



## Understanding the voltage reversal behavior of automotive fuel cells

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### HIGHLIGHTS

- Study of PEFC anode degradation during cell reversal due to hydrogen starvation.
- Evaluation of reversal tolerant anodes with oxygen evolution reaction catalysts.
- Three-dimensional nano-scale resolution X-ray tomography of degradation.

### ARTICLE INFO

#### Keywords:

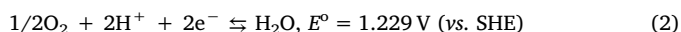
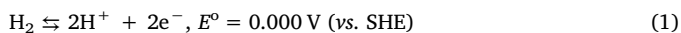
Polymer electrolyte fuel cell  
Hydrogen starvation  
Cell reversal  
Reversal tolerant anode  
X-ray computed tomography  
Degradation

### ABSTRACT

Hydrogen starvation at the anode of a polymer electrolyte fuel cell (PEFC) causes cell voltage reversal followed by water electrolysis and carbon corrosion due to an increasing anode voltage. In addition to the conventional system control technologies to protect the cell from carbon corrosion, water electrolysis catalyst (e.g., IrO<sub>2</sub>) can be employed to protect the anode by promoting proton and electron production at anode by oxygen evolution reaction (OER) over carbon oxidation reaction. Here, we investigate the voltage reversal behavior of membrane-electrode assemblies (MEAs) with reversal-tolerant-anodes (RTAs) with OER catalyst to understand the degradation mechanism using electrochemical diagnostics and X-ray computed tomography. We found that the sustainable reversal time of the RTA MEAs scales with the IrO<sub>2</sub> loading. However, all MEAs irrespective of the presence of IrO<sub>2</sub> eventually fail. They exhibit a self-similar behavior of undergoing water electrolysis followed by the carbon corrosion under the reversal conditions. The cell performance decay is dominated by Ohmic resistance increase from anode structural collapse. From the post-mortem imaging, we do not detect any significant change in the distribution and morphology of IrO<sub>2</sub> particles in the RTAs, suggesting that the RTA failure results from catalytic deactivation of the OER catalyst during cell reversal.

### 1. Introduction

Over the last decade, polymer electrolyte fuel cells (PEFCs) have drawn much attention as a promising candidate for high efficiency and zero-emission power sources for automotive applications, i.e., fuel cell electric vehicles (FCEVs) [1–4]. For FCEVs to be commercially viable, however, the three major challenges of cost, performance, and durability must be resolved. PEFCs are operated by supplying hydrogen to the anode and oxygen (or air) to the cathode, for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), respectively (as shown below and illustrated in Fig. 1a) [4–6]:



