



Short communication

Micro-protective layer for lifetime extension of solid polymer electrolyte water electrolysis

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ABSTRACT

This study uses the reverse electrochemical reaction of Proton Exchange Membrane (PEM) fuel cells, called PEM water electrolysis to produce high concentration hydrogen and oxygen (both 99.99%). The proposed technique can decrease carbon dioxide (CO₂) emissions. However, the oxidation and corrosion of the catalysts and gas diffusion layer (GDL) of the anode side remain challenging problems. The carbon fiber is used as the gas diffusion layer for PEM water electrolysis owing to its low density and porosity as well as its good conductivity even under low compression. Noble metal catalysts are coated with a micro-protective layer (MPL) on one side of the gas diffusion layer to extend the lifetime of PEM water electrolysis. The lifetime can reach over 2000 h at high current density (1400 mA cm⁻²) that is ten times longer than that of a sample coated only with carbon black (XC-72) as the microporous layer. The proposed micro-protective layer can transform active oxygen species to harmless oxygen gas and increase the catalyst's resistance to corrosion and oxidation during water electrolysis.

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1. Introduction

The population growth and continuous development of technology have increased the global usage of petrochemical products. However, a shortage of petroleum, rising energy prices, and global warming are increasing the need for alternative energy methods with pollution-free characteristics and high-energy efficiency. Hydrogen is widely considered the most promising green energy. Fuel cells [1–5] that can directly convert the chemical energy of fuel into DC electricity are widely expected to be used in future energy systems. The electrochemical reaction of fuel cells with hydrogen and oxygen can generate electricity and pollution-free byproduct, water that can be decomposed into hydrogen and oxygen through water electrolysis. Of all the possible approaches to produce hydrogen; pure water electrolysis with a solid polymer electrolyte (SPE) is the most effective and cleanest method [6–8]. General Electric Co. developed the first SPE electrolyser to split water into hydrogen and oxygen gases for space allocations in 1966 [9]. Moreover, the purity of hydrogen or oxygen could reach 99.99% because only de-ionized water (DI water) is used. Along with the development of fuel cells, the SPE electrolyser is able to combine with the solar cell and wind turbine to form an energy storage system to recycle water and be a renewable energy source [10].

Unfortunately, a key component of the electrolytic cell, the gas diffusion layer, corrodes during water electrolysis. The gas diffusion layer is fabricated by either porous carbon materials (e.g., carbon cloth or carbon fiber paper), or metals (e.g., Ti or Ni). The carbon-made gas diffusion layer is lightweight, cheap, and has a small volume. However, it reacts easily with the active oxygen species at high temperatures or potentials. The anode is corroded due to the formation of carbon monoxide or carbon dioxide [11–13]. Previous experiments used non-carbon gas diffusion layer, GDL and metal catalysts (titanium, nickel, and so on) to replace carbon-made GDL [14]. Unfortunately, the effects were relatively limited owing to the formation of the oxidized layer to increase the internal resistance after testing for several hours.

The metallic diffusion layer has a superior resistance to corrosion, however, it still forms an oxidized layer to increase the impedance of the metallic diffusion layer during water electrolysis. Thus, a carbonic diffusion layer is typically applied to fuel cells, whereas water electrolysis devices use a metallic layer due to a high potential for resistance to oxidation and corrosion.

Fuel cells and water electrolysis devices are individual systems and applications. However, this study presents that a novel micro-protective layer (MPL) coated on a carbon-made gas diffusion layer is invented to combine these two devices and test on a novel device to improve the original defects [15–17]. The MPL process is similar to the conventional process, a coating of microporous layer on the gas diffusion layer. This normally involves XC-72, which can enhance the conductivity, prevent the catalyst layer from

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delamination, and reduce the contact resistance of fuel cells. MPL also plays a key role in enhancing the resistance to corrosion and oxidation and transforming the active oxygen species to oxygen gas. This effectively extends the lifetime of an electrolytic cell under high current density even after testing for 1000 h.

