Spatially Resolved Degradation During Startup and Shutdown PEM Fuel Cell Operation

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The durability of polymer electrolyte membrane (PEM) fuel cells is a key challenge to developing commercially viable systems for transportation and stationary power applications [1]. Corrosion of catalyst-support carbon, one of the major degradation mechanisms, is particularly damaging to cell performance as it leads to numerous changes in the catalyst layer: lower porosity (pore space collapse), lower active catalyst surface area and catalyst connectivity, and less hydrophobic surface [1, 2]. Carbon corrosion is accelerated during high-potential excursions which can take place during steady-state operation (local fuel starvation) and transient operation (startup and shutdown).

A segmented cell (Fig. 1) enabled measurements of the internal currents during startup (SU) and shutdown (SD) operation to evaluate the charge exchanged between the active (H_2/Air) and passive (Air/Air) portions of the cell [3]. Carbon corrosion was quantified by measuring the CO_2 emissions at the cathode exhaust. Separate testing protocols for fuel cell startup (SU) and shutdown (SD) were developed to distinguish between the effects of SU and SD on both local and global performance degradation. Humidity was 100 % at all times, while the flow rates were 10 slph for both SU (H_2) and SD (Air). Spatial degradation of the cell was characterized periodically during SU and SD series, by recording the local polarization curves (Fig. 2), local ElectroChemical Surface Area (ECSA) as well as electrochemical impedance spectra (EIS). We explore the influence of the anode Pt loading, cathode Pt loading, and cathode carbon support (varying levels of graphitization, i.e. surface area). This work focuses on ex situ analyses (SEM, TEM, and XRD) of the tested membrane-electrode assemblies (MEAs).

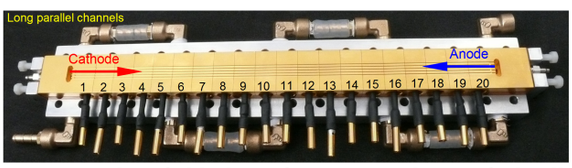
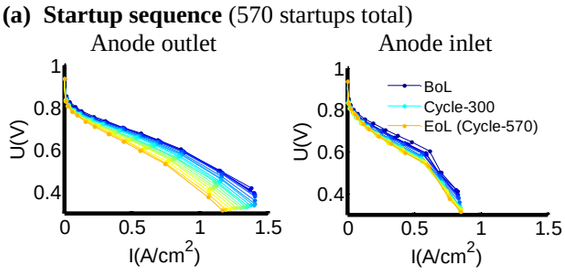


Figure 1. Flow-field plate of a segmented PEM fuel cell, divided into 20 segments along the channel length (active area 1 by 30 cm; 5 parallel channels).

Long repeated SU and SD protocols cause nonuniform ECSA loss and performance degradation along the cell area. The performance decrease is more severe in the regions staying the longest in the presence of oxygen in the anode compartment (i.e. regions of the cell that are in the passive, air/air mode, for prolonged time periods during each startup or shutdown). Regions with higher performance degradation exhibited substantial local ECSA loss, thinning of the cathode catalyst layer, and Pt particle growth. The largest local decay in the performance is exhibited in the anode outlet region after prolonged SU cycling (Fig. 2a). After prolonged SD cycling, local performance loss is largest at the anode inlet (Fig. 2b, Fig. 3). Spatial variation is substantially lower after SD than after SU protocol. Overall, startups are more damaging than the shutdowns in present experiments, regardless of the MEA type, i.e. regardless of the catalyst loading on anode and cathode, or carbon-support surface area at the cathode. Higher degradation caused by startups is corroborated (1) in situ from more CO_2 evolved as well as charge exchanged, higher performance decrease, and more severe ECSA losses, and (2) ex situ from larger Pt particles and thinner cathode catalyst layer (Fig. 3).

(a) Startup sequence (570 startups total)



(b) Shutdown sequence (690 shutdowns total)

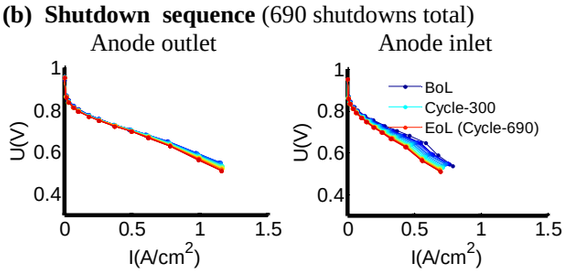


Figure 2. Time evolution of local polarizations curves for individual segments (anode outlet vs. inlet) during (a) startup and (b) shutdown aging protocols (MEA #6).

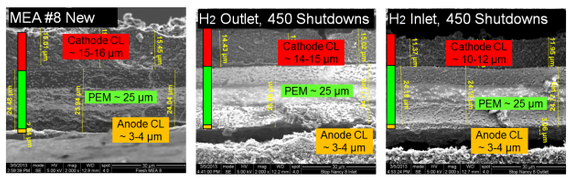


Figure 3. SEM images of non-uniform thinning of the cathode catalyst layer caused by shutdown aging protocol (MEA #8).

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