Reverse-Current Decay in Hydroxide Exchange Membrane Fuel Cells

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In proton exchange membrane fuel cells (PEMFCs), the cathode carbon support corrodes during startup and shutdown by reverse-current decay (RCD). We show for the first time that hydroxide exchange membrane fuel cells (HEMFCs) also undergo RCD. We find that decreasing the oxygen reduction reaction (ORR) activity of the anode catalyst mitigates RCD: a Ru anode causes less corrosion than Pt, Ir, and Pd anodes, as expected from their ORR activities. After an intensive 6 h RCD test, an HEMFC based on Ru shows six times lower internal resistance compared to Pt (1.02 vs. 6.01 Ω cm²). Due to its enhanced ORR activity in base, carbon alone can sustain RCD. To minimize RCD the carbon support should be eliminated from the anode catalyst.

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A reverse-current mechanism of proton exchange membrane fuel cell (PEMFC) degradation was discovered in 2005.1 We summarize it as follows. After a period of inactivity, a PEMFC anode contains only air due to equilibration with the atmosphere. As hydrogen is introduced during device startup, distinct hydrogen and air regions form on the anode (Fig. 1a). In the hydrogen region the device operates normally: the hydrogen oxidation reaction (HOR) occurs on the anode while across the membrane, the oxygen reduction reaction (ORR) occurs on the cathode. Since the two anode regions are electrically connected, electrons produced by HOR in the hydrogen region can move to the stagnant air region and react with protons supplied by the electrolyte to reduce oxygen. Removing positive charge from the electrolyte in this manner lowers the electrolyte potential, ultimately generating an interfacial potential difference sufficient to drive the carbon oxidation reaction (COR) and oxygen evolution reaction (OER) on the cathode in the stagnant air region. This mechanism is called reverse-current decay (RCD) because reduction occurs on the anode where hydrogen is normally oxidized while oxidation occurs on the cathode where oxygen is normally reduced. Related decay processes take place during shutdown and whenever hydrogen is maldistributed on the anode.2,3 Over the course of many startup/shutdown cycles, corrosion of the cathode carbon support leads to significant performance loss.4

Strategies to mitigate RCD include maintaining hydrogen pressure in the anode after shutdown or flushing with an inert gas,5 shorting the electrodes to deprime the cathode potential,6 replacing carbon with a corrosion-resistant support,7,8 and mixing OER catalysts into the cathode to reduce selectivity for COR.8,9,10 However, these strategies add to system complexity or treat symptoms instead of resolving the underlying problem.

The key issue responsible for RCD in PEMFCs is that the anode and cathode catalysts are the same. Pt is the best catalyst available for both HOR and ORR. When a mixture of gases is present at the anode, Pt catalyzes HOR as intended, but also catalyzes ORR. A direct way to stop RCD is to eliminate the interfacial potential buildup altogether by replacing Pt with a specialized anode catalyst that has no ORR activity.

Unfortunately, because PEMFCs operate under harsh acidic conditions, many metals oxidize and subsequently dissolve at PEMFC anode potentials (Fig. 2). Thus, efforts to date to reduce ORR activity have focused on modifying Pt. Genorio et al. completely suppressed the ORR activity of Pt at low overpotential by covering the surface with calix4[4]arene, an organic macrocycle.11 However, they reported only half-cell measurements; it is unclear whether this surface modification approach would be practical in a real device.12

Hydroxide exchange membrane fuel cells (HEMFCs) are an emerging low-cost alternative to PEMFCs.13 Because HEMFCs operate under basic conditions, they intrinsically support earth-abundant non-Pt anode catalysts (Fig. 2), such as Ni.14 Until now RCD has never been studied in HEMFCs, but if it occurs it could present an even more serious issue than in PEMFCs. In a basic environment, CO₂ produced by COR reacts further to the stabler CO₃²⁻ form, increasing the energetic favorability of corrosion.15 Furthermore, the tendency of the HEMFC anode to flood16 may exacerbate hydrogen maldistribution during closed-circuit operation. Despite these differences, we expect the basic mechanism of RCD in HEMFCs to be similar to that of PEMFCs (Fig. 1b). We aim to determine whether RCD affects HEMFCs, and if so, whether it can be mitigated by choosing specialized anode catalysts with low ORR activity.

