Journal of Power Sources 302 (2016) 210–214

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Electro-thermal impedance spectroscopy applied to an open-cathode polymer electrolyte fuel cell

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HIGHLIGHTS

- Electro-thermal impedance spectroscopy applied to a PEFC.
- ETIS corrects for emissivity variation and reflection.
- Electro-thermo-ampligrams identify areas of heat generation.
- Current-related features decoupled from temperature distribution.

ARTICLE INFO

Article history:
Received 5 July 2015
Received in revised form
13 October 2015
Accepted 14 October 2015
Available online 11 November 2015

Keywords:
Electro-thermal impedance spectroscopy
Lock-in thermography
Transfer function analysis
Polymer electrolyte fuel cell
Thermal imaging
Electro-thermography

ABSTRACT

The development of *in-situ* diagnostic techniques is critical to ensure safe and effective operation of polymer electrolyte fuel cell systems. Infrared thermal imaging is an established technique which has been extensively applied to fuel cells; however, the technique is limited to measuring surface temperatures and is prone to errors arising from emissivity variations and reflections. Here we demonstrate that electro-thermal impedance spectroscopy can be applied to enhance infrared thermal imaging and mitigate its limitations. An open-cathode polymer electrolyte fuel cell is used as a case study. The technique operates by imposing a periodic electrical stimulus to the fuel cell and measuring the consequent surface temperature response (phase and amplitude). In this way, the location of heat generation from within the component can be determined and the thermal conduction properties of the materials and structure between the point of heat generation and the point of measurement can be determined. By selectively 'locking-in' to a suitable modulation frequency, spatially resolved images of the relative amplitude between the current stimulus and temperature can be generated that provide complementary information to conventional temporal domain thermograms.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have shown great promise as power sources in a range of applications due to their high efficiency and low temperature operation [1,2]. However, the widespread adoption of PEFCs has been hampered by, amongst other things, a lack of operationally relevant thermal characterisation and *in-situ* diagnostic techniques. Electrochemical Impedance Spectroscopy (EIS) is a powerful technique used to deconvolute the various loss mechanisms in electrochemical systems and devices [3–5]. A small voltage (or current) perturbation is applied over a range of frequencies, while measuring the resultant current (or voltage) response. Transfer function analysis allows processes occurring with different time constants to be identified, such as kinetic, Ohmic and mass transfer impedances in fuel cells [6], which provides valuable information regarding fuel cell performance. This principle can be modified in order to derive new diagnostic techniques – for instance electro-thermal impedance spectroscopy (ETIS).

ETIS is a technique that applies a similar transfer function analysis to EIS; in this instance, a small current (or voltage) perturbation is related to modulation of heat generation, and

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http://dx.doi.org/10.1016/j.jpowsour.2015.10.047
0378-7753/

consequently the measured temperature. The relative amplitude and phase shift between the periodic current stimulus and the temperature response are frequency dependent and can yield information on the electro-thermal properties of electrochemical devices [7–9]. For example, Schmidt et al. [7] applied the technique to a Li-ion pouch cell, measuring the surface temperature at a single point with a thermocouple. The relative amplitude of the thermal response to the current perturbation is analogous to the 'thermal impedance' of the system; a higher thermal impedance through a material results in a lower temperature at the surface of the material. The phase shift between the perturbation and response is analogous to 'thermal capacitance'; the finite thermal diffusivity of a material means that there is a time lag between perturbation and response.

Lock-in thermography is an established technique that typically uses a thermal stimulus (e.g. a heat gun or IR lamp) imposed on a sample, with the resultant temperature modulation measured to give spatially resolved information about heat transfer in a system (identification of cracks in components, for example) [10,11]. Reflected artefacts and variations in emissivity can be rejected, thereby improving image fidelity. However, other forms of modulation stimulus can be used that result in heat generation (e.g. mechanical stress, ultra-sound, electrical current) [11]. Robinson et al. [12] applied lock-in thermography to a Li-ion pouch cell with a periodic current stimulus, highlighting the ability of the technique to identify sub-surface defects; in this instance, gas pockets formed during cell aging. The technique has also been applied to silicon materials for solar applications to identify regions containing recombination-active grain boundaries [13]; in photovoltaic modules to determine shunt values [14,15], and in semiconductors to identify cracks [16].

The power and efficacy of lock-in thermography is governed by the ability to interpret the images. This necessitates appreciation of the factors that lead to phase and amplitude shifts, *a priori* knowledge of the physical structure and materials of the device, and intelligent selection of the modulation frequency. Where the internal structure of devices can be determined using techniques such as X-ray computed tomography, the application of ETIS can provide insight into selection of modulation frequency and interpretation of images [17].