2. Experiment

2.1. Catalyst-coated membrane

The experiment was performed using a self-fabricated electrolytic cell (25 cm² active area) and NRE-212 (50 μm thick, Du Pont) as the solid electrolyte to obtain enhanced performance. The catalyst-coated membrane (CCM) [18–20] was prepared using platinum black (3 mg cm² and 20 wt.% of ion-exchange polymer, Nafion solution in a partial water and alcohol solution) as the cathodic catalyst, and iridium black (catalyst loading and weight percent of ion-exchange polymer is the same as platinum black) as the anodic catalyst. Catalytic mixtures were directly sprayed onto the each side of the Nafion membrane. Spraying membrane would be the optimal method because of the achievement of uniform coating and deep penetration to enhance the performance of water electrolysis. After catalysts were coated, the membrane was dried in vacuum at 80 °C for 1 h.

2.2. Micro-protective layer

A conventional microporous layer was coated with carbon black (XC-72) and polytetrafluoroethylene (PTFE). At the beginning, the untreated GDL was immersed in 5–10% of PTFE solution, and then placed in an oven at an elevated temperature about 350 °C for 1 h to form a waterproof layer. After the waterproof process, carbon black and PTFE were mixed with DI water as the spraying ink. Because the treated GDL became waterproof, the spraying ink was only coated on the surface of the waterproof GDL to form a microporous layer and then it was placed in an oven at 350 °C for 1 h.

The innovative micro-protective layer in this study has a slightly different fabrication procedure from the conventional one. First, the mixture of iridium black, PTFE solution (10 wt.%) and DI water was sprayed onto the untreated carbon paper (Toray TGP-H-090, 280 μm thick) and the loading of iridium black is 3 mg cm². Because the carbon paper is not waterproofed, a small amount of iridium black was sprayed inside, with most of it collecting on the surface. The GDL-coated MPL was then placed in an oven at 350 °C for 1 h. Fig. 1 shows the difference in the structures between these two processes described above.

The CCM was sandwiched between two GDLs (one coated MPL) by a hot-pressing procedure at 20 kg cm⁻² and 130 °C for 3 min to fabricate the membrane electrode assembly (MEA) as shown

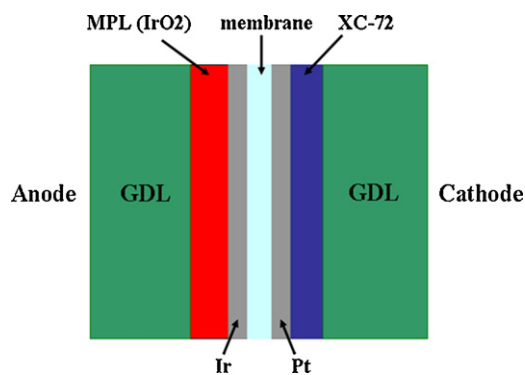


Fig. 2. A standard membrane electrode assembly (MEA) structure. The MPL replaced a microporous layer on the anode side, where the active oxygen species were generated during the water electrolysis reaction.

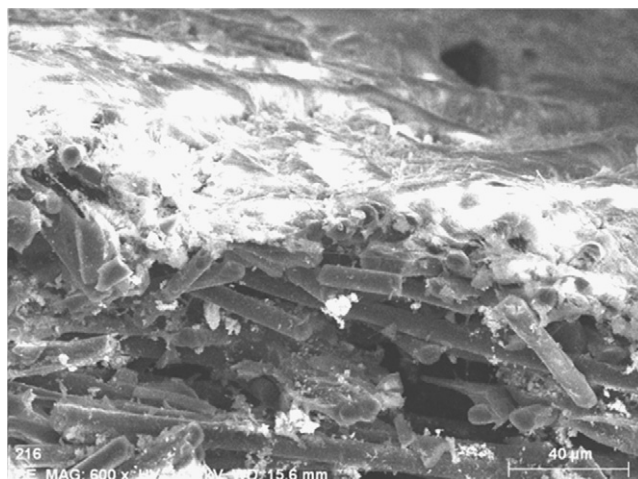


Fig. 3. Cross-section of carbon paper and micro-protective layer. This structure is identical to that shown in Fig. 1(b).

in Fig. 2. The hot-pressed GDL with CCM improved the adhesion to the membrane and reduced contact resistance. However, the mechanical strength and lifetime of the membrane were decreased by the MEA combined with carbon-made GDL. The MEA was then mounted between two flow field plates and current collectors.