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Figure 1. Mechanism of reverse-current decay during startup in (a) PEMFCs (known) and (b) HEMFCs (proposed). Stagnant air (white regions) is displaced by flowing hydrogen and air (shaded regions).
Here we demonstrate for the first time that HEMFCs undergo RCD when some platinum-group metals or carbon are used as anode catalysts. We adapt the model of Reiser et al. to predict an inverse relationship between anode ORR activity and RCD driving force. We test several mononuclear catalysts and confirm that cathode corrosion is slower for anode catalysts with low ORR activity.

Experimental

High-performance 5 cm² membrane-electrode assemblies (MEAs) were fabricated with a robotic sprayer (Sono-Tek ExactaCoat) by a catalyst-coated membrane (CCM) method as described elsewhere. Electrolytes were supplied by Tokuyama Corp. (A201 membrane and AS-4 ionomer solution); catalysts, by Tanaka Kikinzoku Kogyo (or TKK; 50% Pt on high-surface-area C), AkzoNobel (Ketjen C black), and Premetek (20% Ir, Pd, Rh, or Ru, all supported on Vulcan XC-72); gas diffusion layers, by Toray (unwetproofed TGP-H-060 C paper); and fuel cell enclosures, by ElectroChem and Fuel Cell Technologies.

MEAs were tested with a fuel cell test system (Scribner 850e). Internal resistance (IR) was monitored continuously by a built-in current interrupt method. Point IR estimates were obtained by averaging over the final 10 min of a 30 min evaluation period. No back pressure was applied. For each RCD test, two fresh MEAs were used: one “driver” and one “performer”, wired together in either a normal or inverted configuration as shown in Figure 3. Before the test, both MEAs were activated/evaluated by controlling the cell voltage. After the test, the performer was evaluated again to check for any difference caused by RCD (Fig. 4). In this work we assess the extent of carbon corrosion only by characterizing the performer cell before and after RCD. A more direct approach, of potential interest for future work, would be to measure CO2 levels in the exhaust in real time.

In-situ cyclic voltammetry (CV) was performed with a JSM-7400F microscope equipped with an ultra-thin-window energy-dispersive X-ray spectrometer (EDS). Micrographs were obtained at accelerating voltages of 7–10 kV. Deviations given in the summary of EDS data (Table II) indicate one standard error (n = 3).

In the reported measurements, the potential was repeatedly cycled from 0 to 1.2 V vs. the H2 anode. Anode and cathode humidifiers were allowed to cool to 30 °C while connected to feeds (room temp. otherwise), anode and cathode humidifiers at 55 °C, H2 and O2 flow rates of 0.2 L/min. For a Ru/C performer, in steps (a) and (d) the cell voltage is maintained at 0.5 V throughout (dashed lines) to avoid catalyst oxidation.

Figure 3. Experimental configurations for (a) normal and (b) inverted RCD tests. The HEMFC shown in Figure 1b is split along the vertical dotted line into two separate cells. In each test, the cells are connected by two wires. The H2/O2 cell is termed the driver because it provides the low hydrogen oxidation potential required to induce ORR in the performer cell. The performer is the air/air cell whose performance degrades over the course of the RCD test. For all tests, identical Pt/C electrodes, with 0.5 mgPt cm⁻² and 20% ionomer loading, were used for both electrodes and for the performer electrode where CO corrosion occurs (i.e., the cathode in a normal test or the anode in an inverted test). The catalyst in the remaining electrode is used to identify the performer cell (e.g., a “Ru/C performer” consists of a Ru/C anode and a Pt/C cathode).

Theoretical

Reiser et al. modeled electrolyte potential in a small section of a Pt-based PEMFC with a charge-conservation balance, as described in the original work. They solved the resultant second-order ordinary differential equation (ODE) by a finite difference method. We reproduced their work, and here provide some computational details so that others may more easily follow the same approach.

