-212 proton-exchange membrane (PEM) to form the membrane electrode assemblies (MEAs). Nafion dispersion (5 wt% in isopropanol) was used as the binder to form the ionomer film in the catalyst layers. Pd coated Pt wires containing absorbed H [denoted as (Pt)PdH] [14] were used as *in situ* reference electrode (RE). Two spatially separated REs (one located at the anode side and the other at the cathode side) were used to independently record the potentials of anode and cathode under real-time fuel cell operation conditions. The details of the placement of the REs were as previously reported [15].

The fuel cell was operated in DEA mode with no external humidification at anode, i.e. the anode was supplied with dry  $H_2$  (99.999%) via a pressure regulator. The  $H_2$  purge was manually controlled by a valve at the outlet of the anode. A fuel cell test station with 8 auxiliary voltage detectors (Arbin FCTS 200W, USA) was used to control the other tests conditions: air flow rate =  $6 \times$  stoichiometry (unless otherwise specified) and air supply relative humidity (RH) = 0%, 25%, 50% and 80% (when testing the fuel cell with different cathode supply humidities). The impedance of the single cell was recorded using a PGSTAT302N potentiostat (Autolab, Switzerland) containing an electrochemical impedance spectrometer FRA2 module along with a 20 A booster. Two of the auxiliary voltage detectors of the Arbin FCTS were used to detect the potentials of the anode and cathode respectively. The potentials of the anode, cathode and the whole cell, along with the internal ohmic resistance of the cell (i.e.  $R_{hf}$ , the high frequency resistance), were recorded using the combination of the FCTS 200W and the PGSTAT302N to measure the performances of the fuel cells being operated in DEA mode. The small time differences between the operations of the two instruments were corrected using the cell voltages recorded by the two instruments (not shown in Figs. 1–3 for clarity but explained in detail in the caption of Fig. 4).

Micro-pinholes in the PEMs can cause significant  $N_2$  crossover from cathode to anode. Considering the longevity of MEAs running under dry conditions and micro-pinholes in the membrane were previously observed when MEAs failed [9], each test was done using fresh MEA. The OCVs (open circuit voltages) of the MEA maintained the beginning-of-life values of 0.95–1.0 V after testing was completed: this simple test indicates the lack of micro-pinhole formation in the PEM. Unlike the failed MEAs in the longevity tests conducted by Yu et al. [8] and Matsuura et al. [9], scanning electron microscope (SEM) images of an unused MEA and a post test MEA show no detectable structural differences (Supplemental information: Fig. S1 shows the different zones of the MEA (in Fuel Cell test

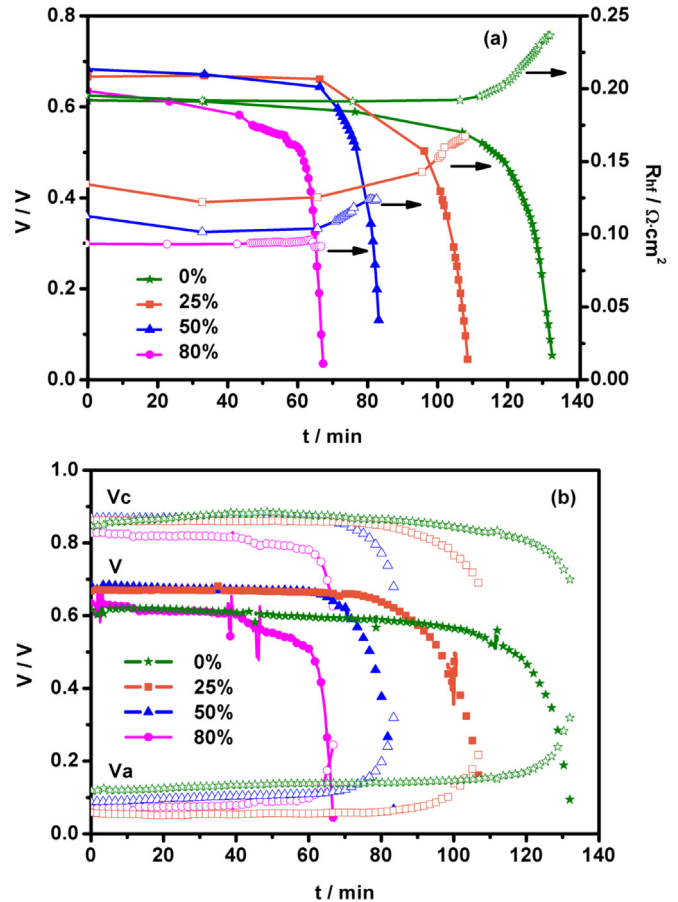


Fig. 1. (a) Chronopotentiometric and internal ohmic resistances ( $R_{hf}$ ) of the DEA-mode fuel cells at  $400\text{ mA cm}^{-2}$  with different air supply RHs. (b) The simultaneously recorded potentials of the anode ( $V_a$ ), cathode ( $V_c$ ), and whole cell ( $V$ ).  $T_{cell} = 50\text{ }^\circ\text{C}$ ,  $H_2$  backpressure = 0.3 atm, anode RH = 0%, air supply = ambient pressure and  $6 \times$  stoich.

assemblies) that were studied and Fig. S2 presents the local SEM images of both the unused and used MEAs at different zones). This confirms the lack of significant micro-pinhole formation in the PEM.

A test protocol was developed to aid the production of repeatable results: After the temperature of the cell and the RH of the air supply reached the set point, the cell was discharge at 0.2 V for *ca.*

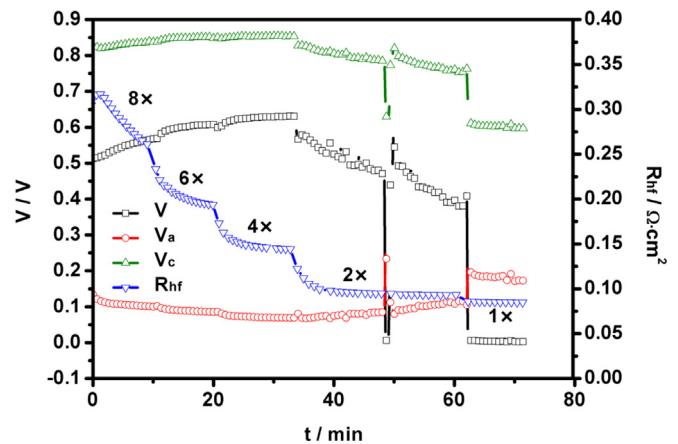


Fig. 2. The changes in the potentials of the anode, cathode, and whole cell and the  $R_{hf}$  values with discharge time for a DEA-mode fuel cell discharged at  $400\text{ mA cm}^{-2}$  when supplied with air at different flow rates.  $T_{cell} = 50\text{ }^\circ\text{C}$ ,  $H_2$  backpressure = 0.3 atm, anode and cathode RH = 0%, air supply = ambient pressure.

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