High-Repetitive Reversal Tolerant Performance of Proton-Exchange Membrane Fuel Cell by Designing a Suitable Anode

Xiangyang Zhou, Hao Ji, Bing Li,* and Cunman Zhang*

ABSTRACT: Hydrogen starvation of the proton-exchange membrane fuel cell can result in high positive anode potentials followed by cell voltage reversal, which causes water electrolysis and carbon corrosion. A common material-based method is to adopt water electrolysis catalysts to promote water electrolysis over carbon corrosion. While, the membrane electrode assembly shows poor-repetitive reversal performance as the fuel starvation tests are repeated in the previous studies. Herein, IrO$_2$/RuO$_2$ nano-composites are prepared by a modified Adams method and characterized by physical and electrochemical measurement. Then, the as-prepared IrO$_2$/RuO$_2$ is used as an oxygen evolution reaction catalyst in reversal tolerant anodes, and the results exhibit an unexpected repetitive reversal tolerant performance with the voltage reversal times become longer as the increase of fuel starvation tests.

INTRODUCTION

Proton-exchange membrane fuel cell (PEMFC) has gained much attention as a promising candidate for the fuel cell electric vehicle (FCEV) due to its zero emission, high efficiency, and high-power density. Over the last decade, the PEMFC has achieved significant progress, but there are still some obstacles like lower durability, high cost, and insufficient infrastructure that must be resolved before its wide commercialization.

Fuel starvation usually occurs when the FCEV is operated under harsh operating conditions, for instance, rapid load change and subzero start-up with the high hydrogen utilization. When the anode is short of fuel, hydrogen is no longer sufficient to provide the needed protons and electrons, so water electrolysis reaction and carbon corrosion will occur as eqs 1 and 2, respectively

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (1)$$

$$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^- \quad (2)$$

Meanwhile, the carbon corrosion could consume the carbon support, damage catalyst layer, weaken the link of the carbon support and Pt particles, and then lead to the severe agglomeration of Pt particles and degradation of cell performance. Besides, the high anode potential usually produces a significant amount of heat and then results in the membrane electrode assembly (MEA) to be electrically shorted and eventually caused a catastrophic MEA failure.

Many control approaches have been developed to prevent the cell voltage reversal in the past years, and the two main methods are system control and material-based solution. For system control strategies, the fuel cell must be intentionally delayed or stopped when the anode potential increases. Moreover, this approach is complex, expensive and impacts the cell performance and leaves the cell susceptible to reversal damage. Meanwhile, the material-based method, which is typically termed as a reversal tolerant anode (RTA), is much simpler and the prevention mechanism does not need active intervention. The highly active oxygen evolution reaction (OER) catalyst is the key to the RTA, which promotes water electrolysis reaction over carbon corrosion. Moreover, the properties of the RTA can be evaluated by the following four aspects: the influence of the RTA on the initial electrochemical performance of the MEA, the first voltage reversal time (VRT), the degradation rate of the MEA before and after the fuel starvation test, and the accumulated VRTs calculated by summing all individual VRTs. But until now, most of the existing research studies have little focus on the accumulated VRTs and the VRT becomes very short after

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the first fuel starvation test. This indicates that the MEA assembled by a reversal tolerant anode shows poor-reversal tolerant performance and the water electrolysis catalysts become deactivated when the fuel cell is operated under repetitive reversal events. Besides, the existence of CO₂ or CO in exhaust gas is not provided in most studies.

Herein, in this manuscript, we designed a MEA with high-repetitive reversal tolerant performance using Pt/C–IrO₂/RuO₂ nanocomposites as an RTA, the electrochemical properties (i.e., polarization, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)), voltage reversal behavior and the volume percentage of CO₂/CO in exhaust gas were investigated. Better than the previous literature reports, the VRT becomes longer as the fuel starvation tests are repeated. Moreover, the accumulated VRT was 78 h, which is almost the longest time in all studies.

RESULTS AND DISCUSSION

Figure 1a shows the X-ray diffraction (XRD) pattern of the OER catalyst; it is quite obvious that the lattice of the as-prepared OER catalyst is similar to the tetragonal rutile structure (JCPDS 15-0870), with typical peaks at about 28°, 35° and 54° represent the (110), (101) and (211), respectively. This indicates that the IrO₂/RuO₂ nanocomposites with the tetragonal rutile structure were successfully prepared via the modified Adams fusion method. Also, the average crystalline size of the OER catalyst is 19 nm, which is calculated by Debye–Schererr. The morphology of the OER catalyst is characterized by scanning electron microscopy (SEM) and shown in Figure 1b, which exhibits numerous bulk and sheet-shaped particles in different sizes.

