Journal of Power Sources 215 (2012) 266–273

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Ex situ testing method to characterize cathode catalysts degradation under simulated start-up/shut-down conditions – A contribution to polymer electrolyte membrane fuel cell benchmarking

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HIGHLIGHTS

- ► Start-up/shut-down test protocol development.
- ► Translation of the automotive stack voltage responses.
- ► Start-up/shut-down degradation mechanism.
- ► Evaluation methodologies for cathode catalysts.

ARTICLE INFO

Article history:
Received 21 December 2011
Received in revised form
18 April 2012
Accepted 6 May 2012
Available online 12 May 2012

Keywords:
Fuel cells
Electrochemical testing method
Start-up/shut-down
Degradation mechanism
Testing standard
Carbon corrosion

ABSTRACT

The paper introduces a novel *ex situ* test procedure that was developed to quantify the ageing of catalyst layers under critical automotive fuel cell conditions during start-up/shut-down phases. It is based on liquid electrolyte measurements, using a thin film catalyst electrode. The overall degradation under start-up/shut-down conditions is assessed by the decay in electrochemically active surface area. Furthermore, contributions from different processes leading to catalyst degradation such as Pt dissolution and Pt particle growth/agglomeration can be separated. Finally, using a differential electrochemical mass spectrometry (DEMS) set-up, also the extent and role of carbon corrosion under these conditions is accessible. The potential of this, compared to *in situ* fuel cell stack tests, rather fast and less costly *ex situ* test procedure is demonstrated in measurements using a commercial, graphitized carbon-supported Pt catalyst. The results of the degradation test and in particular the contributions from different degradation processes such as Pt dissolution, Pt particle growth/agglomeration and carbon corrosion during different stages of catalyst ageing are discussed.

1. Introduction

Proton Exchange Membrane Fuel Cells (PEM FCs), despite being a promising alternative to combustion engines, still face many challenges related to cost and durability. In order for automotive fuel cells to become commercially attractive, the current operational lifetime of 2500 h must be increased to 6500 h [1]. Over this lifetime, an automotive fuel cell will be exposed to over 13,600 start-up events and 500,000 short drive cycles [2], both of which are key drivers for degradation. Cathode catalyst degradation during transient operation causes a gradual decline in performance through the loss of the electrochemical surface area (ECSA) of platinum [3–9]. Considering that the cathode accounts for 55–77% of the total PEM FC stack cost [10–12], it is important to understand the mechanisms of the degradation processes that occur during automotive fuel cell operation. Of particular interest is the degradation during start-up and shut-down (SU/SD) events in a vehicle [13]. During shut-down, air will slowly fill the anode flow field of the fuel cell that initially was filled with hydrogen gas, causing a hydrogen/air front to move through the anode channels. Similarly, during start-up, hydrogen is fed to the anode, creating a H_2/air front. It has been found that the cathode voltage reaches potentials higher than 1.4 V, depending on the velocity of the H_2/air front

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doi:10.1016/j.jpowsour.2012.05.010

filling the anode side of the system [13]. This creates a high interfacial potential difference in the region of the H_2/air interface, causing carbon corrosion and oxygen evolution at the cathode electrode. Catalyst degradation mechanisms under SU/SD conditions are often studied using the PEM FC stack as test object, by *in situ* test methods [13]. These tests, however, can be costly, they do not allow to discriminate between different processes contributing to the overall degradation [14,15], which prevents a deeper understanding of the specific mechanisms for catalyst degradation. The *in situ* tests often require larger amounts of catalyst material and therefore are not always suitable when assessing new research catalysts. In addition, in PEM FC the degradation is difficult to quantify and particularly the amount of dissolved Pt since it is trapped in the membrane and in the ionomer of the catalysts layer. For rapid evaluation of catalyst materials, model studies in liquid electrolyte (*ex situ* characterization) and accelerated degradation tests would be highly desirable. To be useful, the testing method must allow i) for a fast screening of different catalysts and ii) to distinguish between different degradation mechanisms, while being faster, more efficient and, most important, relevant to automotive operational modes. The US Department of Energy (USDoE) has provided two *ex situ* protocols to study catalyst degradation. One involves a potentiostatic hold test at 1.2 V; which it is used to assess the stability of the high surface area carbon support material, and the second one is a dynamic test used to evaluate the durability of the electrocatalytically active nanoparticles under load cycling. The latter consists of 30,000 square wave cycles (SWC) between idle and peak power conditions of 0.6/0.7–0.9/1.0 V [16–18]. The US Fuel Cell Council (USFCC) has also proposed a degradation test, consisting of 1000 SWC between 0.6 and 1.2 V, that is generally accepted for evaluating the electrocatalyst durability, and a 1.5 V potential hold test to examine the carbon support stability, especially of current state-of-the-art graphitized carbon support materials [16]. Though the protocols from the USDoE and USFCC separately evaluate the catalyst stability upon cycling and/or holding at high potentials, they do not properly simulate SU/SD events in a vehicle. Therefore, these tests may not provide as much insight into the specific degradation mechanisms characteristic for these applications. Several groups have suggested different *ex situ* cycling tests at potentials between 0.6 and 1.5 V [19,20] or between 0.85 and 1.5 V [21]. However, degradation tests studying start-up/shut-down cathode events separately and combined in a liquid electrolyte environment have not been reported so far.

