Journal of Power Sources 254 (2014) 1–9

Contents lists available at ScienceDirect

Journal of Power Sources

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

Dead-ended anode polymer electrolyte fuel cell stack operation investigated using electrochemical impedance spectroscopy, off-gas analysis and thermal imaging

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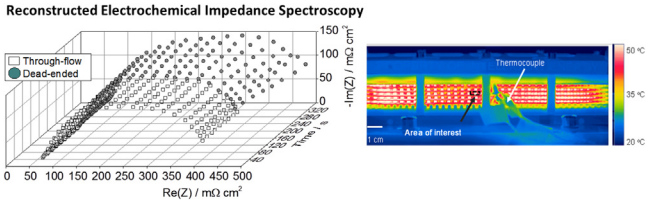
HIGHLIGHTS

- Dynamics of anode dead-end/purge operation investigated.
- Reconstructive impedance allows complete spectra with high temporal resolution.
- Water build-up and N_2 cross-over cause performance loss in dead-end mode.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form
21 November 2013
Accepted 27 November 2013
Available online 16 December 2013

Keywords:
Polymer electrolyte fuel cell (PEFC)
Dead-ended anode
Thermal imaging
Multichannel electrochemical impedance spectroscopy
Reconstructed electrochemical impedance spectroscopy
Gas cross-over

ABSTRACT

Dead-ended anode operation, with intermittent purge, is increasingly being used in polymer electrolyte fuel cells as it simplifies the mass flow control of feed and improves fuel efficiency. However, performance is affected through a reduction in voltage during dead-ended operation, particularly at high current density. This study uses electrochemical impedance spectroscopy (EIS), off-gas analysis and high resolution thermal imaging to examine the source of performance decay during dead-ended operation. A novel, 'reconstructed impedance' technique is applied to acquire complete EIS spectra with a temporal resolution that allows the dynamics of cell processes to be studied.

The results provide evidence that upon entering dead-ended operation, there is an initial increase in performance associated with an increase in anode compartment pressure and improved hydration of the membrane electrolyte. Subsequent reduction in performance is associated with an increase in mass transport losses due to a combination of water management issues and build-up of N_2 in the anode. The purge process rapidly recovers performance. Understanding of the processes involved in the dead-end/purge cycle provides a rationale for determining the optimum cycle frequency and duration as a function of current density.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) operating on hydrogen offer the possibility of zero-emission electricity generation. The technology has shown significant advances in terms of performance and durability, and wide-scale commercialisation in a range of applications is imminent.

Within the broad category of PEFCs a range of design variants and operational modes exist. Dead-ended anode operation is a common mode as it can simplify the system, potentially avoiding flow meters and humidifiers. The configuration typically employs a single pressure regulator before the hydrogen inlet to the stack and a purge valve after the anode outlet [1]. However, dead-ended

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URL: http://www.ucl.ac.uk/electrochemical-innovation-lab

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http://dx.doi.org/10.1016/j.jpowsour.2013.11.125

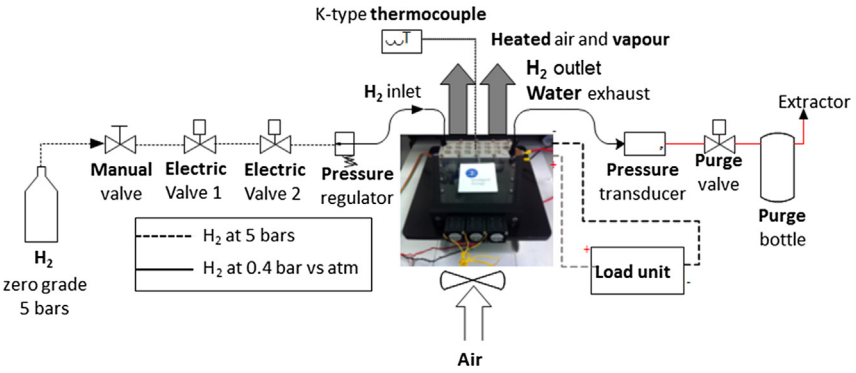

Fig. 1. Illustration of the system test rig.

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(s).

