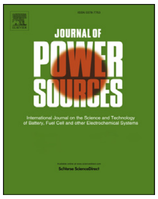
Journal of Power Sources 242 (2013) 244–254

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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



In situ measurement of active catalyst surface area in fuel cell stacks

E. Brightman [a,*], G. Hinds [a], R. O'Malley [b]

[a] National Physical Laboratory, Teddington, Middlesex TW11 0LW, United Kingdom
[b] Johnson Matthey Fuel Cells, Lydiard Fields, Great Western Way, Swindon, Wiltshire SN5 8AT, United Kingdom

HIGHLIGHTS

- Novel in situ technique for measuring active surface area in PEMFC stacks.
- Simultaneous measurement of every cell in an 18-cell stack demonstrated.
- Invaluable tool for state of health monitoring during fuel cell durability tests.

ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form
16 April 2013
Accepted 9 May 2013
Available online 30 May 2013

Keywords:
In situ
Fuel cells
Electrochemical surface area
Galvanostatic measurement
PEMFC stack

ABSTRACT

Measurement of electrochemical surface area (ECSA) of fuel cell electrodes is a key diagnostic of performance and gives a useful parameter for monitoring degradation and state of health in polymer electrolyte membrane fuel cells (PEMFCs). However, conventional methods for determining ECSA require potentiostatic control of the cell, which is impractical in a fuel cell stack. Here we demonstrate for the first time the practical application of a galvanostatic technique that enables in situ monitoring of ECSA in each cell throughout the lifetime of a stack. The concept is demonstrated at single cell level using both H adsorption and CO stripping, and the H adsorption (cathodic current) method is extended to stack testing. The undesirable effects of H_2 crossover on the measurement may be minimised by appropriate selection of current density and by working with dilute H_2 on the anode electrode. Good agreement is achieved with ECSA values determined using conventional single cell voltammetry across a range of MEA designs. The technique is straightforward to implement and provides an invaluable tool for state of health monitoring during PEMFC stack lifetime studies.

1. Introduction

One of the main challenges for the successful commercialisation of polymer electrolyte membrane fuel cells (PEMFCs) is the optimisation of catalyst utilisation, in order to minimise the amount of platinum required. The catalyst layer is typically formed of small particles of polycrystalline platinum or platinum-alloy dispersed on a high surface area support such as carbon black. This helps to maximise the number of catalytically active sites per gram of platinum used and means that the catalytic surface area of a fuel cell electrode is very much higher than the geometrical electrode area. In a PEMFC, not all the platinum is electrochemically active due to discontinuities in the electronic, ionic and gas phases, and the degradation of the electrode over time due to agglomeration and loss of platinum particles is associated with a concomitant decrease in electrochemical surface area (ECSA) [1]. The ECSA of an electrode is therefore an important performance metric that provides an estimate of catalyst utilisation and degradation.

In order to make valid measurements of critical parameters that are applicable to commercial cell and stack hardware, in situ techniques must be developed. Until recently, the ECSA of PEMFC electrodes has only been studied ex situ in aqueous electrolytes, or in single cell configurations. The standard technique for determining ECSA in a single cell is by measurement of the charge associated with the oxidation or reduction of a monolayer of adsorbed species, typically either hydrogen or carbon monoxide (CO) [2,3]. In both these cases, the measurement is made using cyclic voltammetry (CV) with the electrode of interest acting as the working electrode, supplied with an inert gas such as N_2, and the counter electrode supplied with H_2 functioning as a pseudo-reference electrode.

In the method using hydrogen desorption/adsorption, protons present in the electrolyte are reduced to form a monolayer of electro-adsorbed hydrogen on the platinum surface (Eq. (1)). The Pt-H species formed, so-called underpotential deposited hydrogen (H_{upd}), is distinct from the intermediate involved in the hydrogen

---

* Corresponding author. Tel.: +44 (0)20 8943 8564; fax: +44 (0)20 8943 6458.
E-mail address: edward.brightman@npl.co.uk (E. Brightman).

0378-7753/$ – see front matter Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.05.046

evolution reaction, which is driven by application of an overpotential. A detailed explanation of this mechanism is given by Conway and Jerkiewicz [4].

$$Pt_{(surface)} + H_3O^+ + e^- \rightleftharpoons Pt - H_{upd} + H_2O \quad (1)$$

The reaction in Eq. (1) involves a range of adsorption energies due to the polycrystalline nature of the platinum catalyst and so the potential at which this occurs ranges from 0.05 to 0.40 V vs. the standard hydrogen electrode (SHE) [2]. The measurement of ECSA by this method is based on the assumption that each proton is able to occupy one site on the available platinum surface, and that all sites that are active and accessible are occupied during the measurement.

In the CO oxidative desorption method, the platinum catalyst under investigation is exposed to CO, which chemisorbs strongly in a monolayer on the platinum surface. The electrode is then switched to an inert gas supply and the potential swept up to oxidising potentials, showing a sharp peak in current corresponding to oxidation of CO at around 0.7 V vs. SHE.

