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Impact of flow rates and electrode specifications on degradations during repeated startups and shutdowns in polymer-electrolyte membrane fuel cells

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HIGHLIGHTS

- To distinguish between the effects of startup and shutdown on performance degradation.
- The internal currents during SU and SD operation are measured in a segmented cell.
- Cells with different membrane-electrode assemblies are subjected to SU or SD sequences.
- Influence of the cathode and anode Pt loading, and the type of carbon for cathode catalyst support.

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ABSTRACT

Separate testing protocols for fuel cell startup (SU) and shutdown (SD) are developed to distinguish between the effects of SU and SD on performance degradation. The internal currents during SU and SD operation are measured in a segmented cell to evaluate the charge exchanged between the active (H_2/Air) and passive (Air/Air) portions of the cell. Cells with different membrane-electrode assemblies (MEAs) are subjected to SU or SD sequences to evaluate the time evolution of spatially resolved decrease of performance and electrochemical active surface area (ECSA). We examine the influence of the cathode and anode Pt loading, and the type of carbon for cathode catalyst support.

Both the CO_2 emissions and the charges exchanged increase with the common residence time of air and hydrogen in the anode compartment. However, the evolved CO_2 accounts for less than 25% of the total exchanged charge. Startups are consistently more damaging than the shutdowns, evidenced by more evolved CO_2 and charge exchanged, severe ECSA decrease, and higher performance losses.

1. Introduction

Despite recent efforts in PEM fuel cell research and development, sufficient lifetimes for transportation and stationary applications have not yet been achieved within satisfactory cost and performance targets. Fuel cell degradation mechanisms can affect the membrane, the electrodes, the gas diffusion layers (GDLs), the bipolar plates and even the gaskets. Although all these mechanisms are not fully understood, some of the operating conditions that accelerate the degradation of Membrane-Electrode Assemblies (MEAs) are well known [1–5]. Among them, startups and shutdowns (SU/SD) can be extremely harmful to the stability of the PEMFC components, especially the cathode electrode. Compared to the normal (or, steady state) fuel cell operation, SU/SD transients lead to higher rates of electrochemical oxidation of the carbon supporting the cathode Pt catalyst, mainly because of the simultaneous presence of oxygen (air) and hydrogen in the anode compartment [6]. The presence of air in the anode compartment can be avoided or delayed during shutdowns (for instance by closing the inlet and the outlet of the anode compartment to maintain a homogenous concentration while hydrogen slowly permeates through the membrane). Various mitigation strategies have been developed which can limit the degradation due to SU/SD

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operation, however, such mitigation strategies can cause other durability issues and they are challenging to implement, especially when the fuel cell has been stopped for a long time [7,8]. For a review on various mitigation strategies from the patent literature see ref 8 and references within Ref. [8].

When the anode compartment is divided into a part already (still) filled with hydrogen and another part where air is still (already) present, startups (shutdowns) lead to the occurrence of internal currents flowing between the active region (H_2/air) and the passive region (air/air) of the cell. The active portion (top region in Fig. 1a) operates normally (i.e. as a H_2/air fuel cell), with oxygen reduction at the cathode and hydrogen oxidation at the anode (marked in red in Fig. 1). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) The reverse currents appear in the passive part, i.e. the part which is not yet supplied with hydrogen (bottom region in Fig. 1a). These reverse currents can be measured using segmented cells [9–13]. Although they can be, in a very general manner, considered as fuel starvation events, the exact nature of reverse currents is not yet well understood. One of the first interpretations was proposed by Reiser et al. [6] who associated them with high cathode potential excursions, leading to accelerated carbon oxidation of cathode catalyst support [14]. Indeed, the occurrence of carbon corrosion was confirmed by various studies, through the measurement of CO_2 emissions at the cathode exhaust [1–5,15,16] and via post-mortem analyses of aged MEA [1,3,4,17,18]. Furthermore, the post-mortem analyses and the local measurement of CO_2 emissions along the cathode channel [19], ECSA, and performance [8] by various research groups indicate that carbon corrosion occurs heterogeneously over the MEA active surface: carbon corrosion in the cathode catalyst layer (CL) is accelerated in the region of the reverse current flow, and is mainly governed by the common residence time of air and hydrogen in the anode compartment [9,20,21].

