Recovery mechanisms in proton exchange membrane fuel cells after accelerated stress tests

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Xu Zhang [a], Liejin Guo [a, **], Hongtan Liu [b, *]

[a] International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[b] Clean Energy Research Institute, Department of Mechanical and Aerospace Engineering, University of Miami, Coral Gables, FL 33124, USA

HIGHLIGHTS

- Both kinetic and mass transport losses after AST can be partially recovered.
- Kinetic recovery is due to platinum oxide reduction and platinum re-attachment.
- Mass transport recovery is due to removal of oxide groups on carbon surface.
- AST without recovery significantly over-estimates true degradation in PEMFCs.

ARTICLE INFO

ABSTRACT

The mechanisms of performance recovery after accelerated stress test (AST) in proton exchange membrane fuel cells (PEMFCs) are systematically studied. Experiments are carried out by incorporating a well-designed performance recovery procedure right after the AST protocol. The experiment results show that the cell performance recovers significantly from the degraded state after the AST procedure. The results from cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements further show that the performance recovery can be divided into kinetic and mass transport recoveries. It is further determined that the kinetic recovery, i.e. the recovery of electrochemical active area (ECA), is due to two distinct mechanisms: the reduction of platinum oxide and the re-attachment of detached platinum nanoparticles onto the carbon surface. The mass transport resistance is probably due to reduction of hydrophilic oxide groups on the carbon surface and the microstructure change that alleviates flooding. Performance comparisons show that the recovery procedure is highly effective, indicating the results of AST significantly over-estimate the true degradation in a PEM fuel cell. Therefore, a recovery procedure is highly recommended when an AST protocol is used to evaluate cell degradations to avoid over-estimating true performance degradations in PEMFCs.

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1. Introduction

Durability remains to be one of the primary obstacles for the commercialization of proton exchange membrane fuel cells (PEMFCs). Although much progress has been made to improve the durability of components and fuel cell system, the degradation mechanisms and detrimental effects on cell lifetime have not been fully understood.

Among various degradation mechanisms, carbon corrosion is considered to be a one of the most important in PEMFCs [1–4]. In fact, although the thermodynamic equilibrium potential for carbon oxidation is only 0.207 V vs. RHE, the oxidation or corrosion of the carbon support is negligible in a typical PEMFC environment [5]. However, under certain conditions, such as start-up and shut-down process [6,7], or reactant starvation condition [8–10], the potential at the cathode can increase substantially, sometimes reaches to as high as 1.2 V–1.5 V [11]. The elevated potential accelerates the electrochemical carbon corrosion reaction at cathode side dramatically [12,13].

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \tag{1}$$

* Corresponding author.
** Corresponding author.
    E-mail addresses: zhangxuxjtu@gmail.com (X. Zhang), lj-guo@mail.xjtu.edu.cn (L. Guo), hliu@miami.edu (H. Liu).

Corrosion of carbon support weakens or even breaks the bonding between platinum nanoparticles and the carbon support [14,15], causing agglomeration of platinum nanoparticles with adjacent larger particles [16,17]. More serious situation may cause platinum nanoparticles to completely detach from the carbon support [18,19]. The detached platinum particles may reattach on carbon support or even be washed out of the cell system [20–22]. Both the increase of platinum particle size and the loss of catalyst mass result in reduction in the electrochemical active area (ECA). Carbon corrosion also results in significant reduction of the catalyst layer (CL) thickness [23–25], sometimes even cause the collapse of the pore structures [15,26]. The damages to electrode microstructure increase the electrode ohmic resistance and contact resistance between components [27]. Moreover, the mass transport is also reduced due to porosity drop [18,28,29]. Besides, evidences from x-ray photoelectron spectroscopy (XPS) measurements [27,30], gas chromatography [31] and infrared spectrometry [32] have proven that hydrophilic surface oxide groups can form due to carbon corrosion. A more hydrophilic carbon surface affects the water condensation/evaporation equilibrium and capilllary pressure in porous media. The blockage effect of liquid water to reactant transport or even the occurence of flooding can reduce the cell performance drastically [27,33].

Due to the long durations and high cost required for durability studies in PEMFCs, accelerated stress test (AST) has been widely accepted and adopted to evaluate fuel cell degradations [1,11]. U.S. Department of Energy [34] and other research groups [15,18,23,24,32,35–38] have adopted various forms of AST protocols for catalyst support degradation evaluations. Normally high potential hold (e.g., 1.2 V) is recommended. Yet most researchers prefer to adopt much harsher condition to save time. In the literature, the hold voltages ranged from open circuit voltage (OCV) to 1.5 V. Since the rate of carbon corrosion reaction increases exponentially with potential, every 0.1 V increase in potential can reduce the overall test duration dramatically. Spernjak et al. [11] reported that the performance decay rate was eight times faster at 1.3 V than that at 1.2 V under identical settings.