In theory, noble metals such as iridium (Ir), iridium dioxide (IrO₂), platinum (Pt), and palladium (Pd) [21–24] can be used as MPL materials. This study used iridium black as the precursor of iridium oxide because of its conductivity, even after heat treatment at high temperature. Fig. 3 shows a SEM (Scanning Electron Microscope) micrograph of the advanced MPL that the catalytic mixture

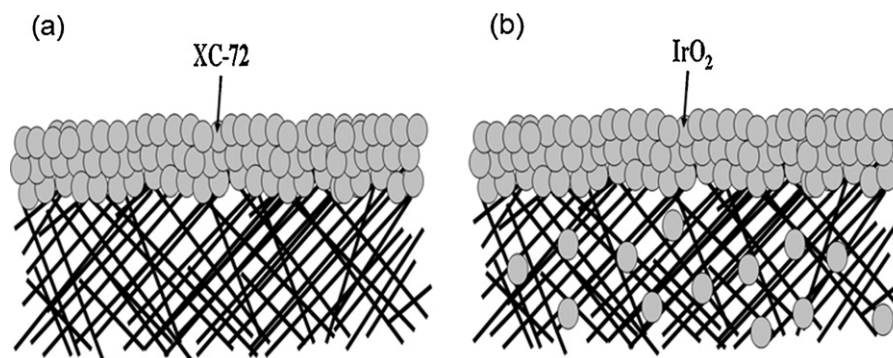


Fig. 1. (a) Schematic cross-section of a conventional microporous layer. XC-72 is almost on the surface of the GDL. (b) Schematic cross-section of self-fabricated MPL coated on one side of the untreated GDL. Partial iridium dioxide (IrO₂) was permeated into the GDL to provide enhanced protection around the carbon structure.

Table 1
EDX elemental analysis of MPL coated carbon fiber.

El	An	Series	Unn. C (wt.%)	Norm. C (wt.%)	Atom. C (at.%)	Error (wt.%)
F	9	K-series	62.46	43.82	37.42	6.7
C	6	K-series	56.88	39.91	53.90	6.3
Ir	77	K-series	9.14	6.41	0.54	0.4
O	8	K-series	7.29	5.11	5.18	0.9
Al	13	K-series	5.37	3.77	2.27	0.3
Na	11	K-series	0.90	0.63	0.44	0.1
Mg	12	K-series	0.50	0.35	0.24	0.1

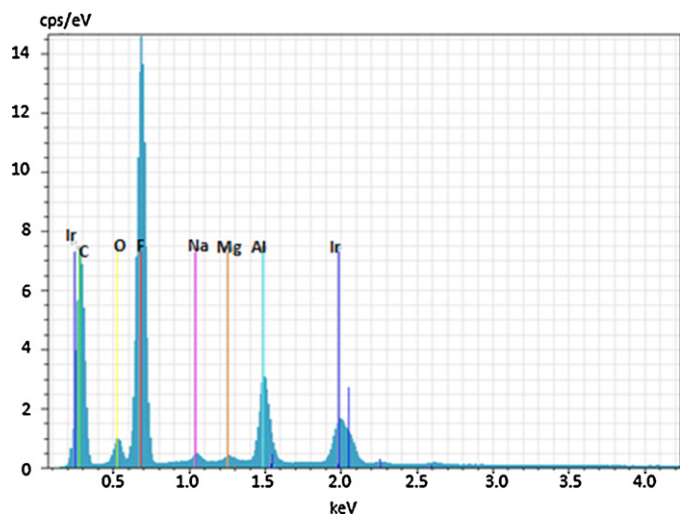


Fig. 4. EDX result of MPL coated carbon fiber. The majority elements are F and C, which are from PTFE and carbon paper, respectively. Iridium is completely replaced conventional carbon black, which is coated on the carbon paper as the microporous layer.

is partially permeated inside to enhance the bonding strength between GDL and MPL, and the EDX elemental analysis of MPL shown in Fig. 4 and Table 1 presents that the major elements are F and C, which are from PTFE and carbon paper, respectively.

