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The maximum potential a PEM fuel cell cathode experiences due to the formation of air/fuel boundary at the anode

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Abstract In this short communication, a misconception about the maximum potential a polymer electrolyte membrane fuel cell (PEMFC) cathode experiences due to the formation of fuel/air boundary at the anode during startup/shutdown is clarified. It is shown, conceptually, that the maximum potential experienced by a cathode in PEMFC under such condition is about twice the potential observed when one connects a driving fuel cell to a driven cell (electrolyzer), both of which having the same physical characteristics and operating under the same conditions.

Introduction

The durability of polymer electrolyte membrane fuel cells (PEMFC) has been one of the major factors that has impeded the commercialization of this technology so far [1–2]. Among the many failure mechanisms, particularly for transportation applications, which require frequent start/stop cycling, one of them is the so-called reserve-current decay mechanism, first reported by researchers at UTC fuel cells [3]. This happens in the following manner: after a PEM fuel cell shuts down, air can occupy the anode

Dedicated to my graduate advisor Dr. John O'M. Bockris in honor of his 85th birthday.

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compartment due to either leakage from the outside air or from crossover through the membrane. Hence, before the startup of a PEMFC, air occupies both the anode and cathode. When hydrogen is introduced into the anode during startup, an H_2/Air boundary is created in the anode, which moves along the anode channel until the air is completely replaced by H_2 (Fig. 1a). A similar situation can occur during the shutdown procedure when the air leaks into the anode from the outside or crosses through the membrane and replaces the hydrogen. This mechanism is also possible during the PEMFC operation when localized hydrogen starvation occurs in the anode where the fuel-starved region can be filled with the crossover air. The presence of an air/fuel boundary in the anode creates a high interphasial potential difference in the cathode region where hydrogen is absent on the anode side (Fig. 1a), causing oxygen evolution, carbon corrosion, and Pt dissolution on the cathode side. This happens because the in-plane proton transfer resistance for a given distance in the polymer electrolyte is an order of magnitude higher than its cross-plane value due to its micro thickness. More specifically, when H_2 enters the anode, which is filled with air initially and the cathode with air, the anode electrode Fermi level goes up due to the rapid kinetics of H_2 oxidation reaction, lowering the anode electrode potential from the air potential (~1.0 V/NHE) to a value where oxygen reduction reaction (ORR) can occur on the anode section filled with air. Since the in-plane proton resistance of the polymer electrolyte is much higher than its cross-plane resistance, the proton for the ORR at the anode side, instead of coming from the anode section where H_2 is oxidized, must come from some place where it can be generated and experience less transport resistance, and that takes place through oxygen evolution reaction (OER) at the cathode section directly opposite of the anode section with air. This has the effect of

Fig. 1 A fuel cell at OCV during a startup with a H₂/air front in the anode channel (**a**) and its simulated equivalent with a dual cell (**b**)
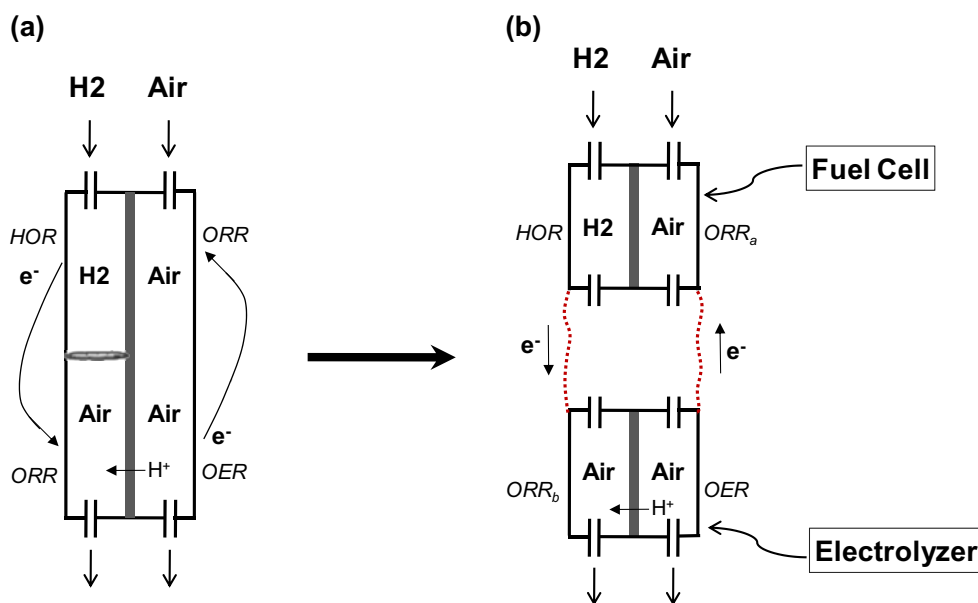
dividing, at the H₂/Air front region, the whole PEMFC at open-circuit-voltage (OCV) into two cells that are in electronic connection where one section, which acts as H₂/Air fuel cell, drives the other section with Air/Air, which acts as an electrolyzer (Fig. 1b).

