Short communication

Performance of gold-coated titanium bipolar plates in unitized regenerative fuel cell operation

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ABSTRACT

The corrosion of the carbon-based bipolar plate was studied under unitized regenerative fuel cell (URFC) operation conditions. At overpotentials higher than 2.0 V vs. normal hydrogen electrode (NHE), cell performance in the electrolyzer mode significantly decreases with time due to the increased ohmic resistance of the carbon-based bipolar plates. During fuel cell operation, the unit cell shows an ohmic resistance of approximately 0.15 Ω. After the operation in the electrolyzer mode, the ohmic resistance of the cell increases up to 1.24 Ω. The surface image of the carbon-based bipolar plate after water electrolysis reaction at 2.0 V shows a drastic corrosion at the contact area of the bipolar plate with the electrode. The corrosion of the rib in the flow-field increases the contact resistance between the electrode and the bipolar plate, which leads to the observed decrease in cell performance. A gold coating of 1 μm on the titanium bipolar plates is very effective in preventing titanium oxidation during the URFC operation. The ohmic resistance of the cells that are prepared with bare titanium and gold-deposited titanium bipolar plates is 0.40 Ω and 0.18 Ω, respectively. In fact, the gold coating serves as a barrier layer, which inhibits the formation of the passive layer on the surface of titanium-based bipolar plates. The cycling experiments in the fuel cell and in the electrolyzer mode indicate that the gold-coated titanium bipolar plates exhibit a stable performance.

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1. Introduction

Bipolar plates are one of the most important components in the unitized regenerative fuel cell (URFC). In addition to distributing the fuel, the bipolar plates serve as separators, current collectors and supports for the membrane/electrode assembly (MEA). The plates also play an important role in heat and water management in URFCs. In order to perform these functions, the bipolar plates should be non-permeable, highly electrical- and thermal-conductive, non-brittle and corrosion resistant [1–3].

Carbon-based materials have been previously used as bipolar plates in the fuel cell due to their high electrical conductivity, good hydrophobicity and chemical stability [1]. However, problems with using carbon-based materials as bipolar plates for the URFC include their poor mechanical strength, poor manufacturability, high cost and very high corrosion rates at high positive overpotentials [4]. The high carbon corrosion decreases the thickness of the bipolar plate, leading to a decrease in the electrical contact between the electrode

and the bipolar plate, which results in a subsequent increase in the ohmic resistance. In addition, oxidation of the carbon surface leads to a decrease in the hydrophobic properties of the carbon bipolar plate. This affects water management in the fuel cell, leading to increased mass transport losses [1,5–7]. These effects cause the performance of the URFC to degrade quickly, resulting in a poor lifetime.

In order to solve these problems, metal-based bipolar plates have been studied recently [1–3]. It is anticipated that the metal-based materials have high mechanical strength, non-permeability, excellent manufacturability and cost-effectiveness. Stainless steel, aluminum and titanium have been seriously considered as the materials for manufacturing the bipolar plates [1–4,8–12].

Titanium is one of the best base material candidates for the bipolar plate of the URFC due to its sturdiness in a highly acidic and humid condition with no corrosion at high positive overpotentials. However, it is expected that when using titanium-manufactured bipolar plates, a passive oxide layer will form, which will increase the contact resistance between the electrode and the bipolar plate, resulting in a poor cell performance [2,11,12].

To overcome this problem, precious metal coatings, such as platinum and gold, have recently been applied to protect the titanium surface from oxidation in a polymer electrolyte membrane fuel cell (PEMFC) [11,12]. In this study, the effect of gold coating on the performance of the titanium bipolar plate is investigated under more

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severe conditions in the URFC. This study describes the performance of the URFC fabricated with gold-coated bipolar plates.

2. Experimental

2.1. Preparation of gold-coated bipolar plate

Titanium blocks (98.9% purity, 7.5 cm × 7.5 cm × 1.2 cm) were used as the bipolar plates. The bipolar plates were machined to form serpentine type flow-fields with a surface area of 5 cm². The depth of the channel in the flow-field was 1 mm. To accomplish a better adhesion of gold on the titanium plate, the titanium plate was mechanically polished with finer grades of grinding papers (SiC grinding paper #2400) on a surface grinder (Phoenix Alpha grinder, BUEHLER). Prior to the gold coating, the titanium plate was immersed in concentrated sulfuric acid (96%) for 1 min and washed with de-ionized water. A Denton Desk II Sputter Coater was used to deposit the gold coating. This system uses a direct current (DC) power source to form the plasma. The basic vacuum pressure was less than 50 mPa. The thickness of the film was measured by a micrometer on a standard smooth surface.