The governing ODE takes the form

\[ \Phi''(x) = \sum_{i=1}^{5} \alpha_i e^{\beta_i \Phi(x)} \]

where \( \Phi \) is electrolyte potential, \( x \) is position on the anode (see x-axis of Fig. 5a), and \( \alpha \) and \( \beta \) are constants. Each summand is an...
We varied the exchange current density (contained in convergence was slowed by under-relaxation for all time steps. After fully recovering the nonlinear problem, the iterations were con- incremental from the linear to the nonlinear ODE at each time step. explicit method, parameter continuation was applied to transition in- finite difference approximation to the linearized ODE. Following an overpotential term corresponding to Figure 1a (anode: HOR or ORR; cathode: ORR, COR, or OER). The presence of the dependent variable inside an exponential function makes the ODE highly nonlinear. On the boundary, \( \Phi'(x) = 0 \).

To obtain \( \Phi(x) \) numerically, we performed a first-order Taylor expansion on the exponential function to yield the linearized ODE

\[
\Phi''(x) = \sum_{i=1}^{5} \alpha_i [1 + \beta_i \Phi(x)].
\]

We discretized the domain onto a grid (\( N = 200 \)) and applied a finite difference approximation to the linearized ODE. Following an explicit method, parameter continuation was applied to transition incrementally from the linear to the nonlinear ODE at each time step. After fully recovering the nonlinear problem, the iterations were continued until convergence criteria were reached. To improve stability, convergence was slowed by under-relaxation for all time steps.

To find the effect of anode ORR activity on electrolyte potential, we varied the exchange current density (contained in \( \alpha \) above) for the anode ORR term and repeated the calculation. Otherwise, we used the same PEMFC parameters as Reiser et al. To be consistent with the original model, the oxidant flowed through the cell was air, although in our experimental HEMFC setup we use pure oxygen. We did not reparameterize the model for an HEMFC; this is a direction for future work, though we expect the results to be qualitatively similar.

**Results and Discussion**

To test our claim that reducing anode ORR activity mitigates RCD, we reproduced Reiser et al.’s Pt-based open-circuit PEMFC startup/shutdown model (Fig. 5a, orange curve). The left half of the electrolyte potential profile shows the hydrogen region, where the cell operates normally. Although the electrolyte is in contact with both the anode and the cathode, its potential is nearer to HOR equilibrium (\( \approx 0 \text{ V}_{\text{RHE}} \)) than to ORR equilibrium (1.23 \text{ V}_{\text{RHE}}) because HOR is much faster. The right half of the profile shows the air region of the anode, where ORR can occur. Proton consumption by ORR lowers the electrolyte potential to about \(-0.6 \text{ V}_{\text{RHE}}\), at which point ORR on the anode is balanced by COR and OER on the cathode.

Then, we modified the model to predict the effect of increasing and decreasing the ORR exchange current density of the anode catalyst (Fig. 5a, all curves). When the anode catalyst is completely inactive, the electrolyte potential profile is essentially flat, indicating that the driving force for RCD is gone: startup and shutdown are no different from normal open-circuit conditions. As activity increases, the electrolyte potential drops monotonically as expected, resulting in a higher difference between the cathode potential (measured to be approx. 850 mV under RCD conditions\(^1\)) and the electrolyte potential, and thus more overpotential to drive OER and COR on the cathode. This trend is quantified in Figure 5b, a plot of average electrolyte potential in the air region versus ORR activity. The large negative slope seen between -12 and -3 on the x-axis is related in part to the curvature of the profiles. At high activity a sharp transition is predicted at the hydrogen-air front, but as the activity is decreased the potential drop becomes not only shallower but also smoother. Since only a 1 mm section of the anode flow channel is shown, the effect of this smoothing is minor when the entire length is considered, but it does indicate that a somewhat smaller region of the cell is maximally affected when ORR activity is low. Overall, the model predictions support our claim that reducing the ORR activity of the anode catalyst mitigates RCD in PEMFCs. Without reparameterizing the model, we assume that this result transfers qualitatively to HEMFCs.