In this work, we propose a potential cycling protocol which was developed from automotive stack voltage responses and which reproduces the main features exhibited during SU/SD processes. Combined electrochemical and mass spectrometric measurements in a differential electrochemical mass spectrometry (DEMS) set-up were employed to follow the degradation of the catalyst during potential cycling with time. The SU/SD degradation process is analyzed to identify which parts of the SU/SD cycle contribute most to degradation. Finally, the physical changes of the catalyst caused by SU/SD cycling are characterized. The results provide a solid basis for an application relevant evaluation of the cathode catalyst durability and degradation under SU/SD operating conditions.

2. Experimental

2.1. Electrochemical and DEMS measurements

The electrochemical and mass spectrometric measurements were performed in a dual thin-layer flow-through DEMS cell, which was connected to a differentially pumped vacuum chamber system with a Pfeiffer Vacuum quadrupole mass spectrometer (QM 422) [22–25]. Potential control was achieved with a potentiostat from Solatron (Analytical Multistat 1480). A thin film of catalyst supported on a glassy carbon stub, was used as working electrode. Two Pt wires served as counter electrodes and a saturated calomel electrode was used as reference electrode. All potentials are referenced against that of a reversible hydrogen electrode RHE. The degradation measurements were conducted in 0.5 M H_2SO_4 electrolyte under controlled flow, with the electrolyte continuously purged with argon. All DEMS experiments were reproduced by rotating ring disk electrodes (RDE) as well, showing similar ECSA degradation behavior as in DEMS.

2.2. Thin film catalyst electrode preparation

Using a commercial graphitized carbon-supported Pt catalyst, a catalyst ink consisting of 2 mg catalyst per cm^3 aqueous solution was prepared. The suspension was ultrasonicated for 30 min at room temperature before a 25 μl aliquot was dispersed onto a mirror polished glassy carbon disk from Sigradur GmbH Germany of 9 mm diameter and then dried under nitrogen. An aqueous Nafion solution was then added following the method proposed by Schmidt et al. [26]. It was shown that the diffusion resistance of the Nafion film is negligible due to its low thickness [26]. The working electrode was transferred to a thin-layer flow-cell. Prior to the electrochemical measurements, the catalysts was electrochemically cleaned by sweeping the potential between 0.06 and 1.2 V, until a steady voltammogram was obtained.

2.3. ECSA loss determination

The platinum ECSA of each catalyst sample was determined using the mean integral charge of the hydrogen adsorption areas, obtained at 10 mV s^{-1} and room temperature, considering a charge of 210 μC cm_{Pt}^{-2} for a full monolayer (ML) of H_{upd} and assuming a H_{upd} coverage of 0.77 ML at the onset of hydrogen evolution [22,27]. Each of the accelerated events included 1000 potential cycles, stopping after 100, 200, 400, 600, 800, 1000 cycles in order to determine the ECSA and the cumulative carbon mass via the CO_2 signal (see below).

2.4. Carbon corrosion

The carbon mass loss was quantified by measuring the CO_2 evolution during the different potential cycle tests in a DEMS set-up. This allows simultaneous measurements of the Faradaic current at a thin film working electrode and online measurements of the carbon corrosion via the resulting CO_2 evolution. Gaseous products such as CO_2 diffuse from the working electrode through a porous membrane to a mass spectrometer; the membrane is provided by Scimat® and has 50% porosity, a thickness of 60 μm and 0.2 μm pore diameter. The mass signal of CO_2 ($m/z = 44$) recorded during potential cycling is then used to determine the carbon weight loss m_{carb} via the following relation:

$$m_{carb} = \left(A_W \cdot Q_{CO_2}\right) \Big/ \left(F \cdot K^*\right) \tag{1}$$

where A_W is the atomic weight of carbon ($A_W = 12.01$ g mol^{-1}); Q_{CO_2} is the charge of the mass spectrometric CO_2 signal ($mz^{-1} = 44$); F is the Faraday constant ($F = 96{,}485$ C mol^{-1}) and K^* the calibration constant of the CO_2 signal. The calibration constant K^*, which allows to calculate the number of CO_2 molecules from the charge in the mass spectrometric CO_2 signal and which is defined by [22]:

$$K^* = \frac{z \cdot Q'_{CO_2}}{Q_F} \tag{2}$$