2.2. Characterization studies

The titanium bipolar plates were characterized by XRD and SEM. The formation of the titanium oxide layer was identified by the X-ray diffraction method using a Rigaku D/max-rc (12 kW) equipped with a rotating Cu anode and a monochromator in a scanned range of 20–80° (2θ). The surface morphology of the titanium bipolar plate after gold coating was investigated by an FEI Quanta 200 Environmental Scanning Electron Microscope.

2.3. MEA preparation

In this study, Nafion 112 was used for the MEA preparation. A commercial E-TEK electrode (30 wt% Pt on Vulcan XC-72, 0.5 mg cm⁻² Pt loading) was used as the anode. The cathode consisted of unsupported Pt black catalyst with a loading of 4 mg cm⁻² Pt prepared by using a brushing technique. The cathode for the cycle test was prepared with unsupported $Pt_{85}Ir_{15}$ catalyst with a loading of 4 mg cm⁻². The PtIr catalyst was physically mixed with 85 wt% of platinum (E-TEK Pt black catalyst) and 15 wt% of Iridium black catalyst, and then applied to the home-made gas diffusion layer (GDL) with microporous layer (MPL). Nafion content in the catalyst layer was 20 wt%. The electrodes and the membrane were assembled by hot-pressing them at 140 °C and 800 psi for 3 min.

The URFC performance was characterized by using a single cell with an electrode area of 5 cm². The cell temperature was maintained at 75 °C. In fuel cell mode, hydrogen and oxygen, humidified to 100% RH were supplied to the anode and the cathode, respectively. In electrolyzer mode, de-ionized water was supplied to the bifunctional oxygen electrode. The I–V curves of the URFCs were galvanostatically measured by using a power supply [13,14]. The schematic diagram for URFC operation is shown in Fig. 1.

3. Results and discussion

Initially, the corrosion of the carbon-based bipolar plate was studied in electrolyzer mode. Positive overpotentials higher than 2.0 V were applied to the cell for 1 h. As shown in Fig. 2(a), the fuel cell performance significantly decreases with time in electrolyzer mode, due to the increased ohmic resistance. During fuel cell operation, the unit cell showed an ohmic resistance of approximately 0.15 Ω. After operating in electrolyzer mode, the ohmic resistance of the cell increased to 1.24 Ω. Fig. 2(b) shows the surface image
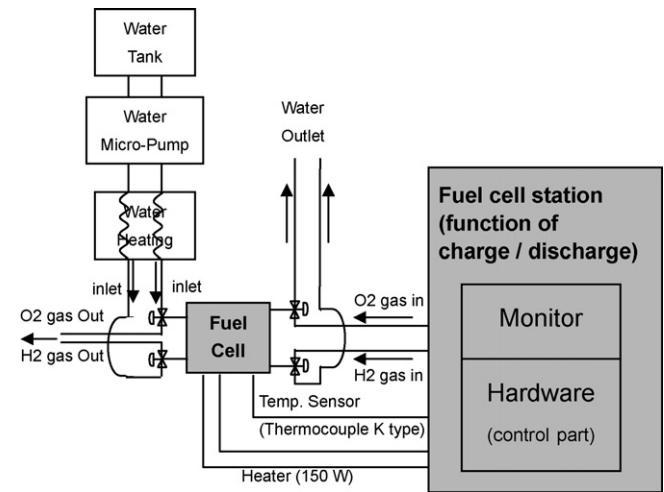

Fig. 1. Schematic diagram for URFC operation.

of the carbon-based bipolar plate before and after water electrolysis at 2.0 V; a drastic corrosion occurred at the contact area of the bipolar plate with the electrode. The corrosion of the rib in the flow-field increased the contact resistance between the electrode and the bipolar plate, which led to the observed decrease in cell performance.