In both methods the surface area is estimated using a conversion factor determined from smooth crystalline platinum surfaces, which is known to be about 210 $\mu C\ cm^{-2}$ for H adsorption [5]. In the case of CO stripping, the charge associated with the oxidation peak of CO is generally assumed to be equivalent to two electrons per CO molecule, and so the conversion factor is assumed to be double that for H adsorption, i.e. ~420 $\mu C\ cm^{-2}$ [3]. The ECSA of the electrode in units of $m^2\ g^{-1}$ is then calculated using the following formula:

$$ECSA = \frac{Q}{\Gamma L} \quad (2)$$

where Q is the integrated charge density ($C\ cm^{-2}$), Γ is the specific charge required to oxidise/reduce a monolayer of the adsorbed species (i.e. 210 or 420 × $\mu C\ cm^{-2}$), and L is the platinum loading of the electrode ($g\ m^{-2}$). The technique can also be used to measure the surface area of platinum per unit geometrical area of the electrode, or roughness factor, without requiring knowledge of the platinum loading L. This value is usually given in units $cm^2_{(Pt)}\ cm^{-2}_{(electrode)}$.

Use of the conventional technique for ECSA measurement in single cells requires potentiodynamic control of the cell. This is impractical in a fuel cell stack, firstly because the potential of individual cells cannot be controlled independently due to the electrical connections between them and secondly because of the prohibitively long time required to measure the ECSA of each individual cell in sequence, particularly for large stacks. A recent publication by Wasterlain et al. has demonstrated a technique for measuring ECSA of cells in a stack by a combined CV technique, which relies on the assumption that the cells behave in a homogeneous way and that the sweep rate is uniform through the stack [6]. However, this assumption is rarely valid, particularly for stacks containing membrane electrode assemblies (MEAs) with different Pt loadings, in which case the potential difference applied to the stack will not be equally divided among the cells and there would be a risk of damaging cells by exposing them to highly oxidising potentials. Furthermore, the experiment requires specialist hardware which is not easily integrated into test systems.

Here we report on a novel galvanostatic technique for measurement of ECSA in fuel cell stacks, which has been developed independently by two separate groups: the present authors and also researchers in Korea. In their recent paper, Lee et al. [7] investigated the use of a current-controlled method to determine ECSA by applying a constant current to the cell and measuring the rate of change of the electrode potential. This gives equivalent information to a CV, as previously shown by Stevens and Dahn for ex situ Pt/C samples in aqueous electrolyte [8]. Lee et al. showed that by applying a fixed current to a PEMFC, a reliable estimate of ECSA could be obtained in situ, in a method that could be easily applied to stack assemblies.

The present work describes the results from the parallel development of this technique at the National Physical Laboratory (NPL), using both H adsorption/desorption and CO stripping, and moreover, extends the application of the method to a viable stack diagnostic procedure carried out on commercially relevant hardware at Johnson Matthey Fuel Cells (JMFC). We demonstrate an easily-implemented test procedure taking steps to minimise the impact of hydrogen crossover, and investigate the sensitivity of the technique to electrode loading, membrane permeability, and degradation.

2. Experimental

2.1. Single cell tests

2.1.1. Test setup

The single cell tests were performed on MEAs supplied by JMFC (Pt/C anode/cathode, perfluorosulfonic acid (PFSA) membrane), using a Greenlight FCATS-G50 fuel cell test stand. The test stand was used for gas flow control and humidification, while a separate Gill AC potentiostat (ACM Instruments Ltd.) was used to perform the voltammetric/potentiometric measurements. The reference and counter electrode connectors of the potentiostat were attached to the anode current collector of the fuel cell, while the working electrode was connected to the cathode current collector of the fuel cell. (N.B. For simplicity, the fuel cell cathode and fuel cell anode are nominally referred to as “cathode” and “anode” throughout, even though in certain measurements either anodic or cathodic processes may be occurring at these electrodes.) Three-way switching valves were fitted to facilitate switching of the cathode gas supply between air, N_2 and 1% CO in N_2.

All measurements were carried out at room temperature and atmospheric pressure. For the H desorption/adsorption experiments, the fuel cell cathode was supplied with humidified nitrogen (100% relative humidity (RH)) at a flow rate of 0.5 standard litres per minute (SLPM), while the anode was supplied with humidified hydrogen (100% RH) at a flow rate of 0.5 SLPM and functioned as a reversible hydrogen electrode. The cell was allowed to equilibrate before commencing the voltammetry tests, during which time hydrogen diffusing through the membrane adsorbed on the cathode catalyst surface, resulting in a steady state potential of ~0.1 V. The importance of this hydrogen crossover rate on the measurements will be discussed further in due course.

For the CO stripping tests, hydrogen was again supplied to the anode at a constant flow rate of 0.5 SLPM. The cathode was exposed to 1% CO in N_2 (BOC Special Gases Ltd, UK) flowing at 0.5 SLPM for approximately 15–20 min. Before the measurements were made, the gas supply was switched to pure N_2 at the same flow rate until the cell potential was steady, which took around 20 min.

In all experiments, the fuel cell anode was used as a pseudo-reference electrode (assumed to be 0.0 V vs SHE), and potentials are quoted with respect to this.

2.1.2. Cyclic voltammetry

The MEAs were characterised with a standard CV test in order to obtain a benchmark value of the ECSA for comparison with the galvanostatic method. For the measurement using H adsorption/desorption, the cell potential was swept at 10 $mV\ s^{-1}$ between 0.05 V and 0.80 V. For cyclic voltammetry experiments using CO stripping, the potential was swept between 0.05 V and 1.2 V at 5, 10