In fact, the authors of [3] explained this phenomenon as described above and proved its existence by electrically connecting two identical fuel cells in parallel where one acts as power sources and the other as an electrolyzer. Another paper by researchers at Plug Power reports similar results with reformate [4]. However, both papers report an incorrect potential that was experienced by the cathode of their fuel cells at OCV when an H₂/Air boundary is simulated using two identical cells.

In this study, a conceptual framework is presented which provides an explanation for the maximum potential experienced by the FC cathode due to the formation of H₂/Air boundary during a startup/shutdown and local fuel starvation. Several mitigation strategies have been developed and reported by UTCFC in patent publications. These strategies will not be discussed in this note.

Conceptual basis for the maximum potential experienced by the cathode in the presence of anode air/fuel boundary in a PEMFC at OCV

The concept can be explained diagrammatically by current–potential relations based on either Butler–Volmer equation or experimental I–V data from PEM fuel cells. Since the conclusion of this paper will not depend on the magnitude of the overpotentials or the IR, a somewhat schematic current–potential curves representing the reactions involved

in a PEM fuel cell will be used to illustrate the concept.[1] The only condition for the validity of our conclusion requires that the in-plane proton transfer resistance for the polymer electrolyte membrane in a fuel cell is greater than the sum of Faradaic resistance of the oxidation reactions at the cathode and the cross-membrane proton transfer resistance.

Now, let us consider the consequence of connecting two identically built fuel cells (Fig. 1b); one acts a driving cell with H₂/air at anode/cathode and the other acts as an electrolyzer with air/air at anode and cathode. As mentioned above, this simulates the presence of a fuel/air front during the startup/shutdown of a PEMFC. Before the electrical connection, the driving cell has an OCV of ~1 V and the driven cell an OCV of 0 V. At the moment the two cells are electrically connected, current starts to flow through the external circuit, and the driving cell voltage decreases while the driven cell voltage increases following the oxygen reduction curve at electrolyzer cathode and oxygen evolution curve on electrolyzer anode, respectively. Once the driving cell voltage V(FC) approaches the opposing cell voltage V(driven) of the driven cell, there establishes a dynamic equilibrium between the driving force and opposing force where a net current flows through the electrical leads. Thus, at such a steady-state condition, the maximum potential the cathode of the electrolyzer experiences is the sum of driving cell voltage, driven cell

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[1] The I–V curves used are not too far from real situations because of the use realistic-looking FC data and Tafel slopes for the oxygen evolution/reduction reactions on Pt in acid, although the FC data do not represent any specific fuel cell.

voltage, and the overpotential for fuel oxidation at driven cell anode, i.e.,

Maximum interphasial potential a cathode experiences　　(1)

$= V_{FC} + V_{driven} + overpotential\_for\_HOR.$

This concept is shown in Fig. 2 where two assumptions were made to make the illustration simple: (a) Both anode and cathode for the fuel cell with the fuel/air front have the same electrochemical active area (ECSA) or made with the same catalyst with the same loading etc. (b) It is understood that the high positive potential at the cathode can cause water oxidation to evolve O_2, carbon corrosion, and Pt dissolution (slows down due to oxide growth) [5]; among these, OER has lower overpotential and faster kinetics compared to the other two (if that is not the case, Pt or carbon could not be used to evolve oxygen before they themselves corrode away) [6–7]. Therefore, only OER curve is chosen for Fig. 2.

