Electrochimica Acta 203 (2016) 198–205

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Nitrogen Blanketing and Hydrogen Starvation in Dead-Ended-Anode Polymer Electrolyte Fuel Cells Revealed by Hydro-Electro-Thermal Analysis

Quentin Meyer[a], Sean Ashton[b], Sergio Torija[b], Chris Gurney[b], Pierre Boillat[c,d], Magali Cochet[c], Erik Engebretsen[a], Donal P. Finegan[a], Paul Adcock[b], Paul R. Shearing[a,*], Dan J.L. Brett[a,*]

[a] Electrochemical Innovation Lab, Department of Chemical Engineering, UCL, London, WC1E 7JE, United Kingdom
[b] Intelligent Energy, Charnwood Building Holywell Park, Ashby Road, Loughborough, Leicestershire, LE11 3GB, United Kingdom
[c] Electrochemistry Laboratory (LEC), Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland
[d] Neutron Imaging and Activation Group (NIAG), Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland

ARTICLE INFO

Article history:
Received 30 January 2016
Received in revised form 22 March 2016
Accepted 5 April 2016
Available online 6 April 2016

Keywords:
Dead-ended anode
bypass effect
neutron imaging
nitrogen blanketing
current and temperature mapping

ABSTRACT

Dead-ended anode operation has a number of practical advantages that simplify system complexity and lower cost for polymer electrolyte fuel cells. However, dead-ended mode leads to performance loss over time which can only be reversed by performing intermittent purge events. This work applies a combined hydro-electro-thermal analysis to an air-cooled open-cathode fuel cell, presenting experimental functional maps of water distribution, current density and temperature. This approach has allowed the identification of a 'nitrogen blanketing' effect due to nitrogen cross-over from the cathode and a 'bypass' effect where a peripheral gap between the gasket and the GDL offers a hydrogen flow 'short circuit' to the border of the electrode. A consequence of high local current density at the margin of the electrode, and resulting high temperatures, may impact the lifetime of the cell in dead-end mode.

1. Introduction

Polymer electrolyte fuel cells (PEFC) fuelled with hydrogen are among the most promising energy conversion technologies for a broad range of applications, including portable, stationary and automotive power delivery. Dead-ended anode operation enables significant design simplification, with the replacement of humidifiers, and flow controllers by pressure regulators [1]. However, it causes reversible performance decay, and intermittent purging of the anode chamber is required to sustain effective operation. Greater insight into the mechanism of fuel cell operation during dead-ended mode is required in order to optimise the purging programme and ensure that irreversible degradation does not result. *In-situ* diagnostic techniques provide one of the most effective ways of studying the performance of fuel cells; combined mapping of current density, temperature and water distribution is applied here to give an unprecedented level of understanding into dead-ended fuel cell operation.

1.1. Current and temperature mapping in fuel cells

Initiated by Cleghorn et al. [2] and Brett et al. [3] over 15 years ago, current mapping in polymer electrolyte fuel cells have provided great insight into fuel cell operation. The technique has identified a range of current density distribution profiles associated with factors such as: uneven fuel consumptions [3–6], operating conditions [7–9], stoichiometric ratios [10–13], reactant flow orientation [5,9], and water management issues [14].

Temperature distribution has also been extensively investigated, identifying areas of higher electrochemical activity, hot-spot formation and fuel depletion. Thermocouples can provide a crude measure of temperature inside fuel cells [15–18], but cannot provide high spatial resolution, and as they need to be inserted inside the fuel cell, this often requires design modifications which may affect reactant flow and fuel cell performance. Infrared thermal imaging can provide very high spatial and temperature resolution [19–24], but requires use of modified fuel cells with an

* Corresponding authors. Tel.: +44 20 7679 3310.
E-mail addresses: p.shearing@ucl.ac.uk (P.R. Shearing), d.brett@ucl.ac.uk, http://www.ucl.ac.uk/electrochemical-innovation-lab (D.J.L. Brett).

http://dx.doi.org/10.1016/j.electacta.2016.04.018
0013-4686/

infrared transparent window, and/or cells with open channels (such as open-cathode fuel cells [25–28]) or can only image the outer surface of a cell or stack [29,30].

Combined temperature and current mapping studies allow the impact and interactions of these two parameters on the overall performance to be assessed [17,20,31–33]. However, capturing the water content may provide insights on how the temperature and current density fluctuate, and therefore should ideally be measured at unison.

1.2. Neutron imaging in fuel cells

Neutron imaging can identify water in the in-plane orientation (with the membrane plane parallel to the beam) and through-plane orientation (with the membrane plane perpendicular to the beam), enabling differentiation of water content in the cathode and the anode [34–36], the effect of different cell designs [37], and operating conditions on the water distribution throughout the cells [38–53]. Neutron imaging has been combined with other modelling and experimental techniques, such as current mapping [54], CFD model validation [38,53,55], optical imaging [56], neutron scattering [49] and localised EIS [45]. The authors have recently combined neutron imaging with current and temperature mapping in a single device [57], linking water formation/evaporation with current density and temperature under steady state conditions.