To overcome the corrosion of the carbon-based bipolar plate for URFCs, titanium was used as the base material for construction of the bipolar plates. Fig. 3(a) shows the performance of the fuel cell prepared using titanium-based bipolar plates. Before fuel cell
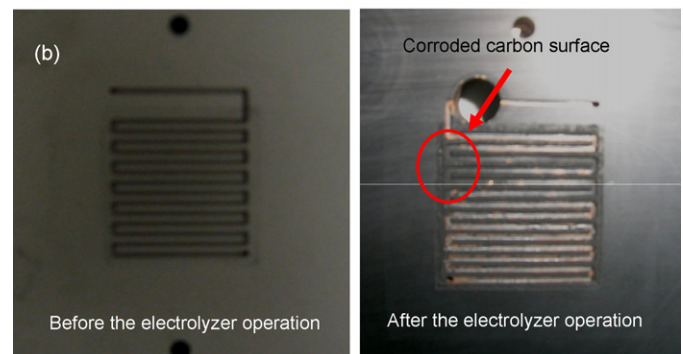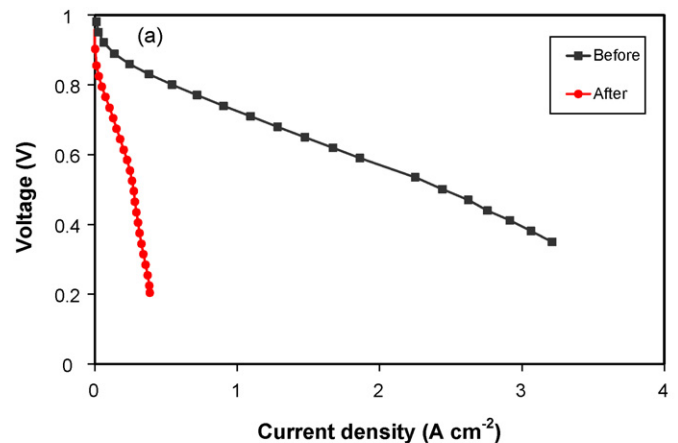

Fig. 2. (a) I–V curves of unit cell with carbon-based bipolar plate in fuel cell mode at 75 °C (before and after operation of the unit cell in electrolyzer mode at 2.0 V for 1 h, 4 mg cm⁻² of Pt black catalyst). (b) Corrosion on the surface of carbon-based bipolar plate before and after operation of water electrolysis reaction at 2.0 V for 1 h.
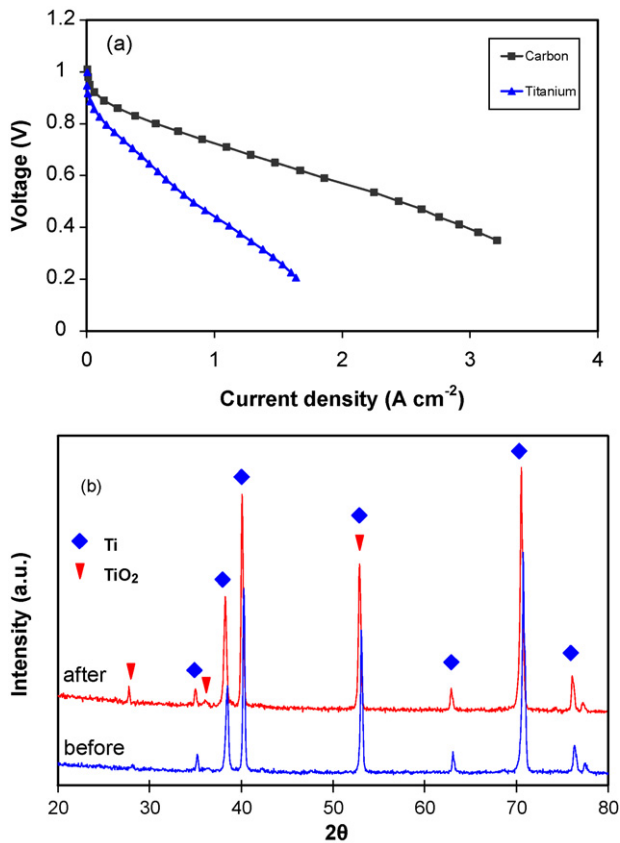
Fig. 3. (a) *I–V* curves of each unit cell with different bipolar plates in fuel cell mode (4 mg cm^{-2} of Pt black catalyst). (b) The formation of titanium oxide layer.

Fig. 4. The surface morphology of titanium-based bipolar plates after gold sputtering.

operation, initially similar electrical conductivity values for carbon- and titanium-based bipolar plates were measured. After assembly of the unit cell, the performance of the fuel cell constructed with titanium-based bipolar plates was lower than that of the fuel cell constructed with the carbon-based bipolar plates. The poor performance of the fuel cell constructed with titanium-based bipolar plates results from the formation of a passive oxide layer during the fuel cell operation. The XRD studies presented in Fig. 3(b) show the formation of a titanium oxide layer on the surface of the titanium metal with a resistance of 0.4 Ω compared with 0.15 Ω measured for the carbon-based bipolar plates. Due to the oxide formation that occurred during fuel cell operation, peaks were observed on Ti bipolar plates at 27.9°, 35.1°, and 53.1°, which are typical for a rutile TiO$_2$ structure.

