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On the impact of water activity on reversal tolerant fuel cell anode performance and durability



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Water is essential to both carbon corrosion and oxygen evolution reaction (OER).
- Addition of OER catalyst in anode does not guarantee prolonged reversal durability.
- Performance of OER catalyst surprisingly drops at water-excess condition.
- OER catalyst's performance exhibits volcano type dependence on water activity.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have gained significant



ABSTRACT

Durability of polymer electrolyte fuel cells in automotive applications can be severely affected by hydrogen starvation arising due to transients during the drive-cycle. It causes individual cell voltage reversal, yielding water electrolysis and carbon corrosion reactions at the anode, ultimately leading to catastrophic cell failure. A popular material-based mitigation strategy is to employ a reversal tolerant anode (RTA) that includes oxygen evolution reaction (OER) catalyst (e.g., IrO₂) to promote water electrolysis over carbon corrosion. Here we report that RTA performance surprisingly drops under not only water-deficient but also water-excess conditions. This presents a significant technical challenge since the most common triggers for cell reversal involve excess liquid water. Our findings from detailed electrochemical diagnostics and nano-scale X-ray computed tomography provide insight into how automotive fuel cells can overcome critical vulnerabilities using material-based solutions. Our work also highlights the need for improved materials, electrode designs, and operation strategies for robust RTAs.

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attention as highly efficient and clean power source for fuel cell electric vehicles (FCEVs) due to their high power density, high efficiency, and zero-emission features [1–6]. For the automotive fuel cells to be commercially viable, three major challenges of cost, performance, and durability must be resolved. Automotive fuel cells have several major components, i.e., membrane-electrode assembly (MEA), gas diffusion layer (GDL), and bipolar plate, in order to produce electricity. Among the critical components of fuel cells, the electrodes in the MEA, mostly based on carbon-supported



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platinum (Pt/C) catalysts, are of paramount importance to generate electricity for vehicles efficiently. As Fig. 1 shows, under normal fuel cell operating conditions, hydrogen and oxygen (in air) gases are supplied to the anode and cathode, respectively, where the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) respectively occur as follows [3,4]:

 $H_2 \leftrightarrows 2H^+ + 2e^-, E^0 = 0.000 V (vs. SHE)$ (1)

$$1/2O_2 + 2H^+ + 2e^- \leftrightarrows H_2O, E^0 = 1.229 V (vs. SHE)$$
(2)

where, E^o is the standard electrode potential and SHE is the standard hydrogen electrode.

Although often overlooked, hydrogen starvation at the anode arising from either a hydrogen supply malfunction or hydrogen channel blockage by liquid water or ice is a critical issue for FCEVs that can be exacerbated when FCEVs are operated under transient conditions such as start-up and rapid load change [5,6]. When an anode in PEFC stack is starved of hydrogen, the anode lacks a facile Faradaic source of protons and electrons at low potentials and it thus capacitively charges due to the external current from the high cumulative voltage of the adjacent cells stacked in series. With charging, the anode half-cell potential (Ean) increases relative to the cathode's (E_{ca}) and the individual cell voltage (E_{cell}) reverses (that is, $E_{cell} = E_{ca} - E_{an} < 0$ V). With continued charging, the anode halfcell potential becomes sufficiently high for the oxygen evolution reaction (OER), i.e., water electrolysis, to provide protons and electrons. If the water electrolysis cannot support the full current. the anode half-cell potential further increases leading to Faradaic carbon oxidation (i.e., the carbon corrosion shown in Fig. 1) [5-9]. Although carbon corrosion is thermodynamically favorable, water electrolysis proceeds at a higher rate because it seems to be kinetically favorable [10]. However, the sluggish carbon corrosion reaction becomes sufficiently fast at high voltages (i.e., >1 V) to cause severe carbon corrosion [4-7]. The presence of platinum also aggravates carbon corrosion at high anode-half-cell potentials [11,12]. Carbon corrosion typically occurs through oxidation of carbon into carbon dioxide (CO₂) or carbon monoxide (CO) as follows [7–10]:

$$C + 2H_2O \implies CO_2 + 4H^+ + 4e^-, E^0 = 0.207 V (vs. SHE)$$
 (3)

$$C + H_2O \leftrightarrows CO + 2H^+ + 2e^-, E^0 = 0.518 V (vs. SHE)$$
(4)

Thus, if unabated, these cell voltage reversal events typically cause the MEA to be electrically shorted due to a significant amount of heat generated in the membrane as the anode potential increases to high values, eventually resulting in catastrophic cell failure [4–6]. Unlike the inherently transient start-up/shut-down carbon corrosion degradation [13,14], cell reversal degradation is a sustained process that must be survivable for several hours over the lifetime of the fuel cell stack. The anode's voltage rise and cell reversal must be intentionally stopped or delayed through system control strategies. Many control approaches to reversal tolerance have been developed over the past decade, such as cell voltage and exhaust gas monitoring [10,15] and flushing of the anode compartment to eliminate accumulated nitrogen and/or water [16]. However, these control strategies can limit the robustness of operation, hinder performance, and leave the cell susceptible to reversal damage.

Instead of complex active control system, a material-based solution that robustly prevents degradation without active intervention is desired. One such approach is a reversal tolerant anode (RTA) [4,6]. The key to an RTA is inclusion of highly active OER catalyst into the anode that promotes oxygen evolution over carbon corrosion. A variety of water electrolysis or OER catalysts, e.g., IrO₂, RuO₂, TiO₂, Ir_xSn_{1-x}O₂, PtIr, IrRu, etc., have been added into anodes to suppress the drop of E_{cell} (i.e., the increase in E_{an}) such that facile carbon corrosion potentials are avoided [4,6,10,17]. One of the constraints of the OER catalyst for RTAs is their stability in acidic media and, to a lesser degree, their robustness to a limited number of potential swings between roughly 0 and 2 V vs. SHE. Another challenge with RTAs is the associated material cost. Most FCEVs use a large-sized stack (e.g., 100 kW) to propel the vehicle which consists of several hundreds of unit cells in series, with MEAs having active areas on the order of several hundred square centimeters [18]. This entails significant amounts of OER catalyst and requires a careful design and operation of PEFCs to maximize the RTA OER catalyst's effectiveness.

A key aspect of a successful RTA strategy is that, it is effective under all operating conditions, including high temperature (i.e., >80 °C) and extremely high and low relative humidity (RH). Operation of fuel cells at high temperature is normally desirable



Fig. 1. A schematic illustration of fuel cell operation under normal and hydrogen starvation conditions. On the left, electrochemical reactions at the anode and cathode under the normal hydrogen supply condition are shown. On the right, electrochemical reactions under the hydrogen-starved condition for the MEA with and without an RTA are shown.

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