3. Results and discussion

The MEA performance of water electrolysis was measured at ambient environment. Similar to fuel cells, the proposed MEA

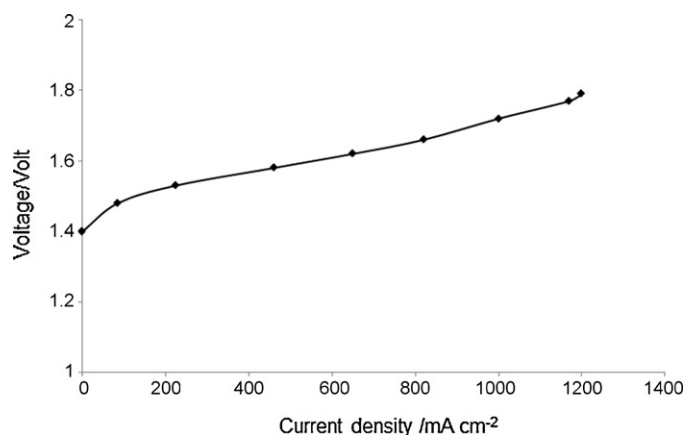


Fig. 5. Current–voltage performance of self-fabricated CCM with MPL operated at ambient atmosphere pressure and room temperature. Anode catalyst loading: Ir 3 mg cm⁻²; cathode catalyst loading: Pt black 3 mg cm⁻².

required time to activate the catalysts in the beginning. In theory and practice, the reaction activity of the catalysts could be enhanced while increasing the temperature to improve the performance of SPE water electrolysis [25,26]. However, this study focuses on the effects of MPL lifetime extension at high current density. Therefore, the water electrolytic unit cell operated at high current density and ambient environment during water electrolysis reaction. Fig. 5 shows the voltage profile with different current densities. The hydrogen production rate depended on the current. For the lifetime test, the maximum current was set 40 A (around 1400 mA cm²), meaning that the water electrolytic cell could generate hydrogen at approximate rate 300 ml min⁻¹.

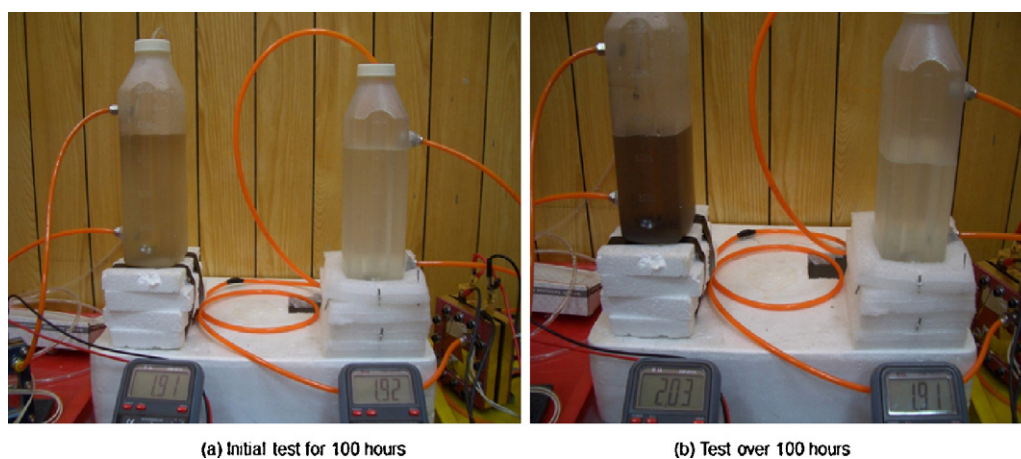


Fig. 6. The two water electrolytic cells were initially exhibited roughly the same performance when operating at 1400 mA cm⁻². However, the color of the left tank turned into brownish color for 100 h as shown in (a). The voltages and colors of the two cells showed marked differences after testing over 100 h as shown in (b). The right cell with MPL protection still operated at the expected voltage (1.91 V) and current density (1400 mA cm⁻²), and the water was still clear. However, the degradation of the left cell was visible. The water tank exhibited in dark brown and the voltage rose to 2.03 V.