For HEMFCs, there are many possible choices for the anode catalyst. Aside from cost, typical selection criteria are high oxidative stability and high HOR activity. To avoid the issue of oxidation, we consider here only four of the most thermodynamically stable catalysts shown in Figure 2 (Ru, Pd, Ir, and Pt), all of which also have some ORR activity. Ru is an especially exciting option because a PtRu/C anode catalyst recently showed exceptional HEMFC performance.\(^{19}\)

We propose that in addition to high stability and HOR activity, low ORR activity is also desirable. Literature measurements of the ORR activities of these catalysts are shown in Table I.\(^{20-26}\) Based on the modeling results above, if we control for HOR activity, we hypothesize that differences in ORR activity of these anode catalysts will dictate the extent of cathode carbon degradation in an experimental RCD test.

Our experimental RCD test protocol (Fig. 3a) is analogous to that of Reiser et al. To simulate startup/shutdown conditions without cycling, we employ two cells: a “driver” and a “performer”. Hydrogen and oxygen are allowed to flow through the driver as usual, while the performer inlets and outlets are simply exposed to stagnant air. Shorting the cells together achieves a perpetual startup-like configuration.

To determine whether degradation took place in an RCD test, we evaluated the performer cell beforehand and afterward by connecting it to hydrogen and oxygen feeds, controlling the cell voltage, and measuring IR and current (Fig. 4). To minimize sources of degradation other than RCD, we chose mild test conditions (moderate temperature and full humidification) and used different MEAs, prepared identically with a robotic sprayer (Sono-Tek), for each test.
Table I. ORR activities of HEMFC anode catalysts measured by rotating disk electrode.

| Disk material | Source | Reported (V) | Standardized (V_{RHE}) | Electrolyte | Rotation rate (rpm) |
|---------------|--------|--------------|------------------------|-------------|---------------------|
| Pd            | Vracar et al. (1986) | 0.07 vs. SHE | 0.85 | 1 M LiOH | 2 |
| Pt            | Tarasevich (1973) | 0.06 vs. SHE | 0.83 | (pH 13) | 6100 |
| IrO₂          | Chang and Wen (1996) | -0.19 vs. Ag/AgCl | 0.82 | 1 M KOH | 2500 |
| Ru            | Anastasijevic et al. (1986) | -0.23 vs. Hg/HgO | 0.71 | 0.1 M NaOH | 2500 |
| C             | Taylor and Humffray (1975) | -0.40 vs. Ag/AgCl | 0.62 | 0.8 M NaOH | 2000 |

*Not reported or not available

Initially, we limited our experiments to Pt-based electrodes to determine whether RCD affects HEMFCs. Evaluation of a Pt/C performer before and after a 2 h RCD test (Fig. 6a) showed a clear performance drop (from 1310 to 336 mA cm⁻²) and IR increase (from 0.129 to 0.477 Ω cm⁻²), consistent with the loss of electron- and ion-conducting pathways that is expected to accompany electrode corrosion. In-situ CV of the cathode showed that RCD rendered the Pt surface inaccessible (Fig. 7). Despite the disappearance of the Pt peak in the CV, after a 6 h test, EDS revealed Pt enrichment in the cathode (from 44 to 82 wt%, Table II). After a 24 h test, SEM revealed cathode thinning (by approx. a factor of two, Fig. 8b). The higher brightness in the cathode after RCD indicates clustering of heavy Pt atoms. However, in this longer test no trend was observed in the EDS, suggesting that Pt enrichment does not occur uniformly over the cathode. Regardless, performance loss, IR increase, catalyst inaccessibility, (possible) cathode Pt enrichment, and cathode thinning are all signatures of RCD in PEMFCs. Based on this evidence we conclude that RCD does affect HEMFCs.

We confirmed this conclusion by running a control: a 2 h test in which the driver and performer were never shorted together so that no RCD took place. The Pt performer showed minor current loss (1350 to 1150 mA cm⁻²) and IR gain (0.128 to 0.138 Ω cm⁻²), suggesting little or no corrosion as expected. After a longer 24 h control test, the anode and cathode both appeared uncorroded in SEM (Fig. 8a).