Here, for the first time, ETIS is applied to a PEFC to determine the frequency, polarisation, and spatially-dependent behaviour of the system and to inform interpretation of lock-in images (electro-thermo-ampligrams). The open-cathode configuration allows for direct visualisation of the gas diffusion layer (GDL) and comparison of channel and land features. A printed circuit board (PCB) current collector is used to achieve this fuel cell configuration.

2. Experimental

2.1. Open-cathode fuel cell design

The PEFC consisted of two printed circuit board (PCB) current collectors (anode and cathode), a membrane electrode assembly (MEA), gaskets and two end-plates. PCBs have been widely used as current collectors for fuel cells [18–20]; here the PCB geometry was 1.6 mm thick and contained a 38 μm layer of copper, which was coated with a proprietary carbon-based ink for corrosion protection. The gaskets used for gas manifolds were made of silicone and were 0.4 mm thick, and those used as seals between the end plate and current collector were 0.15 mm thick. A double-serpentine flow-field geometry was used for the anode and a parallel vertical flow-field was used for the cathode. A schematic of the design is shown in Fig. 1. The 1 mm slits in the cathode flow-field where the GDL is exposed to the atmosphere are referred to as 'channels' and the 1 mm wide sections of PCB material between the channels are referred to as 'lands'.

The cathode end-plates were made from aluminium and contained a 13 cm^2 square open window for direct visualization of the flow-field. The size of this window was larger than the active area of the cell and had negligible effect on the electrochemical performance of the cell. A torque of 3.6 Nm was applied to each of the four tie bolts to compress the cell and achieve a similar performance as achieved by Obeisun et al. in previous studies [18,19].

2.2. MEA fabrication

The electrolyte, Nafion 117 (Fuel Cell Store, USA), was pretreated at 80 °C in 3% H_2O_2 (Sigma Aldrich, UK) and then 1 M H_2SO_4 (Sigma Aldrich, UK). The MEAs were produced in-house using the electrolyte and ELE0237 Johnson Matthey 0.4 mg cm^{-2} platinum electrodes (Johnson Matthey Fuel Cells, UK) with an active area of 9.6 cm^2. The MEAs were pressed (Carver 4122CE, USA) at 170 °C for 4 min with an applied pressure of 3100 kPa.

2.3. Thermal imaging

Thermal imaging was performed using a 640 × 512 focal plane array InSb camera (SC5000MB FLIR, UK). The camera was calibrated for the temperature range in question (15–60 °C) with the images being recorded using commercially available software (ResearchIR, FLIR ATC, Croissy-Beaubourg, France) at 100 frames per second. ETIS was performed by fixing the location of the camera in relation to the cell and selecting identical pixels through the range of frequencies examined. The emissivity of the cathode GDL was calculated to be in excess of 0.95 over the temperature range observed during the experiments.

Thermal images were post-processed using commercially available software to obtain temporal temperature data and lock-in images (Altair LI, FLIR ATC, Croissy-Beaubourg, France). In this study, because the stimulus is electrical current and the area of interest is the amplitude ratio, images are referred to as 'electro-thermo-ampligrams'.

2.4. Fuel cell testing

A fuel cell test station (840 Advanced Fuel Cell Test System, Scribner Associates, USA) was used to supply dry hydrogen gas to the fuel cell anode. Hydrogen (99.995% purity, BOC plc, UK) was supplied at ambient temperature at a rate of 100 mL min^{-1}. The cathode was open to the atmosphere.

An IviumStat potentiostat (Alvatek, UK) was used to apply single frequency current perturbations with 3 mA cm^{-2} amplitudes between 100 μHz and 1 Hz to the fuel cell and measure the voltage response. The current was measured with a current probe (Tektronix A622, RS Components Ltd., UK) and recorded in a data acquisition unit (USB 6363 Multifunction DAQ, National Instruments, USA) which amplified the signal to an equivalent stimulus signal within the specifications of the thermal imaging camera (0–10 V).

3. Results and discussion

In order to determine the suitable amplitude of the current perturbation and determine the linearity or response, the temperature responses to 1, 2, 3, and 5 mA cm^{-2} peak amplitude current perturbations were investigated. Supplementary figure (Figure S1) shows the thermal responses in the time domain under a 0.1 Hz current perturbation with a 30 mA cm^{-2} direct current (dc) offset. It can be seen that a 3 mA cm^{-2} current perturbation was