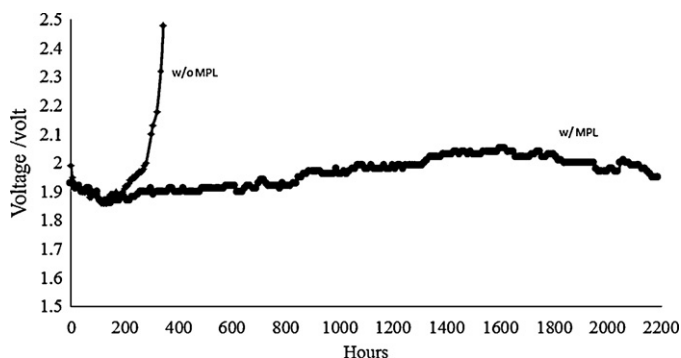


Fig. 7. Time–voltage curves measured at current density 1400 mA cm^{-2} . The lifetime of the sample without MPL is deteriorated rapidly after 200 h, and the lifetime of the sample with MPL can extend to more than 2000 h.

Another water electrolytic unit cell using two GDLs with microporous layers coated with XC-72 was operated under the same conditions. To determine MPL resistance to corrosion and oxidation and its ability to transform active oxygen species into harmless oxygen gas, the catalyst layers for both cells were the same.

The performance of these two SPE water electrolytic cells was roughly equal for the first 100 h. However, a huge difference in the color of water appeared later; the tank connected to the water electrolytic cell with MPL contained clear water. The other water tank became a brownish color because the carbon corroded the GDL structure and XC-72 microporous layers as shown in Fig. 6(a), reacting with the active oxygen species to form CO or CO₂. A substantial amount of the carbon structure separated, rendering the water black as shown in Fig. 6(b). The corrosion became more evident thereafter, as the performance of the water electrolytic cell without MPL worsened.

The two water electrolytic cells operated at the same conditions of 1400 mA cm^{-2} , and the power was not turned off until the last lifetime tests. The voltage of the cell without MPL protection increased to 2.5 V after 200 h, and water tank turned dark brown. We then stopped the lifetime test of the water electrolytic cell without MPL. The performance of the water electrolytic cell with MPL matched the expectation because the MPL provided outstanding protection and further transformed the active oxygen species into oxygen to prevent from reacting with GDL. Though water electrolysis occurred over more than 2000 h, the water remained relatively clean. The lifetime comparison of the water electrolysis with and without MPL protection as shown in Fig. 7 shows that the voltage profile of electrolysis with MPL protection was still stable after 2000 h; however, the voltage profile of the electrolysis without MPL protection substantially increased after 200 h test. It means that the surface of GDL has oxidized to increase the internal resistance.

4. Conclusion

Water electrolysis has been used to produce hydrogen for decades [27–30]. Favorable considerations for the commercial use of water electrolysis include its low weight, high performance, and relatively low price. The cost of catalyst, iridium black is lower than that of commercial platinum black. In the viewpoint of the hydrogen volume generated, the hydrogen volume generated from the cell without MPL is needed several MEAs to reach the same hydrogen volume generated from the cell with MPL and single MEA. The cost of raw materials of the cell without MPL is much higher than that of the cell with MPL. The academic point of view to reduce the cost is to increase the surface to volume ratio of the catalyst [31–33]. When the surface to volume ratio reaches the maximum, the cluster size of catalyst achieves the minimum or

a monolayer, hence the rapidest reaction can be achieved. There are different methods to reduce the cluster size of catalyst and increase the surface to volume ratio as well as the specific surface area (BET). The method of the electrostatic stabilization of catalyst is to charge the metallic ions to prevent from aggregation and then these charged ions are reduced by the reducing agent, strong electron donors to form nanoparticles. The other method called, steric stabilization is to put long molecular chains onto each ion that is pushed away from each other. Also these two methods can be combined to prevent the catalyst from agglomeration [34–37]. The loading of the catalyst can be reduced due to the smaller cluster size.

The experiment in this study used almost the same components and structures as PEM fuel cells, and coated a MPL on one side of the GDL to prevent it from corroding and oxidizing under high current density condition. As expected, the MPL shows outstanding protection in this experiment to extend the lifetime over more than 2000 h at high current density, 1400 mA cm^{-2} , which is almost 10 times longer than that of the other water electrolytic cell without MPL protection. The MPL can be made from iridium, iridium dioxide, platinum, ruthenium, and so on. Iridium dioxide was chosen as the material for the MPL because it is still conductive after the heat treatment process at 350°C . Iridium oxide also has anticorrosion and antioxidation effects, and can transform active oxygen species into harmless oxygen gas.

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