The electrochemical performance of the OER catalyst has a great influence on the reversal performance of the MEA under fuel starvation, so the CV and LSV curves of the OER catalyst are shown in Figure 1c,d. At voltammograms below 0.4 V, the desorption of H and underpotential deposition occur. In the oxygen region of potential above 0.4 V, the OER catalyst causes the adsorption–desorption of OH groups. Besides, the electrochemically active surface area (ECSA), calculated from 0.4 to 1.4 V in Figure 1c, of the OER catalyst is 227 C g⁻¹. Also, the potential is 1.564 V at the current density of 10 mA cm⁻². This result indicates that the as-obtained OER catalyst is a good candidate for the application of the MEA during fuel starvation.

To investigate the influence of the addition of the OER catalyst in the PEMFC catalyst, we compared the electrochemical performance of JM and JM-O catalysts and the results are displayed in Figure 1c,d. It is quite clear that the CV curves are similar in shape of the two catalysts, but the Pt−H adsorption and desorption peaks position shifted to the left by approximately 0.02 V after the addition of the OER catalyst. The ECSAs, which calculated by the charge transfer of hydrogen desorption and adsorption, of JM and JM-O catalysts before accelerated degradation testing (ADT) cycles of the durability test, the JM catalyst exhibits a great loss of 20.3% in the ECSA, whereas the JM-O catalyst exhibits a loss of 16.4%. The half-cell test shows that the addition of the OER catalyst in JM can improve durability and has just an 18 m² g⁻¹ decrease in the ECSA.

The rotating disk electrode (RDE) test indicates that the addition of the OER catalyst may have not much influence on the electrochemical performance of the MEA, so the initial electrochemical performance of the two MEAs (MEA-1 and MEA-2) were performed. As shown in Figure 2a, the polarization performance of MEA-1 shows a bit better, and its performance parameters are presented in Figure 2c. Under the current density of 1000 mA cm⁻², its cell voltage is 0.697 V, which is 5 mV higher than that of MEA-2. Besides, its maximum power density is 941.4 mW cm⁻², which is 35.8 mW cm⁻² higher than that of MEA-2. In situ CV curves as well as ECSA parameters of MEAs are presented in Figure 2b,d. It is quite clear that the CV curves at the cathode of two MEAs almost overlap, and the ECSAs are 63 and 61 m² g⁻¹ for MEA-1 and MEA-2, respectively. However, the ECSA at the anode of MEA-1 is 55 m² g⁻¹, which is 10 m² g⁻¹ lower than that of MEA-2. This may be due to the addition of the OER catalyst, which can improve the ECSA of the catalyst, increase the Ohmic impedance, and then decrease the electrochemical performance at high current densities. Through the comparison of the MEA initial single-cell performance of MEAs, it can confirm that after the introduction of the OER catalyst at the anode, the electrochemical performance of the MEA has a little drop and is much better than that of ref 18.

The as-prepared RTA has not much influence on the initial electrochemical performance of the MEA, while it can obviously improve the reversal performance under fuel starvation. As observed in Figure 3a, MEA-1 can only survive for about 0.67 min, while the VRT of MEA-2 is about 66 min. Besides, it can be seen that, upon starting, the cell voltage suddenly dropped to approximately −0.8 V followed by slowly decreasing to about −1.3 V, which can be attributed to the OER, water electrolysis, and minor carbon oxidation. In the previous studies and in this manuscript, along with the increase of the reversal time, the OER catalyst becomes
deactivated and the cell voltage rapidly declines to $-2.0\, \text{V}$. Also, this can be proved by the analysis of exhaust gas in Figure 4, which also indicates that the carbon oxidation process mainly occurs as $\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + 2\text{H}^+ + 2\text{e}^-; \quad E_0 = 0.518\, \text{V}$ versus SHE. As mentioned above, the carbon corrosion can degrade the fuel cell performance. Meanwhile, Figure 3b shows a slow drop of the cell voltage and power densities at different current densities, for example, the potential decrease values are only 5 and 24 mV for MEA-1 and MEA-2 at 1000 mA cm$^{-2}$, respectively. This can be owing to the short reversal time for MEA-1.

To evaluate the repetitive reversal performance and obtain accumulated VRTs of MEA-2, fuel starvation tests were conducted four times. Figure 5a shows accumulated voltage reversal time series of cell voltage during fuel starvation tests. For a clear presentation, the first two times of reversal tests are shown in the inset. The as-prepared MEA-2 shows an unexpected repetitive reversal tolerant performance with VRTs of 66, 194, 1614, and 4693 min for the four reversal tests individually. This discovery shows almost the best repetitive reversal performance and the longest accumulated VRT until now. Subsequently, the reversal tolerant declines significantly as the fuel starvation tests are repeated in the previous studies. The reasons for high-reversal tolerant performance will be explained in detail later. Moreover, the high voltage (approximately 0.7 V) at the cathode can cause carbon corrosion and lead to performance degradation. As described above, shown in Figure 5b,c, after the first reversal test, the cell voltage degradation and degradation rate at 1.0 A cm$^{-2}$ are only 24 mV and 3.5%, respectively. Meanwhile, the cell performance rapidly decreases after the second fuel starvation test, which can be attributed to the carbon corrosion (both at the anode and cathode) and the increase of Ohmic resistance during the long VRTs. The EIS at 0.2 A cm$^{-2}$ (Figure 5d) also illustrates the same result. Ohmic resistances at high frequencies, measured by the intercept of the real axis
related to its total mass content, distribution, "the repetitive fuel starvation tests can be owe to the high starvation tests.