Fig. 4 shows the surface morphology of the titanium bipolar plate after gold sputtering. The thickness of the coating was approximately 1 μm which was selected based on the durability and stability studies of URFC using Ti bipolar plates with different gold coating thickness values ranging from 0.1 to 1.5 μm. When less than 0.8 μm thick coatings were employed, the cycling performance in both electrolyzer and fuel cell modes decreased rapidly because of the deterioration of the gold coating. An insufficient and non-uniform barrier film (gold) was formed in Ti surface. The observed deterioration of the barrier film resulted in an increase of the contact resistance due to the formation of TiO$_2$. In the case of coatings which were between 0.8 and 1.5 μm thick, the cycling performance increased drastically. From these preliminary results, we chose 1 μm thick gold coating to plate Ti bipolar plates and used for our cycling studies. The cell performances before and after the gold sputtering are shown in Fig. 5. The results indicated that, in fuel cell mode, the performance of the unit cell significantly increased when gold-coated titanium was used as a bipolar plate; this per-
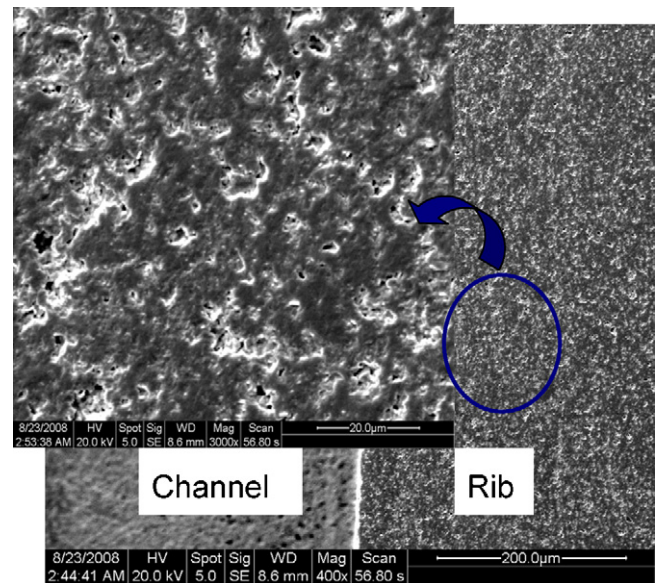
formance increase was due to the observed decrease of the ohmic resistance. The ohmic resistances of the cells prepared with bare titanium and gold-deposited titanium bipolar plates showed resistances of 0.4 Ω and 0.18 Ω, respectively. The formation of a gold coating layer on the titanium-based bipolar plates improved the
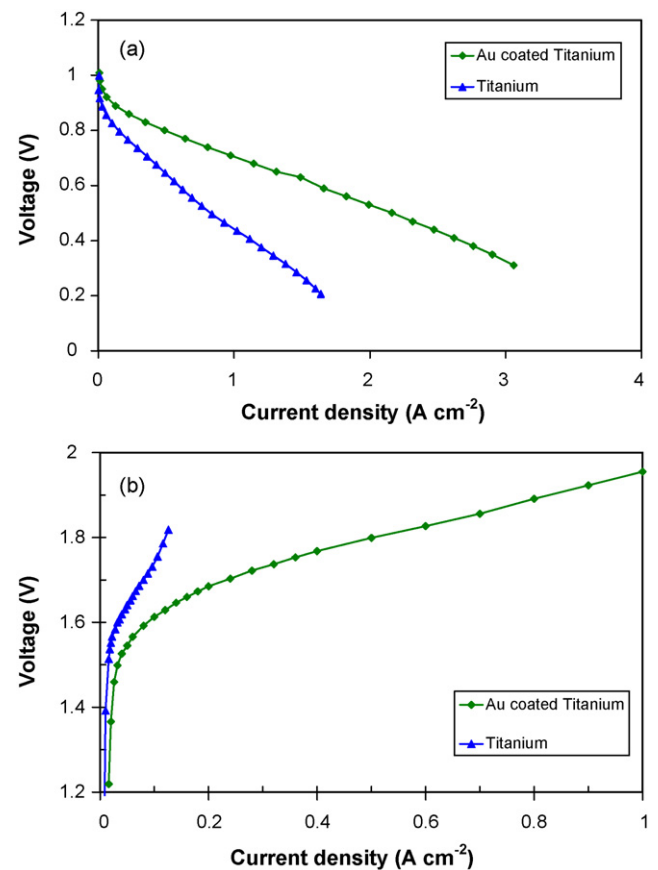