The most reliable indicator that RCD has occurred is increased IR. Unlike current density, IR is directly comparable across catalysts. Prior to RCD, the IR should be roughly similar regardless of catalyst choice as long as the same electrolytes are used, whereas current density varies widely due to differences in HOR activity. However, IR is still an imperfect indicator of RCD, since electrode corrosion is not the only way in which a fuel cell’s IR may increase. Two additional ways should be mentioned. First, the membrane may degrade during normal operation through mechanisms unrelated to RCD, for

Figure 6. Evaluation of (a) a Pt/C performer and (b) an inverted C black performer before and after a 2 h RCD test. Solid symbols indicate initial evaluation; open symbols, final evaluation; triangles, current density; and circles, IR. In (b), some IR points at t < 5 min are missing because the current was too low to perform the measurement. (a) Materials: catalyst loading of 0.5 mgPt cm⁻² Pt/C with 20% ionomer for both anode and cathode. (b) Materials: catalyst loading of 0.5 mgPt cm⁻² Pt/C with 20% ionomer for the anode, and 1.0 mg cm⁻² C black with 30% ionomer for the cathode. Test conditions: cell at 50 °C, anode and cathode humidifiers at 55 °C, H₂ and O₂ flow rates of 0.2 L/min.

Figure 7. In-situ cyclic voltammograms of a Pt/C performer cathode before (black) and after a 1 h (blue) or 2 h (red) RCD test. Different but identically prepared MEAs were used for all three tests. Materials: same as Figure 6a. CV conditions: cell at 30 °C, humidifiers at 50 °C, scan rate of 10 mV s⁻¹, anode (reference electrode) flow rate of 0.2 L/min H₂, cathode (working electrode) flow rate of 0 L/min N₂ (reduced from 0.05 L/min just before scanning).
example via nucleophilic attack by hydroxide ions. Second, if the cell performance drops for any reason, including but not limited to RCD, the membrane may dehydrate as a result. At low current density (i.e., low performance) the cell produces less water, so the membrane becomes a less efficient ion conductor. These additional mechanisms explain the small IR increase observed in the control, which we term “baseline degradation”. After establishing that a performer with a Pt/C anode undergoes RCD, we repeated the RCD test for performers with Ru/C, Pd/C, and Ir/C anodes. In all cases the performer cathode and both driver electrodes were still Pt/C. Differences in HOR activity did not directly affect the RCD test since an identical Pt/C driver anode was exposed to hydrogen each time, and the IR increases observed may be compared across tests since the degradation occurred in identical Pt/C performer cathodes. Thus, we attribute the observed differences in cathode degradation rate to differences in anode ORR activity. Pd/C and Ir/C performers degraded similarly to the Pt/C performer after a 2 h RCD test ($\Delta_{IR} = 0.294-0.516 \, \Omega \, cm^2$). Table III, as expected from their similar ORR activities. Ru/C, the most promising candidate based on its low ORR activity, was compared to Pt/C in greater detail. But it does explain why the Ru/C cell showed a high IR even before evaluation. For the C black performer, evaluation after a 2 h inverted RCD test revealed performance and conductance losses (Fig. 6b). The validity of this inverted RCD approach was confirmed in an additional experiment: a Pt/C performer that underwent a 6 h inverted RCD test and one that underwent a 6 h normal RCD test showed similar degradation, suggesting that normal and inverted tests are comparable. For the C black performer, evaluation after a 2 h inverted RCD test revealed performance and conductance losses (Fig. 6b) which we believe are due to similar factors. The effect is even more pronounced after a longer RCD test or with a low-performance catalyst. All of the anode catalysts we tested are supported on carbon. Unlike in acid, carbon in base is known to have appreciable ORR activity (Table I). Therefore, it is conceivable that a carbon support alone is sufficient to catalyze ORR on the HEMFC anode and trigger RCD, regardless of the “active” metal. To check this possibility we eliminated the metal and tested C black as the catalyst. However, carbon has no HOR activity, an HEMFC with a carbon-only anode would be impossible to evaluate as a fuel cell. Thus, we modified our experimental setup and performed an “inverted” RCD test as follows. A performer was prepared with a Pt/C anode and a C black cathode. After the initial evaluation, for the RCD test the performer was wired to a driver in a cross configuration with anode connected to cathode and vice-versa, so that the Pt/C performer anode would corrode instead of the C black performer cathode (Fig. 10). This indicates slower corrosion; an RCD-immune performer would not decrease the driver’s OCV at all. Note that to prevent oxidation, the Ru/C performer was evaluated at a higher cell voltage (0.5 vs. 0.1 V; see Fig. 4, dashed line). This inconsistency does not compromise the results: the RCD test itself was unchanged, and in a 6 h test the IR of a Pt/C performer increased similarly whether evaluated at 0.5 or 0.1 V (Fig. 9, dashed gray line). But it does explain why the Ru/C cell showed a high IR even before RCD ($t = 0$). At a higher cell voltage, the current is lower, so the cell produces less water and the membrane is less hydrated during evaluation. Water production is also important in the final evaluation regardless of the cell voltage chosen. After RCD the cell is corroded, and so performs worse and produces less water. In turn the electrolyte dries out, which decreases conductivity and additionally may facilitate chemical degradation of the electrolyte during evaluation, since water functions as a diluent. Accelerated degradation of the membrane is apparent in Figure 6a: whereas in the initial evaluation IR remained constant between $t = 10$ min and $t = 30$ min, in the final evaluation IR increased by 0.080 $\Omega \, cm^2$ over the same time period. The effect is even more pronounced after a longer RCD test or with a low-performance catalyst. After a 6 h RCD test, the Ru/C performer showed six times lower IR than the Pt/C performer (1.02 vs. 6.01 $\Omega \, cm^2$, Fig. 9, solid lines). Additionally, during the RCD test itself when the performer and driver cells were shorted together, the open-circuit voltage (OCV) of the two-cell system was higher for the Ru/C performer (Fig. 10). This indicates slower corrosion; an RCD-immune performer would not decrease the driver’s OCV at all.