wt % ratio of Pt:C increases to 4.42 after the 4th time fuel interface

EDX combined with SEM, the results (Table 1) show that the percentage of the elemental composition was analyzed by the leads to the aggregation of Pt particles. Besides, the mass carbon corrosion, which destroys the framework of carbon and distribution and the content of the OER catalyst. Moreover, the electrochemical performance of the OER catalyst is not

affected by the content and the distribution of the OER catalyst. Therefore, the mass activity and specific activity of the OER catalyst as well as the better “three-phase interfaces” are the main reason for the high-reversal tolerant performance of the MEA.

As mentioned above, carbon supports in the anode catalyst layer oxide to carbon monoxide and carbon dioxide during fuel starvation test. Then, more active sites of the OER catalyst are exposed in the catalyst layer, followed by increasing the mass activity and specific activity as well as the utilization rate of the catalyst. Besides, a better “three-phase interfaces” may be formed after carbon corrosion where protons, electrons, and water can simultaneously interact with the OER catalyst.

■ CONCLUSIONS

In summary, the IrO2/RuO2 catalyst was synthesized by a modified Adams method, then characterized by physical and electrochemical evaluation before used as an additive at the anode for the MEA. In the half cell, the Pt/C (JM) catalyst with the addition of the OER catalyst exhibits improved durability and a little decrease in activity. In addition, the cell voltage at 1000 mA cm−2 and the maximum power density under normal operation were just decreased 2.8 and 8.7% by adding a 20 wt % IrO2/RuO2 nanocomposite to the anode electrode. While MEA-2 shows an unexpected repetitive reversal tolerant performance, the VRT becomes longer as the fuel starvation tests are repeated and the accumulated VRTs can reach up to 78 h. This could be due to the increase of mass activity, specific activity, and utilization rate of the OER catalyst as well as the better “three-phase interfaces” during the reversal tests. As a result, the prepared MEA using the Pt/C–IrO2/RuO2 nanocomposite catalyst could be a good candidate for FCEVs.

■ EXPERIMENTAL SECTION

Material Synthesis and MEA Fabrication. IrO2/RuO2 nanocomposites (OER catalyst) were synthesized through the modified Adams method. Briefly, 20 g of sodium nitrate, 0.17 g of ruthenium trichloride, and 0.196 g of chloroiridic acid were stirred in 20 mL of isopropyl alcohol for 8 h to ensure that the mixture was well distributed. Then, after completely dried

\begin{align*}
\text{Voltage} & \quad \text{reversal behavior of single cell during fuel starvation test: (a) cell voltage behavior during cell reversal tests. (b) Cell polarization curves before and after each fuel starvation tests. (c) Normalized cell voltage at 1.0 A cm}^{-2}. (d) EIS of fuel cell before and after each reversal test.
\end{align*}
under the vacuum state at 80 °C, the mixture was calcinated at 400 °C for 1 h. Finally, the product was washed by centrifugal separation with excessive deionized water and ethanol followed by freeze drying overnight.

Catalyst-coated membrane (CCM)-type MEAs where the catalyst slurry was directly sprayed on the membranes (Gore, active area of 25 cm²) were used in this research. The slurry for the cathode was prepared by complete mixing 5 wt % Naflon solution (Dupont), isopropanol, ultrapure water, and 60 wt % Pt/C catalyst (Johnson Matthey HiSpec 9100). The difference between MEA-1 and MEA-2 is 20 wt % IrO₂/RuO₂ with respect to the Pt/C catalyst was added to the anode of MEA-2, and the mass ratio of Naflon and catalyst is 1:3. The Pt loadings of the cathode and anode were 0.4 and 0.2 mg cm⁻², respectively. Then, the MEAs were fabricated by fixing a pair of

Table 1. EDX Analysis on the Element Ratios from Selected Areas of the Anode Catalyst Layer of the Four MEAs

| element | reversal 1 (wt %) | reversal 2 (wt %) | reversal 3 (wt %) | reversal 4 (wt %) |
|---------|------------------|------------------|------------------|------------------|
| C       | 39.69            | 32.14            | 27.19            | 15.14            |
| O       | 5.75             | 5.19             | 6.42             | 4.54             |
| Ir      | 8.12             | 9.97             | 9.36             | 9.56             |
| Ru      | 3.89             | 3.6              | 4.51             | 3.86             |
| Pt      | 42.55            | 49.09            | 52.51            | 66.94            |

Figure 6. SEM images of MEA after fuel starvation: reversals (a) 1, (b) 2, (c) 3, and (d) 4 for anode.