Fig. 5. *I–V* curves of unit cells with titanium-based bipolar plates before and after gold coating in (a) fuel cell mode and (b) electrolyzer mode (4 mg cm^{-2} of Pt black catalyst).
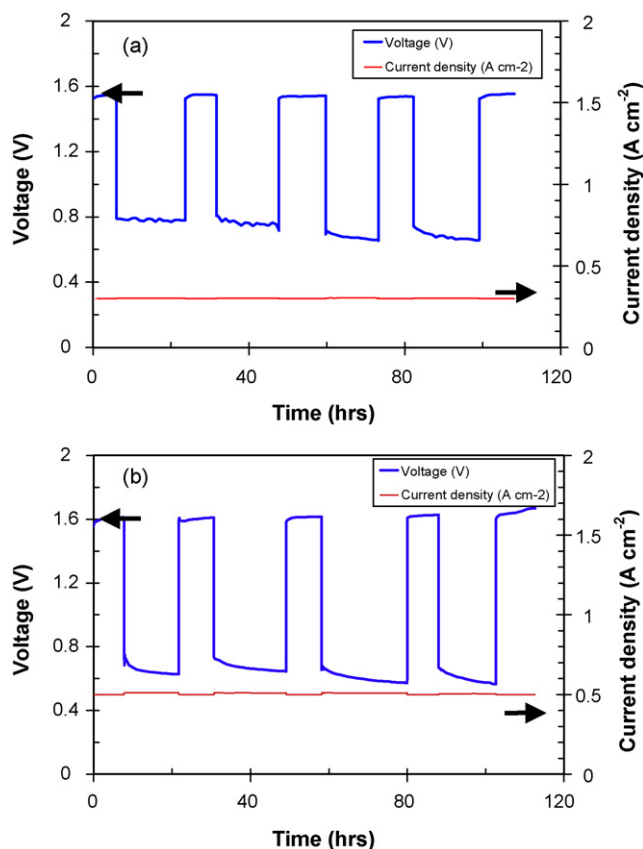
Fig. 6. (a) The cycling stability test with the conventional carbon bipolar plate. (b) The cycling stability test with the gold-coated titanium-based bipolar plate ($4\,\mathrm{mg\,cm^{-2}}$ of $Pt_{85}Ir_{15}$ black catalyst).

cell performance. In fact, the gold coating served as a barrier layer, which inhibited the formation of a passive layer on the surface of titanium-based bipolar plates, resulting in high cell performance. As shown in Fig. 5(b), similar results were obtained when the URFC was operated in electrolyzer mode.

In the present investigation, we have not carried out any studies to measure the passive film thickness that is formed on the Ti bipolar plates. However, Ti forms thin passive layer ($\sim$2 nm) when exposed to high potentials in 0.1 M H_2SO_4 (pH 0.9) [15,16]. Moreover, prior to the gold coating, we performed variety of surface cleaning procedures to make sure that the surface oxide present on the Ti plates is completely removed.

Fig. 6(a) and (b) shows the stability in the cycling test, which is based on the conventional carbon and gold-coated titanium-based bipolar plates, respectively. During the cycling test, the unit cell with the carbon bipolar plate showed a degradation rate of $2.0\,\mathrm{mV\,h^{-1}}$ at an applied current density of $0.3\,\mathrm{A\,cm^{-2}}$ in fuel cell mode. The unit cell with the gold-coated titanium-based bipolar

plate showed a degradation rate of $0.4\,\mathrm{mV\,h^{-1}}$ at the applied current density of $0.5\,\mathrm{A\,cm^{-2}}$ in fuel cell mode. Besides the fact that a higher current density was applied to the unit cell with the gold-coated titanium-based bipolar plate, the degradation rate of the voltage was five times lower than that of the unit cell with the conventional carbon-based bipolar plate. The results obtained in this study indicate that a gold coating on the titanium bipolar plates is very effective in preventing titanium oxidation during URFC operation.

4. Conclusion

Gold coatings have been applied in this study to protect the titanium surface from oxidation under severe corrosion conditions in URFC operation. In fuel cell mode, when the gold-coated titanium was used as a bipolar plate, the performance of the unit cell significantly increased. The observed increase in the performance was due to a decrease in the electrical contact resistance between the electrode and the bipolar plate. The 1 μm gold coating serves as a barrier layer inhibiting the formation of a passive layer on the surface of titanium-based bipolar plates. Similar results were obtained when the URFC was operated in electrolyzer mode. When high current densities were applied in the cycling test to the unit cell with the gold-coated titanium-based bipolar plate, the voltage degradation rate was five times lower than that of unit cell with the conventional carbon bipolar plate. The gold coating on the titanium bipolar plates is very effective in preventing titanium oxidation during URFC operation resulting in a stable performance in both fuel cell and electrolyzer modes.

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