Short communication

In-situ electrochemically active surface area evaluation of an open-cathode polymer electrolyte membrane fuel cell stack

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HIGHLIGHTS

- In-situ method to evaluate the ECSA of electrodes in an open-cathode PEMFC stack.
- Open-cathode evaluation made possible in nitrogen-purged gas-tight enclosure.
- Unlike cyclic voltammetry, all cells in a fuel cell stack measured simultaneously.
- High precision achieved using high data acquisition rates and low pass filtering.
- Electrode capacitance and hydrogen crossover rate obtained in the experiment.

GRAPHICAL ABSTRACT
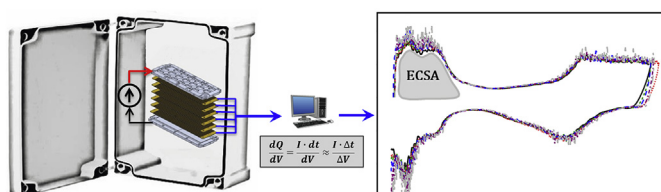
ABSTRACT

The ability to evaluate the electrochemically active surface area (ECSA) of fuel cell electrodes is crucial toward characterising designs and component suites in-situ, particularly when evaluating component durability in endurance testing, since it is a measure of the electrode area available to take part in the fuel cell reactions. Conventional methods to obtain the ECSA using cyclic voltammetry, however, rely on potentiostats that cannot be easily scaled to simultaneously evaluate all cells in a fuel cell stack of practical size, which is desirable in fuel cell development. In-situ diagnostics of an open-cathode fuel cell stack are furthermore challenging because the cells do not each possess an enclosed cathode compartment; instead, the cathodes are rather open to the environment. Here we report on a diagnostic setup that allows the electrochemically active surface area of each cell anode or cathode in an open-cathode fuel cell stack to be evaluated in-situ and simultaneously, with high resolution and reproducibility, using an easily scalable chronopotentiometry methodology and a gas-tight stack enclosure.

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1. Introduction

The evaluation of the electrochemically active surface area (ECSA) of fuel cell electrodes is a key diagnostic and development tool, useful for characterising component suites or batches, optimising designs, and periodically evaluating electrode health throughout durability testing. For polymer electrolyte membrane fuel cells (PEMFC) ECSA measurements are typically achieved using cyclic voltammetry (CV) in a single cell setup using a two-electrode configuration, whereby the electrode of interest is designated the working electrode (WE) whilst the opposite electrode acts as both counter (CE) and reference (RE) electrode(s). In such an

experiment, humidified nitrogen and hydrogen are fed to the WE and CE/RE compartments, respectively. The WE potential is then ramped linearly in the anodic sweep to oxidise adsorbed hydrogen, before reversing in the cathodic direction to electrochemically reduce protons back to adsorbed hydrogen on Pt. The ECSA can then be obtained through the integration of the H_2 adsorption/desorption [1,2] (or similarly using 'CO-stripping' [2]) charge that occurs on Pt-based catalysts, and subtracting double-layer capacitance (and hydrogen crossover contributions in PEMFCs) for precision.

Although CV offers valuable information, there are a number of limitations to the approach, particularly when expanding the methodology to the evaluation of multiple cells in a PEMFC stack. CV cannot be performed on multiple cells by controlling stack potential because even the slightest difference between the current/voltage relationship of individual cells will result in a non-linear and irregular distribution of cell voltage scan rates, as demonstrated in Ref. [3]. Measuring each cell of a stack individually using CV is meanwhile tedious and laborious, while the sophisticated multi-channel potentiostat hardware that is required for automated or simultaneous measurements is prohibitively expensive. CV is also not faultless; relying on precise linear voltage ramps rather than the voltage steps that often plague modern digital potentiostats, along with *iR*-compensation of the cell resistance to ensure a linear voltage sweep is obtained so that ECSAs are measured and integrated accurately. An alternative, chronopotentiometry approach to evaluating the ECSA of Pt-based catalysts that overcomes many of the limitations of CV, however, has been previously described to evaluate catalyst samples in aqueous electrolyte [4], and more recently demonstrated on closed-cathode PEMFC stacks [3,5,6]. Lee et al. [5] evaluated the ECSA of the cathodes using the anodic sweep in a 5-cell PEMFC stack by measuring each cell sequentially. Brightman et al. [6] went further to measure the cathodes of 18-cells simultaneously using the cathodic, whilst also investigating the influence of hydrogen concentration on the anode CE/RE on measurement; however, a limited 1 Hz data acquisition time-resolution of measurement hardware and decision not to subtract the hydrogen crossover or double layer capacitance was found to largely limit precision and accuracy. Chatillon et al. [3] meanwhile contrasted the chronopotentiometry approach with the more conventional linear sweep- and cyclic-voltammetry methods a 3-cell stack, finding that overall uncertainty in the measured ECSA to be within 5%, although it was suggested the number of cells within the stack may play a role in the success of the method. Previous studies have, however, neither evaluated the ECSA of the anode electrode, nor conclusively demonstrated the precision of the method to evaluate multiple cells simultaneously in the pseudo-CVs of both anodic and cathodic currents due to hardware limitations [5,6], cell balance issues [6] and/or small sample size [3].