If the fuel is H_2 and its oxidation overpotential is small, then the maximum potential a PEMFC cathode experiences due to an H_2/air front will be twice the observed potential when two equivalent fuel cells at-OCV are electrically connected to each other, as shown in Fig. 1b:

Maximum interphasial potential a cathode experiences　　(2)

$= 2 \times Observed\_steady\_state\_cell\_potential.$

However, the authors of [4] stated that the cathode of electrolyzer cell experiences about twice the OCV voltage of the PEM fuel cell, i.e., ~2.0 V. This is conceptually incorrect and never happens in practice in PEMFC as long as Pt is used as electrode material. Because based on Fig. 2, for the cathode to experience about twice the OCV
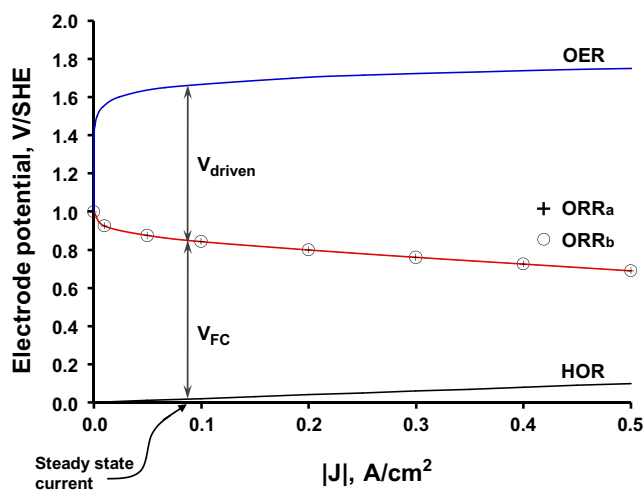

Fig. 2 Schematic current–potential relations involved in the fuel cell and electrolyzer cell shown in Fig. 1b. The steady-state current condition is established as soon as the fuel cell voltage is equal to the opposing driven cell voltage
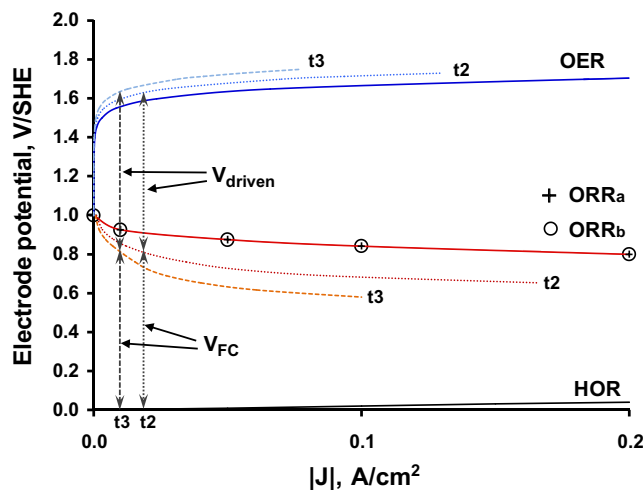

Fig. 3 Schematic current–potential relations showing the effect of time for the shorted dual cell

of a PEM fuel cell, oxygen evolution (with carbon corrosion and Pt oxidation) reactions must have infinite overpotential, and that is not the reality. The researchers at Plug Power, in fact, observed 0.82 V when they connected two fuel cells with the configuration as depicted in Fig. 1b. This means that their cathode experienced $2 \times 0.82 = 1.64$ V, neglecting the overpotential for H_2 oxidation, which is small at such fuel cell potential (0.82 V). Unfortunately, they added the observed 0.82 to the OCV, 0.93 V, of the driving cell to obtain a value of 1.75 V, as though the driving cell were producing net current at its OCV.