1.3. Dead-ended anode operations in an air-cooled open cathode fuel cell

Dead-ended anode operation is a common mode for operating fuel cells as it can simplify the fuel cell system, potentially avoiding flow meters, humidifiers, and drastically reducing hydrogen losses (slippage). It employs a single pressure regulator before the hydrogen inlet to the stack and a purge valve after the anode outlet [1]. However, dead-ended anode operation leads to a gradual voltage loss; therefore, a purge valve is intermittently opened at regular intervals, leading to instantaneous recovery of cell voltage/stack voltages. This gradual voltage loss has been measured and modelled [58–62], highlighting the influence of several factors. Nitrogen cross-over from the cathode to the anode, across the electrolyte membrane, has been reported to have a significant influence [60,63], which has been confirmed by controlling the nitrogen-to-hydrogen ratio at the anode inlet [64]. The extent of N_2 crossover from cathode to anode (the permeation factor) is of particular relevance for dead-ended operation and has been shown to increase with increasing current density and temperature [63,65]. Water management has been studied using neutron imaging [37,42], and by the application of a transparent cell [66], highlighting water accumulation towards the exhaust of the cell. However, these studies both used humidified cathodes; therefore, the reported water accumulation is caused by back diffusion from the cathode to the anode, leading to accumulation and flooding.

The stack used in this study is an air-cooled, open-cathode fuel cell, operated with dry fuel and oxidant. Unlike passive air-breathing systems typically limited to a maximum current density of $\sim$0.6 A cm^{-2} due to heat and water management issues [67–72], in the ‘air-cooled, open-cathode’ configuration, air is forced through the cathode channels using fans, which improves performance and enables higher current densities to be attained [73–77]. In air-cooled, open-cathode systems the temperature depends on the voltage and current density [67,78], air cooling flow rate [73,76], and heat transfer characteristics of the stack. In practice, the temperature management is normally performed using a single-point thermocouple inserted in the centre of the cell [18,29,75], or for development work using multiple micro-thermocouple measurements at various locations in the fuel cell [15,79,80].

The authors have previously studied dead-ended operation, on a cell with dry fuel and air, using techniques such as mass spectrometry (revealing nitrogen accumulation), thermal imaging and electrochemical impedance spectroscopy [29], as well as combined current and temperature mapping, revealing large gradients between the fuel inlet and exhaust [33].

Here, we present the results obtained by applying the recently developed hydro-electro-thermal analysis [57] technique to an air-cooled, open-cathode fuel cell operated in dead-ended anode mode, to capture dynamic operation, combining current and temperature mapping with water mapping during dead-ended operation.

2. Experimental

2.1. Current and temperature mapping

Current and temperature mapping were performed using a 16-segment printed circuit board sensor plate, with a 4 cm^2 resolution, recording every 0.5 s (S++ Simulation Services, Germany), described previously [57].

The sensor plate was imaged at the NEUTRA beam line of the SINQ neutron source (NEUTRA, Paul Scherrer Institut, Villigen, Switzerland) prior to its insertion in the stack and was found to be 80% transparent to the beamline neutron spectrum, which is suitable for neutron imaging. Therefore, the combined neutron imaging and current and temperature mapping is possible with this choice of hardware. The sensor plate is inserted between the first and the second cell, to measure the average current and temperature distribution of both cells.

Fuel cell testing—A 2-cell (60 cm^2 active area) air-cooled/air-breathing fuel cell stack was used for testing (Intelligent Energy Ltd., UK). The membrane electrode assembly was composed of commercially available gas diffusion layers (GDLs) and catalyst coated membrane (CCM) with Pt loading of 0.1 and 0.4 mg cm^{-2} on the anode and cathode, respectively.

The test station [29] supplied dry hydrogen (99.995%) at ambient temperature to the anodes and air was forced through the stack using a single fan (SanAce 36, Sanyo Denki) to the open-cathode channels. The exhaust hydrogen flow rate in through-flow mode was measured using a thermal mass flow meter (MassVIEW, Bronkhorst) to be 4.7 SLPM, which ensures a stoichiometric ratio of 2 at 1 A cm^{-2}. The fans, which provide cooling and air supply to the cathode, were controlled by a programmable power supply (3649A Agilent). The current drawn from the PEFC was controlled using an electronic load (PLZ664WA, Kikusui) in galvanostatic mode. An in-house computer controlled system controls the air, hydrogen, cooling and electrical valves (LabVIEW, National Instruments) as well as recording and presenting data using a data acquisition card (USB 6363, National Instruments). Ambient temperature, pressure (absolute) and relative humidity (RH) were measured at 25 °C $\pm$ 0.2 °C, 0.97 $\pm$ 0.02 bar and 40% RH respectively, during all tests. The operation of this fuel cell in terms of cathode design, cooling and active channels and materials, has been described in previous reports [29,30], and is summarised in Fig. 1. The cathode is operated in through-flow mode, with an air flow rate of 4×10^{-3} m^3 s^{-1}.

2.2. Neutron imaging

Neutron radiography was performed at the neutron imaging facility NEUTRA of the SINQ spallation source (Paul Scherrer Institut, Switzerland) [81]. Thermal neutrons provided by the source are extracted from a moderator tank in the thermal energy