As the hold voltage increases, the real degradation during carbon corrosion becomes more complicated. Not only does high voltage cause carbon corrosion, but also results in other concomitant damages to the fuel cell. The degradation of cell performance often refers to irreversible performance decay. However, the reversible losses probably increase simultaneously and accumulate in a durability test. The recoverable loss should be eliminated from the overall performance degradation in order to correctly evaluate the true performance degradation. Unfortunately, previous AST protocols, including those from DOE and most of those in the literature, have no descriptions of the reversible losses or process to eliminate the reversible losses. Zhang et al. [39] employed a proprietary recovery procedure in their test protocol to study the membrane chemical degradation. The voltage loss was observed to be fully recoverable. Owenjan et al. [40] run a periodically voltage recovery step throughout their experiment protocols when studying the impact of Pt loading on cell performance. The recovery was realized by holding the cell voltage at 0.3 V for 2 h. Dhanushkodi et al. [41,42] also introduced a recovery procedure in their study of carbon corrosion and platinum dissolution in PEMFCs. During the recovery process, hydrogen was fed to anode and no oxidant gas (only nitrogen) was passed through the cathode for 4 h. The cell load was turned off. Both of the recovery processes were believed to be able to remove contaminants, reduce platinum oxide and drain the excess water out of cell. However, no details for the process were provided. Recently, Zhang et al. [43] reported restoration of recoverable activity loss of carbon-supported platinum catalyst by a refreshing operation conducted ex situ using a system with three electrodes. They attributed the restoration to the reduction of the platinum oxide and partially removal of the CO formed during carbon corrosion.

It is obvious from the above that most previous durability studies primarily concentrated on material/component degradations and performance decays, the mechanisms of degradations and the distinction between reversible and irreversible degradations are still not fully understood. Hence, in this study, a systematic AST and recovery procedure is conducted to study the mechanisms of performance degradation and the mechanisms of performance recovery of PEMFCs after AST. In the experiment, a well-designed recovery protocol is incorporated right after each AST interval. The recovery of the cell performance during this procedure is comprehensively characterized. The mechanisms of degradation as well as performance recovery are analysed based on electrochemical characterization results. Moreover, the cell performances with and without recovery procedure are compared to show the over-estimation of the performance losses by using the AST technique.

2. Experimental

2.1. The experiment setup

A single PEMFC with an active area of 16 cm^2 is used in this study. The membrane used is Nafion@ 212-based catalyst coated membrane (CCM, Shanghai Pearl Hydrogen Power Source, China). The catalyst loading is 0.4 mg cm^{-2} at both anode and cathode sides. Two identical pieces of carbon paper (Toray 060, Toray Industries. Inc., Japan) with micro porous layers (MPL) are used as gas diffusion layers (GDL). A pair of graphite flow filed plates (FFPs) with 10 single serpentine flow channels are employed. The flow arrangement for anode and cathode sides is co-flow. The widths of channels and ribs are 2 mm, and the depth of channels is 1 mm. The membrane electrode assembly (MEA), FFPs and two gold coated copper current collector plates at both sides are precisely aligned and compressed together by a cell hardware (Fuel Cell Technologies. Inc., USA) with a torque of 7 N m.

After assembled, the single cell is connected to a fuel cell test station (FCTS-16, Fuel Cell Technologies. Inc., USA). Operating parameters, such as cell temperature, reactant gas flow rates, gas humidification and back pressure, can be precisely controlled. A potentiosat/Galvanostat (HCP803, Bio-Logic. Inc., France) is employed to control and monitor the discharging current and cell voltage. The following characterization techniques are also implemented by this system.

2.2. Performance characterization

A well-designed conditioning process is used to fully activate the cell initially. Then a series of performance characterizations are performed at the beginning-of-life (BOL) and right after each AST interval to assess both the performance degradation and performance recovery. In the performance characterization process, 100% humidified hydrogen and 100% humidified air are passed through the anode and the cathode respectively. Polarization curves (IV) are measured by sweeping the voltage from OCV to 0.2 V with a rate of 1 mV s^{-1}. As the sweeping rate is sufficient slow, the cell can be considered to be in quasi-steady state. The current at 800 mV, 600 mV and 300 mV were recorded. Electrochemical impedance spectroscopy (EIS) is conducted at 150 mA cm^{-2}, and 300 mA cm^{-2}, representing a low and a high current, respectively. The AC-amplitudes applied are 5% of the cell current and the frequency ranges from 10 kHz to 100 mHz. In all above measurements, the hydrogen and air flow rates are kept constant at 168sccm and