The researchers at UTC Fuel Cells did not make the same claim as the authors of [4]; instead, they developed a one-dimensional mathematical model to obtain the electrolyte potential profile for this phenomenon so that the cathode potential could be calculated. However, they made one conceptual error in their modeling: They used the total number of electrons in the exponential for the rate equation as though the rate-determining electron transfer step involves multiple electrons, which is not expected for thermal electron transfer reactions with an activation barrier higher than kT (a separate note will be published regarding this issue). They observed 0.85 V when they shorted two fuel cells with the configuration as shown in Fig. 1b, which means that the actual interphasial potential difference experienced by the cathode directly opposite of the anode air side is 1.70 V (2×0.85 V). Their modeling predicted a lower value of 1.44 V perhaps mostly because of the error mentioned above and of course other simplifications in the model.

The above arguments made for Fig. 2 assume that the electrodes are stable in the potential region where they establish a steady-state condition and reactant supply is

maintained constant. What happens if these two conditions are not maintained, which is the reality?

Let us consider three realistic possibilities:

1. *Reactant supplies are constant, as in the simulated condition*:

It is well known that Pt is not stable at the electrolyzer anode due to the high positive potential required to evolve oxygen. This high potential not only alters the surface structure of Pt as time passes, increasing the overpotential for OER, but also corrodes the catalyst support carbon, leading to catalyst agglomeration and thus reduction of the catalyst surface area [7]. These effects in combination raise the overpotential at the electrolyzer anode; since the driving cell potential cannot be increased further from its steady-state value, current has to decrease to generate a higher driving cell voltage for the driven cell. Besides, the low ORR currents at the two cathodes also degrade the performance of the driving cell and increase the over-potentials for ORRs, leading to further decrease in current. With the combination of such competing factors, the electrolyzer anode potential increases with time initially and then decreases until the driving force stabilizes at a very low current. This situation is depicted schematically in Fig. 3 where t2 and t3 mean with increasing time the driving force and the current decrease.

2. *Reactant supply is not constant—this is the real situation PEMFCs experience during the startup/ shutdown:*

When H_2 is introduced into the air-filled anode (Fig. 1a), O_2 is rapidly depleted due to the ORR at the lower section of the anode, raising the overpotential for this reaction and thus leading to a higher resistance to the driving cell. This factor in combination with those mentioned in situation 1 will limit the positive potential cathode experiences to a lesser value and shorter duration. Thus, a rapid introduction of H_2 into air-filled anode will degrade the cathode less than a slower introduction of fuel into the anode, as has been observed by Plug Power researchers [4].

3. *Local fuel starvation during the PEMFC operation:*

This situation is more complicated than the above two cases, but a general statement could be made that when the fuel cell is in operating mode, its power is consumed in driving the external load so that less power is available for carrying out electrolysis at the cathode section which is just at the opposite side of the fuel starved spot on the anode. However, if the cell is at OCV with some fuel-starved region in the anode, then the damage at cathode side would be much more severe than cases 1 and 2. It is because the smaller fuel-starved spot presents itself as a small electrolyzer to a much larger fuel cell area with larger current. Larger current means more oxidation at the cathode side.

Thus, one can make a simple prediction based on the above analysis: When fuel enters the anode of a PEMFC during startup (air at both electrodes and no fuel-starved spot during startup), as the fuel length increases in anode channel, it is equivalent to increasing the fuel cell active area for the driving cell and thus more power to drive the current at an electrolyzer that is shrinking in size. This means that cathode exit section suffers much more damage than cathode inlet region during startup.

Conclusions

For low-temperature PEM fuel cells at open circuit condition, the maximum interphasial potential a cathode electrode experiences during the startup/shutdown due to a fuel/air front in the anode is twice the observed steady-state cell potential in simulated dual-cell condition, and it decreases with time in realistic situations due to the rapid depletion of oxygen in the anode. Due to the decreasing amount of oxygen with time in the anode during startup, cathode exit region experiences more oxidative damage than its inlet region.

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