Despite the apparent success and number of advantages the chronopotentiometry approach, it is not yet widely adopted, and expanding such in-situ diagnostic techniques to open-cathode air-cooled PEMFC technologies [7], today's most cost-effective PEMFC stack and system architecture in the sub-10 kW power range, is not necessarily straightforward and is until now unreported. Open-cathode air-cooled PEMFCs are a fuel cell architecture where (i) the cathode is fully exposed to ambient air (i.e. each cell does not possess an enclosed cathode compartment with common fuel/oxidant supply manifold), (ii) no external humidification of fuel or oxidant is required, (iii) fans are used to supply both oxidant and coolant air-flow simultaneously, and (iv) the component development begins at the stack rather than single-cell level. In contrast, for conventional air, liquid or evaporatively cooled closed-cathode PEM fuel cell architectures, the fuel/oxidant humidity, stoichiometry and cooling can be controlled separately. In-situ diagnostics of

closed-cathode architectures are therefore easier because the oxidant gas supply can be easily exchanged with an inert gas.

Here we describe the practical use of the chronopotentiometry methodology to precisely, accurately and simultaneously evaluate the ECSA, capacitance and hydrogen crossover current for either the anode or cathode of all 6-cells in a state-of-the-art open-cathode air-cooled PEMFC stack — made possible through the use of a gas-tight stack enclosure.

2. Experimental

Experiments were carried out using Intelligent Energy's in-house test stand and an air-cooled open-cathode 6-cell stack, described previously [7], incorporating a state-of-the-art gas diffusion layer and catalyst coated membrane (Gore Fuel Cell Technologies) component suite with Pt loadings of 0.1 and 0.4 mg cm^{-2} on anode and cathode, respectively. An IP65 rated polycarbonate box (Azcon, 7200-2082C Enclosure) was modified to accommodate the gas and electrical fittings required to house the stack in an inert nitrogen atmosphere. Grade N5.5 hydrogen was fed as reactant to the CE/RE. An in-house humidifier was used to provide continuous flow of humidified gases (100% RH), with all tests carried out at ambient temperature (~25 °C) and atmospheric pressure. An Autolab PGSTAT302 N was used in galvanostatic mode to control current through the fuel cell stack in a two-electrode setup, while individual cell voltages were measured differentially and logged at a 1 kHz time-resolution using a National Instruments DAQ card (isolated USB-6215) and custom LabVIEW software.

The methodology was then carried out as follows: the WEs of the fuel cell stack were supplied with humidified nitrogen at a flow rate of 0.5 L min^{-1}, while the CE/REs were supplied with humidified hydrogen at either: (i) 100 mbar for the fuel cell cathode ECSA measurement, or (ii) a 1% hydrogen/nitrogen mixture at a rate of 0.1 L min^{-1} (open-cathode) for the fuel cell anode ECSA measurement. The cells were allowed to equilibrate until oxygen was completely purged from the enclosure, and hydrogen had adsorbed on the catalyst surface of the WE (via diffusion through the PEMFC membrane), resulting in a steady-state potential of ~0.05 V$_{Cell}$. The chronopotentiometry measurement commenced by applying a fixed positive current until a maximum potential limit of 1.20 V$_{Cell}$ was reached by any one of the test cells. The current was then inverted until the voltage fell to 0.05 V$_{Cell}$, where the applied current was then removed. Note that the upper limit of 1.2 V$_{Cell}$ was set to avoid oxidation of the carbon catalyst support [8], while the lower limit of 0.05 V$_{Cell}$ was set to avoid hydrogen evolution at the WEs. Current densities in the ranges of ~10–30 mA cm^{-2} and ~1–10 mA cm^{-2} were used for cathode and anode measurements, respectively. Three measurement repeats were made at each current, and all data collected was used in the data analysis.

3. Results and discussion

3.1. Pseudo cyclic voltammograms

In this study we have measured the potential transients of each cell in a stack by applying a set of currents, first positive to induce oxidation of the Pt surface and then reversed at ~1.15 V$_{Cell}$ to induce the reduction of the Pt surface. Typical voltage vs. time curves for a range of currents between 12 and 33 mA cm^{-2} are given in Fig. 1(a). Using the method described in Ref. [4] each potential transient may be converted into pseudo-CV form using the equation: $dQ/dV = I \bullet dt/dV \approx I \bullet \Delta t/\Delta V_i$ and plotting the dQ/dV vs. measured cell voltage, as shown in the corresponding pseudo-CVs in Fig. 1(b), where Q is the charge density, I is the experiment current, t is the experiment time, and V is the measured cell voltage.