Figure 7. (a) SEM images and (b) EDS mapping of MEA-2 after four time reversal tests.
During the polarization and EIS measurements, the inlet gases fuel cell testing system; the cell temperature was fuel starvation tests were all measured on a Greenlight (G20) di
catalyst was collected by a Philips PW 3040/60 powder
diffraction with Cu Kα radiation at a rate of 0.05° s−1 from
to 90°. The morphologies of the OER catalyst and the tested MEA were observed by SEM equipped with an energy-dispersive X-ray spectrometer (EDX).

Electrochemical Evaluation. The RDE test at room temperature was used to investigate the electrochemical performance of catalysts. A 2 mg catalyst was suspended in 4.0 M NaOH/isopropanol solution (1:30 wt %), followed by ultrasonic dispersion for 1 h to make catalyst ink. The ink (6 μL) was deposited onto a glassy carbon disk electrode (GCE, 0.196 cm²). The electrochemical performance of the OER catalyst was investigated in a glass cell filled with 0.5 M H₂SO₄ in a three-electrode system. CV and LSV were carried out under N₂-saturated solution at a scan rate of 50 mV s⁻¹ by sweeping from 0.05 to 1.4 V versus RHE and 5 mV s⁻¹ from 1.2 to 1.75 V versus RHE. The JM catalyst with (named JM-O) and without an OER was investigated in a glass cell filled with 0.1 M HClO₄ in a three-electrode system. CV was carried out under N₂-saturated solution at a scan rate of 50 mV s⁻¹ by sweeping from 0.05 to 1.15 V versus RHE. LSV from 0.05 to 1.15 V versus RHE was measured under O₂-saturated solution at a scan rate of 5 mV s⁻¹ at 1600 rpm. ADT was conducted between 0.6 and 1.1 V versus RHE for 5000 cycles at a scan rate of 100 mV s⁻¹ to evaluate the stability of the different catalysts.

The current density—voltage polarization curves, EIS, and fuel starvation tests were all measured on a Greenlight (G20) fuel cell testing system; the cell temperature was fixed at 80 °C. During the polarization and EIS measurements, the inlet gases were H₂ and air for the anode and cathode, respectively; the gas pressure and flow ratio of the anode and cathode were 130/120 kPa and 1.7:3, respectively; and the relative humidity was 80% for both the anode and cathode. EIS was carried out at a current density of 0.2 A cm⁻² using a frequency range from 0.1 Hz to 1 kHz.

Before the fuel starvation test, the fuel cell was operated for 1 h under the condition with N₂/air, 130/120 kPa pressure, 0.3/0.3 slpm, and 100%/100% relative humidity inlet gases for anode/cathode to ensure that there is no impurity gas exist. During the reversal tests, a constant current density of 0.2 A cm⁻² was applied to the cell, thus simulating the generation and movement of protons and electrons during the fuel cell operation. The volume percentage of CO₂/CO in exhaust gas at the anode was measured by a gas mass spectrometer. The stack voltage was recorded, and the cell would shut down when the stack voltage reached −2.0 V. Then, the cell polarization and EIS were performed the next day; besides, the fuel starvation test was repeated until the cell voltage at a 1.0 A cm⁻² decrease to approximately 30% or the number of fuel starvation tests meet the need for the scientific research in this work.

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catalyst for automotive polymer electrolyte fuel cell anodes. *J. Electrochem. Soc.* 2018, 165, F3094–F3099.

(16) Mandal, P.; Hong, B. K.; Oh, J. G.; Litster, S. Understanding the voltage reversal behavior of automotive fuel cells. *J. Power Sources* 2018, 397, 397–404.

(17) Mandal, P.; Hong, B. K.; Oh, J.-G.; Litster, S. 3D Imaging of Fuel Cell Electrode Structure Degraded under Cell Voltage Reversal Conditions Using Nanoscale X-Ray Computed Tomography. *ECS Trans.* 2015, 69, 443–453.

(18) Jang, I.; Hwang, I.; Tak, Y. Attenuated degradation of a PEMFC cathode during fuel starvation by using carbon-supported IrO$_2$. *Electrochim. Acta* 2013, 90, 148.

(19) Zhou, F.; Andreasen, S. J.; Kær, S. K. Experimental study of cell reversal of a high temperature polymer electrolyte membrane fuel cell caused by H$_2$ starvation. *Int. J Hydrogen Energy* 2015, 40, 6672–6680.