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Comparing shut-down strategies for proton exchange membrane fuel cells

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HIGHLIGHTS

- Five different shut-down strategies for PEMFCs were evaluated in a single cell.
- H_2 purge of the cathode and O_2 consumption are the most effective strategies.
- The H_2 purge strategy had a total degradation rate of 23 μV cycle^{-1}.
- The present degradation rate is low, considering the use of unprotected start-ups.

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ABSTRACT

Application of system strategies for mitigating carbon corrosion of the catalyst support in proton exchange fuel cells (PEMFCs) is a requirement for PEMFC systems, especially in the case of systems for transport application undergoing thousands of start-ups and shut-downs (SU/SD) during its lifetime. This study compares several of the most common shut-down strategies for 1100 cycles SU/SD cycles at 70 °C and 80% RH using commercially available fuel cell components. Each cycle simulates a prolonged shut-down, i.e. finishing each cycle with air filled anode and cathode. Furthermore, all start-ups are unprotected, i.e. introducing the H_2 rich gas into an air filled anode. Finally, each cycle also includes normal fuel cell operation at 0.5 A cm^{-2} using synthetic reformate/air. H_2 purge of the cathode and O_2 consumption using a load were found to be the most effective strategies. The degradation rate using the H_2 purge strategy was 23 μV cycle^{-1} at 0.86 A cm^{-2} using H_2 and air at the anode and cathode, respectively. This degradation rate may be regarded as a generally low value, especially considering that this value also includes the degradation rate caused by unprotected start-ups.

1. Introduction

Considerable attention has been focused on the degradation of the catalyst support in proton exchange membrane fuel cell (PEMFC) electrodes since the work published by Reiser et al. [1]. Under fuel starvation conditions or during start-ups and shut-downs (SU/SD), H_2 and O_2 may coexist at the anode compartment, forcing the cathode to reach high potentials and resulting in severe corrosion of the carbon support [1]. This loss of carbon significantly increases catalyst degradation rates, characterized by a decrease in electrochemically active surface area (ECSA) [2]. Carbon corrosion may also result in considerable changes to the electrode morphology e.g. thinning of the electrode [3,4], formation of cavities [5], and decreased electrode porosity, usually referred to as electrode collapse [6]. The combined effect of these physical changes results in severe degradation of the fuel cell performance, especially at high current densities where mass transport may become limited by the altered electrode morphology [6,7].

The four main strategies to avoid this problem are: *i*) to find new carbon materials as catalyst support that are able to sustain corrosion [8,9], *ii*) not to use carbon as a support for the Pt catalyst [10–12], *iii*) to add catalysts with high activity towards the oxygen evolution reaction (OER) to the Pt-based cathode [13] and/or to add catalysts with low activity towards the oxygen reduction reaction (ORR) to the Pt-based anode [14] and *iv*) to apply system strategies to minimize or avoid carbon corrosion at the cathode. Although strategies *i*–*iii* are considered by fuel cell system developers to be promising alternatives to address issues related to SU/SD, many of

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these alternative materials are still under development and often not commercially available. Thus, today's fuel cell system developers that are in need of low cost alternative to avoid issues related to SU/SD, usually turn to strategy *iv*.

An effective system approach to minimize the detrimental effects caused by unprotected SU/SD is to control certain fuel cell operating parameters. Cho et al. [4,15] showed that low cathode humidity and low cell temperature during SU/SD may increase the lifetime of the fuel cell. On the other hand, simply controlling these operating conditions is thought not to be sufficient to achieve required automotive lifetime targets, i.e. 5000 h of operation, including 30.000 SU/SD with less than 30 mV decay at rated power [16].

There has been a great deal of research in the area of system strategies for the mitigation of carbon corrosion during SU/SD. Yu et al. [17] have recently reviewed this area of research and reported that the most common strategies involve: *i*) minimize the residence time of the H_2/O_2 front at the anode, *ii*) completely prevent the H_2/O_2 front at the anode and *iii*) control the cathode potential. Strategies involving gas purge, such as N_2-purge of the anode [18], air-purge of the anode [19,20], exhaust gas recycling purge of the anode [21] and H_2-purge of the cathode [22,23] have been reported to be very successful. In addition, auxiliary loads, also called dummy loads, have been implemented to consume residual O_2 from the cathode [24,25] or residual H_2 from the anode [26] and have also been reported to be very successful.

The authors of this paper are aware that established fuel cell system developers, e.g. UTC, General Motors Corporation (GM), Honda, Ford, Toyota, Nissan, and Daimler have all carried out a great deal of research in this area and most certain already have a strategy in place for their particular systems. However, there is a lack of consensus on what are the most appropriate ways to start-up and shut-down a PEMFC. Future fuel cell system developers will still have to deal with this issue, carrying out their own expensive and time consuming research. In an effort to partially alleviate that burden, this study compares a few of the most common shut-down strategies.