| Electrode | Anode | Cathode |
|-----------|-------|---------|
| Abundance (wt%) | 43.6 ± 2.6 | 52.7 ± 2.2 |
| | 82.2 ± 0.9 | 14.6 ± 0.3 |
| | 3.7 ± 0.5 | 3.2 ± 1.2 |

### Table II. Elemental composition of catalyst layers in a Pt/C performer cell after a 6 h RCD test.

### Table III. Summary of short-term RCD tests with various performer anode catalysts.

| Performer anode | IR ($\Omega \, cm^2$) |
|-----------------|---------------------|
| $t = 0$         | $t = 2$             |
| Pt/C            | 0.130               | 0.477               |
| Pd/C            | 0.152               | 0.668               |
| Ir/C            | 0.107               | 0.401               |
| Ru/C            | 0.465               | 0.798               |

Figure 8. Scanning electron micrograph of a Pt/C performer MEA (a) before and (b) after a 24 h RCD test. To provide the most direct comparison possible, the performer shown in (a) was held at OCV for 24 h while being fed hydrogen and oxygen. The only difference between (a) and (b) is whether the performer was connected to a driver during the test period to induce RCD.
remaining 70% still indicates significant corrosion, so we conclude that the ORR activity of carbon is sufficient to trigger RCD. Extending the inverted RCD test length to 6 h yielded another moderate IR increase (Fig. 9, dashed blue line). Overall, our results show that like Ru/C, C black alone is ORR-active enough to drive RCD, but at a greatly reduced rate compared to Pt/C. To completely eliminate RCD, carbon-free or supportless anode catalysts may be needed.

In summary, the extent of RCD as judged by IR followed the ORR activity trend from Table I. Pt/C, Ir/C, and Pt/C anodes all caused similar cathode degradation as expected from their similar ORR activities. Catalysts with lower ORR activity, namely a Ru/C anode and, in an inverted test, a C black cathode, caused significantly less degradation than Pt/C.

Conclusions

We have shown that HEMFCs, like PEMFCs, undergo RCD during startup and shutdown. RCD can be curtailed directly without increased system complexity by replacing Pt with an ORR-inactive anode catalyst. Among the alternative platinum-group metals studied, Ru is one promising option due to its lower ORR activity but its tendency to oxidize may limit its practical application.

For this approach to mitigating RCD, HEMFCs are superior to PEMFCs because their lower operating potential supports a wider range of non-precious-metal HOR catalysts, many of which have low ORR activity. Due to its enhanced ORR activity in base, we find that the anode carbon support alone suffices to induce RCD, albeit slowly. We recommend low ORR activity as a new design consideration for the development of HEMFC anode catalysts.

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