In previous works, we proposed that the reverse currents can be decomposed into capacitive and faradic contributions [9,11]. Recent results [10] indicated that the charge corresponding to CO_2 emissions stands for only a few tenths of the faradic contribution. Consequently, around 80% of the reverse current is driven by phenomena other than complete carbon oxidation, such as reversible or irreversible catalyst oxidation, partial carbon oxidation, and water splitting. One of the objectives of the present work is to delineate the contribution of carbon oxidation to the charge measured from the internal currents. The internal currents during SU and SD operation were measured in a segmented cell to evaluate the charge exchanged between the active and passive portions of the cell. Carbon corrosion was quantified by measuring the CO_2 emissions at the cathode exhaust. Separate testing protocols for startup (SU) and shutdown (SD) were developed, and are used to distinguish between the effects of SU and SD on performance degradation along the cell area. Cells with several different MEA materials were subjected to a series of SU or SD tests to explore the influence of anode and cathode Pt loading, cathode carbon support and gas flow rates. For this, we studied the time evolution of CO_2 emissions at the cathode exhaust, spatially resolved performance, and Pt Electro Chemical Surface Area (ECSA).

2. Experimental work

2.1. Segmented fuel cell design

This work was performed using a segmented cell with an active area of 1 cm × 30 cm, described in Ref. [9] and shown in Fig. 2. Flow field on both cathode and anode consists of five parallel channels, 30 cm long. Channel dimensions are 0.7 mm in depth × 1 mm in width on the cathode and 0.5 mm × 1 mm on the anode. Lands are 1 mm wide. The cathode compartment was machined in a brass plate, which was then segmented and gold plated. The current was collected independently from 20 electrically insulated segments along the channel length. PTFE sheets (50 μm thick) were inserted between the adjacent segments to ensure electrical insulation. The anode flow-field plate was machined in a non-segmented brass block which was then gold plated.

Hydrogen and air flow in opposite directions (counter-flow) in the anode and cathode compartments. The cathode segments are numbered from 1 to 20 in the direction of the air flow during normal fuel cell operation (segment #1 = air inlet/H_2 outlet, segment #20 = air outlet/H_2 inlet), as shown in Fig. 2. During shutdown operation, the air is injected through the hydrogen inlet on the anode side. The cell temperature was controlled using a cooling circuit (coolant channels in both end-plates) and a thermostatic bath. The fuel cell was operated at 80 °C and atmospheric pressure (i.e. zero backpressure). Humidity of all inlet gases was held constant, at 90% RH.

2.2. MEA materials

Membrane-electrode assemblies (MEAs) were fabricated by Ion Power Inc., using Pt/C catalysts from Tanaka Kikinzoku Kogyo K.K. Four different MEAs were tested (Table 1): the reference MEA had cathode/anode Pt loadings of 0.2/0.08 mg_{Pt}/cm^2 the cathode and

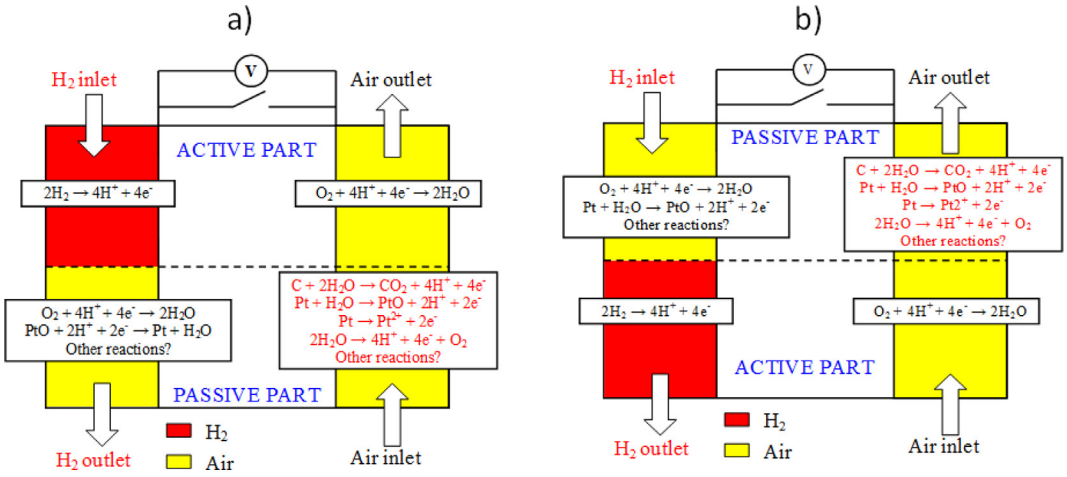

Fig. 1. Schematic of reverse currents and possible electrochemical reactions occurring in the passive part of the cell during startup (a) and shutdown (b).