The primary aim of the study is to find suitable shut-down procedures for PEMFC-based auxiliary power units (APUs) running on hydrogen rich gas. This however does not exclude that the investigated shut-down strategies could be applicable on other PEMFC applications. The strategies are named: *i*) *No purge*, *ii*) *Air purge*, *iii*) *H_2 consumption*, *iv*) *O_2 consumption* and *v*) *H_2 purge*. With the exception of the *No purge* shut-down, these strategies are evaluated in a single cell set-up for 1100 SU/SD, using commercially available fuel cell components. Each cycle is intended to simulate a prolonged shut-down, i.e. finishing each cycle with air filled anode and cathode. Furthermore, all start-ups are unprotected, i.e. H_2 rich gas is introduced into an air filled anode. Finally, each cycle also includes normal fuel cell operation at 0.5 A cm^{-2}, which better simulates realistic fuel cell conditions preceding a shut-down, e.g. water at the cathode and oxide-free Pt surface. It is not the aim of this paper to give a detail description about the involved mechanisms of each particular strategy. However, the effectiveness of the individual strategies to protect the cathode from degradation is discussed.

2. Experimental

2.1. Fuel cell hardware and electrochemical characterization

A fresh commercially available 50 μm membrane electrode assemblies (MEAs) (25 μm membrane) with loadings of 0.45 mg cm^{-2} Pt-alloy on the anode and 0.4 mg cm^{-2} Pt on the cathode was used in each of the shut-down strategy. The same type of gas diffusion layer (GDL), with micro porous layer (MPL) (Sigracet®), was used at both anode and cathode. Fig. 1 illustrates the experimental set-up used to carry out the study. The in-house fuel cell has previously been described in detailed by Ihonen et al. [27,28]. The fuel cell had cylindrical current collectors made of graphite KC-673 (Svenska Tanso AB), having an active area and flow field of 7 cm^2. The design of the flow field consisted of a single spiral flow channel with width, height and land of 1 mm and the clamping pressure was set to 6 bar (60 N cm^{-2}). The measurements were carried out at zero backpressure, at a cell temperature of 70 °C and with gases humidified at 65 °C (Globe Tech inc.). Furthermore, to avoid condensation between the humidifiers and the cell, the temperature of the pipes was set to 77 °C. These conditions were used in all the shut-down strategies, as well as in the electrochemical evaluation.

The gas flow rates were set using mass flow controllers (Brooks Instruments B. V) controlled by LabVIEW software and two NI USB-6008 data acquisition devices (DAQs). The same LabVIEW software was used to control all solenoid valves, and the diaphragm pump used as recirculation pump at the anode. Fig. 1 also shows the solenoid valves between the humidifiers and the cell, which prevents the leakage of gases into the cell from the humidifiers, when required. Furthermore, the solenoid valves at the anode and cathode exhausts prevented the diffusion of air into the cell, when required. An Autolab potentiostat also controlled with the same LabVIEW software was used as load to perform all shut-down strategies. An IM6 unit together with an EL101 Booster (Zahner Elektrik) was used to perform all the electrochemical characterizations, including cyclic voltammetry, H_2 crossover measurements, polarization curves using H_2 at the anode and either O_2 or air at the cathode, and electrochemical impedance spectroscopy (EIS). Table 1 summarizes the operating conditions used for each characterization method.

2.2. Scanning electron microscopy (SEM)

SEM imaging was carried out using a Hitachi S-4800 FE SEM. The analysis of the MEAs cross-sections was obtained by the freeze and break technique described elsewhere [29].

2.3. Shut-down strategies

The shut-down strategies evaluated in this studied are: *i*) *No purge*, *ii*) *Air purge*, *iii*) *H_2 consumption*, *iv*) *O_2 consumption* and *v*) *H_2 purge*. Table 2 summarizes the type and duration of each implemented action during one full cycle. All five strategies began with the same start-up sequence, consisting in the simultaneous introduction of synthetic reformate gas (45% H_2, 23% CO_2 and 32% N_2) into an air filled anode and of air into the cathode (unprotected start-up). This was followed by a 10 s open circuit voltage (OCV) and a 40 s load at a constant current density of 0.5 A cm^{-2}. After the 40 s normal operation the fuel cell is shut-down using one of the above strategies. Finally, all strategies finished their respective cycles with an air purge of both the anode and the cathode, which simulates a prolonged shut-down.

The *No purge* shut-down consisted in not doing anything to either minimize the time or to avoid the H_2/O_2 front at the anode during shut-down. The cell was allowed to reach OCV after the 40 s load at 0.5 A cm^{-2}, the reformate gas and air were shut off and both the anode and cathode exhausts were left opened for at least 820 s. This strategy was only implemented for a total of 230 SU/SD cycles.

The *Air purge* shut-down, a strategy probably used by many fuel cell system developers, consisted in minimizing the time for the H_2/O_2 front at the anode during shut-down. The cell was allowed to reach OCV after the 40 s load at 0.5 A cm^{-2}. Then, the reformate gas was shut off and the solenoid valve between humidifier and anode