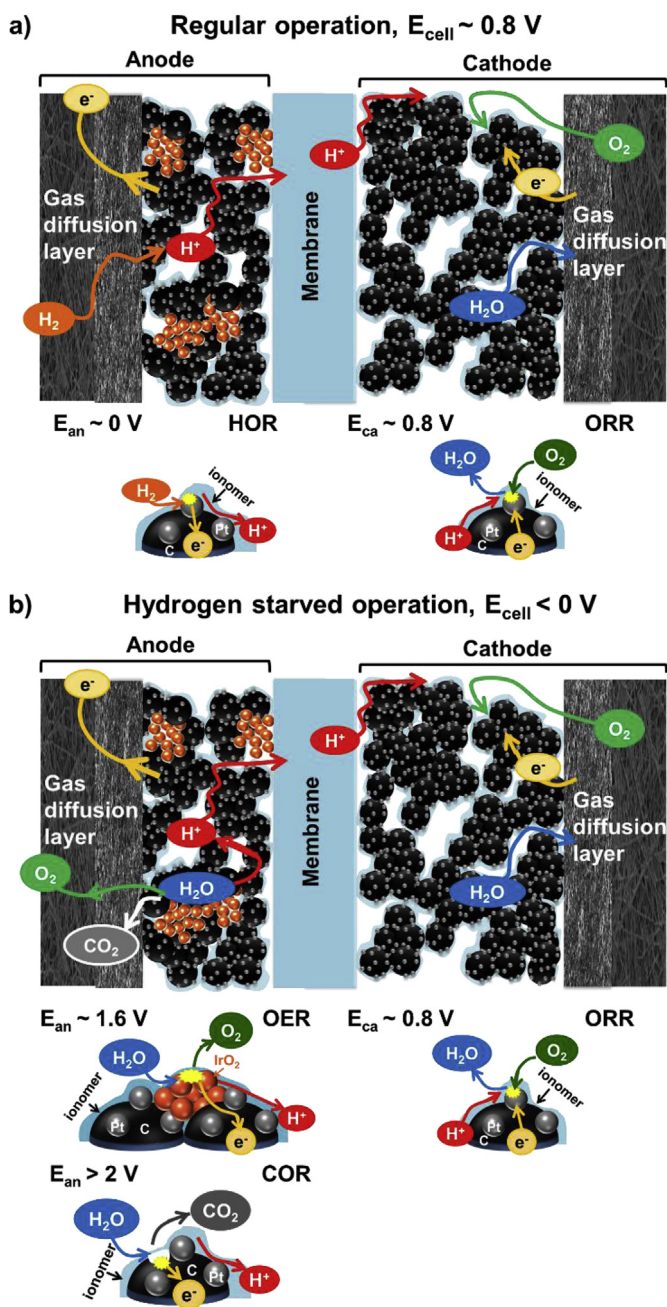
where  $E^\circ$  is the standard electrode potential and SHE is the standard hydrogen electrode.

The major components of an automotive fuel cell participating in the production of electricity are: membrane-electrode assembly (MEA), gas diffusion layer (GDL), and bipolar plate. Among these components, the MEA is one of the most critical and expensive components, which is actively responsible for generating electricity for FCEVs. Thus degradation and durability of MEAs have been investigated extensively under a variety of operating conditions, e.g., start-up/shut-down [7,8], freeze-thaw cycling [9,10], potential cycling [11], high potential holding [12–14], fatigue [15], dry-wet cycling [16], etc. However, another critical challenge towards ensuring robust PEFCs is the occurrence of partial/complete hydrogen starvation in the MEA's anode, mostly resulting from hydrogen supply malfunction or hydrogen channel blockage by liquid water flooding, ice formation, or foreign

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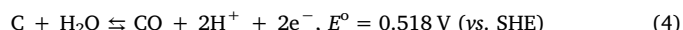
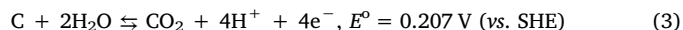
<sup>1</sup> These authors contributed equally to this work.



**Fig. 1.** (a) Schematic of a PEFC and its regular operation on hydrogen where the HOR proceeds at the anode and the ORR occurs at the cathode. (b) Schematic of PEFC operation during cell reversal from hydrogen starvation where the ORR continues at the cathode and the OER and COR occur on the Pt/C catalyst or OER on an RTA catalyst (e.g.,  $\text{IrO}_2$ ) at the anode.

impurities [17,18]. Hydrogen starvation has been a critical issue of FCEVs. It can be exacerbated when FCEVs are operated under transient conditions such as start-up and rapid load change. When the anode is starved of hydrogen, the anode requires an additional source of electrons and protons and its voltage ( $E_{\text{an}}$ ) increases relative to the cathode voltage ( $E_{\text{ca}}$ ) due to charging until the cell voltage ( $E_{\text{cell}}$ ) reverses (that is,  $E_{\text{cell}} = E_{\text{ca}} - E_{\text{an}} < 0 \text{ V}$ ) and the anode voltage becomes sufficiently large to drive the Faradaic current water electrolysis (i.e., the oxygen evolution reaction (OER)) and carbon oxidation (or corrosion) reactions (CORs) [17,18]. Although carbon corrosion reaction is thermodynamically favored at lower anode voltages, the kinetics is sluggish and requires higher voltages (i.e.  $> 1 \text{ V}$ ) [6,17–23]. Whereas water electrolysis is the favored reaction when the potential hits 1.23 V or