The gradual voltage loss has been measured and modelled [2–6], highlighting the influence of several factors. Nitrogen cross-over from the cathode to the anode, across the Nafion membrane, has been reported to have a significant influence [4,7,8]. This has been confirmed by controlling the nitrogen-to-hydrogen ratio at the anode inlet [9]. The extent of N_2 cross-over 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 [7,10]. Similarly, water back-diffusion (cathode to anode) has been studied using neutron imaging before and after anodic purge [11] and found to increase with increasing current density [12]. The effect of dead-ended operation on degradation processes has been investigated [9,13] along with the effect of carbon corrosion in this mode of operation [14]. However, without a clear understanding of what is happening during dead-end/purge processes it is difficult to reconcile the cause of degradation, and take measures to avoid it.

Monitoring temperature transients and distribution in fuel cells is a useful way to study their operation [15], and offers potential insight into the dead-end/purge process. Thermocouples can provide a crude measure of temperature inside fuel cells [16–19] but have accuracy limited to ±1 °C and cannot easily provide high spatial resolution. Moreover, thermocouples need to be inserted inside the fuel cell, which often requires modifications of design. Alternatively, thermal imaging can provide very high spatial and temperature resolution [15,20–25]. Here, a thermal imaging camera is used to perform localised measurements on an air cooled stack to characterise heat generation, and dissipation, in the stack.

Electrochemical impedance spectroscopy (EIS) is an established and powerful tool for fuel cell characterisation [26–28], providing insightful information on the various resistive losses occurring in operational fuel cells. EIS has been used to characterise PEFC response to CO poisoning [29], decouple anode and cathode operation [30], and the effect of specific components (e.g. platinum loading, membrane thickness, GDL structure) [26]. EIS has also found applications in distributed localized measurements [31,32], fault detection and flooding/drying events [33,34].

However, EIS has not been used for dead-end/purge analysis due to the challenge of capturing the process on the relatively short duration of the purge event. The present work uses single-frequency high-frequency impedance measurements, along with a novel 'reconstructed impedance' method that combines the result of consecutive repeatable cycles to build up full EIS during through-flow/dead-ended operation.

2. Experimental

2.1. Test station operation

Fuel cell stack operation was carried out using a 5-cell, 60 cm^2 active area electrode, air-cooled open-cathode stack (Intelligent Energy Ltd., UK). The membrane electrode assembly is composed of commercially available gas diffusion layers and commercially available state-of-the art membrane with Pt loading of 0.1 and 0.4 mg cm^{-2} on the anode and cathode, respectively.

This test system (Fig. 1) supplies dry, non-heated, hydrogen (with a purity of 99.995%) into the anodes and air is blown by three fans to the active cathodes and cooling channels (Fig. 2). The fans, which provide cooling and air supply to the cathode, are controlled by a programmable power supply (3649A Agilent). The fans maintain the stack's temperature between 20 and 50 °C with PID controllers. The fuel cell is electrically loaded using a commercial programmable load (Agilent 6060B). An in-house computer controlled system coordinates the air, hydrogen, cooling and electrical valves (LabVIEW, National Instruments). Through-flow and dead-ended operations were achieved by having the purge valve opened and closed, respectively. Ambient temperature, pressure

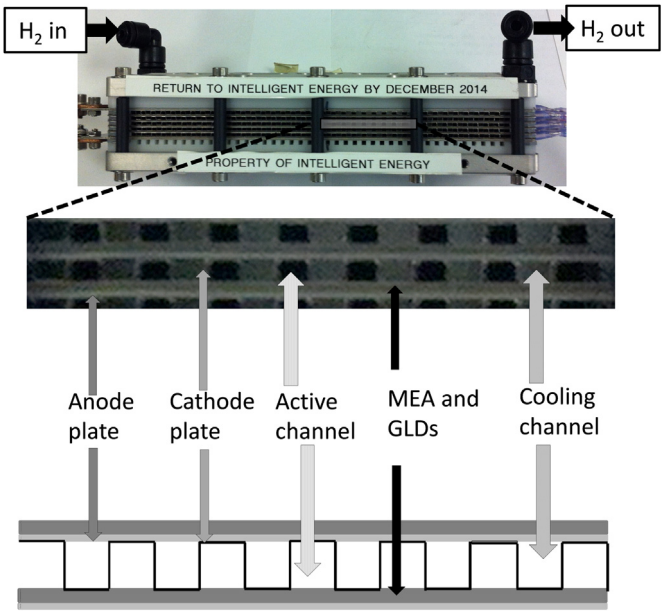

Fig. 2. Picture and simplified scheme of the fuel cell stack showing 'active' and 'cooling' channels. MEA: membrane electrode assembly. GDL: gas diffusion layer.