higher and it becomes the major reaction when the anode is at lower potentials during reversal [19–23]. However, it is universally observed that after a short time, water electrolysis reaction deactivates and carbon corrosion proceeds, driving the anode potential even higher (i.e., more negative cell voltage). Carbon corrosion typically occurs through oxidation of carbon into carbon dioxide ( $\text{CO}_2$ ) or carbon monoxide (CO) as follows [19–23]:



Cell voltage reversal events can lead to significant heat generation, which can create pin-holes in the membrane causing the MEA to be electrically shorted, eventually resulting in catastrophic cell failure [6,17,18]. This can only be prevented if the rise of anode voltage (that is, the cell voltage drop below 0 V) is intentionally stopped or delayed through either system control strategies such as cell voltage and exhaust gas monitoring [21,24] and flushing of the anode compartment to eliminate accumulated nitrogen and/or water [25], or implementing new electrode materials. The materials-based solution is typically termed as reversal-tolerant-anode (RTA), which uses an oxygen evolution reaction catalyst to promote water electrolysis over carbon corrosion [6,18,21,23], as illustrated in Fig. 1b. The RTAs are considered to be a passive solution that is always present and does not require active cell voltage monitoring, greatly increasing the stack robustness. In order to resolve the voltage reversal issues, FCEV developers have mostly employed system control strategies [21,24,25], but to develop more durable and nearly zero-defect FCEVs, additional support from materials-based solutions is imperative.

In the case of materials-based solutions against cell reversal, a variety of OER catalysts (e.g.,  $\text{IrO}_2$ ,  $\text{RuO}_2$ ,  $\text{TiO}_2$ ,  $\text{Ir}_x\text{Sn}_{1-x}\text{O}_2$ , PtIr, IrRu, etc.) have been incorporated into anodes to make RTAs [6,18,21,23]. Most FCEVs typically use a large-sized stack to propel the vehicle which consists of several hundreds of unit cells employing MEAs with an active area of several hundred square centimeters [26], which implies a large consumption of expensive OER catalyst in employing RTAs. This requires a careful operation and design of PEFCs with RTA, to maximize the utilization of the expensive catalysts.

Given the catalyst cost, it is important to develop RTAs that utilize the OER catalyst at low loadings. Thus, it is important to understand the fundamental aspects of cell reversal degradation as a function of RTA loading in order to improve RTA designs. We have studied the voltage reversal behavior of MEAs with three different amounts of OER catalyst loading: 0, 5, and 50 wt% with respect to the amount of Pt catalyst in anode. We term these MEAs as RTA 0 wt%, RTA 5 wt%, and RTA 50 wt% respectively in the following sections of the paper. We have simulated fuel starvation in a single cell set-up using electrochemical diagnostics (i.e., polarization, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV)) and high-resolution three-dimensional (3D) imaging by nano-scale X-ray computed tomography (nano-CT). Our analysis focuses on the similarities and scaling of the degradation phenomena with varying OER catalyst loading in RTAs. Of particular focus, is the diagnosis of the performance loss origin, the degradation process, and the scaling of the reversal survival duration with OER catalyst loading.

## 2. Results and discussion

For this fundamental study, we developed a well-defined testing cycle that allowed us to examine degradation in terms of the number of reversals and time spent in reversed state. Fig. 2a shows the cell voltage during a cell reversal test, in this case the first two reversals of an MEA with a conventional anode are shown. During each reversal test, we first operated the fuel cell at 65 °C with a constant current density of  $0.2 \text{ A cm}^{-2}$  while supplying fully-humidified hydrogen and air to the anode and cathode, respectively, for the first 0.5 min. We then switched

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