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Effect of fabrication methods of bifunctional catalyst layers on unitized regenerative fuel cell performance

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ABSTRACT

In order to understand the origins of performance variations in unitized regenerative fuel cells (URFCs), bifunctional catalyst layers (BCLs) fabricated with two different methods, i.e., ink deposition on membrane or GDL, were designed in this paper. The performances of the two different methods were evaluated, and their reaction dynamics were measured by electrochemical impedance spectra. The different BCLs, caused by the different preparation processes, were found to influence the fuel cell performance. The cell potentials of the URFCs using platinum sprayed onto the gas diffusion layer (GDL) are above 0.100 V higher than those with platinum sprayed onto the membrane at 800 mA cm^{-2} in fuel cell (FC) mode. The mass transport resistances of the URFCs at different operation modes were also compared. It was proved that the platinum layer formed by applying platinum onto the GDL could prevent the cell from water flooding in FC mode. However, it was found that the cell performance changed slightly in water electrolysis mode with different BCLs. The electron conduction path was also found to be hindered by an IrO_2 agglomerate, which led to a decrease in cell performance. The highest and lowest round-trip efficiencies of the URFC with different BCLs were 42.1% and 22.3%, respectively, at 800 mA cm^{-2}.

1. Introduction

A regenerative fuel cell (RFC) can be operated as an electrolyzer, splitting water into hydrogen and oxygen with the help of electric power from renewable energies. The RFC system can also create electrical power with the stored hydrogen and oxygen in the fuel cell (FC) when the power is needed. The advantage of these types of cells compared to batteries such as Ni/MH or Li-ion is the non-existent self-discharge of RFCs and the opportunity to store great quantities of energy that can be converted to electricity [1,2]. However, applications of the RFC system have been limited to space and military uses by its high cost, complexity and the low round-trip storage efficiency [3,4]. To resolve the former two problems, a unitized regenerative fuel cell (URFC) system was developed, where the electrolyzer and fuel cell are combined into one unit, and only one of the two modes can be operated at one time. This arrangement uses only one electrochemical cell and therefore makes it possible to build a simpler and more compact RFC system [5].

In order to improve the round-trip efficiency of the URFC, one key issue is the fabrication of stable and highly active bifunctional catalyst layers (BCLs), which can be used for both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER). It is well known that the best electrocatalyst for ORR is platinum (in its reduced form). Early research by Swette et al. [6], showed that iridium oxide (IrO_2) would be a good candidate for OER. So far, bifunctional electrocatalysts for oxygen redox reactions of the URFC have included Pt–Ir [7], Pt–Ru–Ir [8], Pt–IrO_2 [9,10] and Pt–IrO_2–RuO_2 [11,12], among which IrO_2 and RuO_2 were prepared by the Adams method [13]. However, the most applicable OER catalyst is iridium oxide since iridium and ruthenium suffer from instability [14].

Some of the above-described bifunctional oxygen electrode catalysts were obtained by mixing an efficient electrocatalyst for oxygen reduction-Pt black, and an efficient electrocatalyst for oxygen evolution-Ir or IrO_2 or RuO_2, while others were made by using alloyed PtIr or $PtIrO_x$ or $PtRuO_x$. An OER catalyst does not exhibit a high catalytic activity for the oxygen reduction reaction, while an ORR catalyst may display a low catalytic activity for the oxygen evolution reaction. In addition, as we know, the reactions occurring at the cathode of the URFCs are the reduction and evolution of oxygen as follows:

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \qquad (1)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^- \qquad (2)$$

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According to (1) and (2), in fuel cell mode, the oxygen gas is reduced to liquid water, but, in water electrolysis mode, the reactant is the liquid water and the product is oxygen gas. The different reactants and products in the two different modes also require a suitable bifunctional catalyst layer to obtain the highest round-trip efficiency.

There are several ways to prepare catalyst layers for a fuel cell: the so-called indirect decal method, the gas diffusion layer (GDL)-based method and the membrane-based method [15]. For the decal method, a transfer film is brushed with catalyst ink, dried and hot-pressed onto the electrolyte film. The GDL-based method implies that the catalyst ink is directly painted or sprayed onto the GDL. Fabricating the catalyst layers with the membrane-based method usually consists of spraying the catalyst ink directly onto a dry, blank membrane. The latter two methods have the advantage that the catalyst loading can be adjusted very precisely by simply weighing the membrane electrode assembly (or the GDL) before and after coating with the catalyst ink. Applying the electrodes by the decal method contains the risk of uneven or incomplete catalyst transfer from the transfer film to the membrane. We therefore restricted our research to the GDL- and membrane-based methods.

The water management, which is vital to ensuring the high performance and long life of the fuel cell, will differ in different fabrication processes. It has been shown that, if the cathode is flooded by excess water, the cell performance decreases [15]. Furthermore, although IrO_2 is a good conductor ($\rho = 49\,\mu\Omega\,\mathrm{cm}$ at 300 K) as a metal oxide, the resistivity of IrO_2 is five times larger than that of Pt ($9.85\,\mu\Omega\,\mathrm{cm}$ at 293 K) [16]. The addition of the OER catalyst IrO_2 in the URFC may change the mass transport in fuel cell mode. Up to now, no reports have related the influence of fabrication methods of bifunctional catalyst layers (BCLs) composed of identical bifunctional catalysts to cell performance, especially the round-trip efficiency of a URFC.

In this paper, eight bifunctional oxygen catalyst layers with two different preparation methods were designed. Pt and IrO_2 catalysts were used as bifunctional catalysts. The performances of the URFCs in two different modes were evaluated. The electrochemical impedance spectra (EIS) of the URFCs were measured to study the effects of different bifunctional catalyst layers on cell performance. The round-trip efficiencies of the URFCs were also compared.

2. Experimental

2.1. *Preparation of bifunctional catalyst layers and membrane electrode assemblies for URFCs*

Prior to fabricating the electrodes, a homogeneous suspension composed of PTFE and carbon powder was sprayed onto wetproof carbon paper (TGP-060, Toray Inc.) to form the GDL with a sublayer [17]. The proton exchange membranes (PEMs, Nafion 1035, DuPont) were treated for 1 h in 5 wt.% H_2O_2 solution at 80 °C, 30 min in distilled water at 80 °C, 1 h in 0.5 M H_2SO_4 solution at 80 °C and finally 30 min in distilled water at 80 °C.

To prepare a hydrogen catalyst layer, a homogeneous ink consisting of Pt/C catalyst (28.4 wt.%, T.K.K. Corp.), Nafion solution (5 wt.%, DuPont) and isopropanol was sprayed directly onto one side of a Nafion 1035 membrane. The prepared catalyst-coated membrane was then dried at room temperature for 24 h to evaporate the residual solvents. The Nafion content was 25 wt.% and the Pt/C loading was 0.5 mg cm^{-2} for the hydrogen side.

The oxygen catalyst layers were made as shown in Fig. 1. Pt (Pt black, T.K.K. Corp.) and home-made IrO_2 were used as bifunctional catalysts. IrO_2 was made by proprietary modification of Adams-type fusion of the iridium salt in a nitrate flux [18]. All the bifunctional catalyst layers were prepared by spraying technique. To form C1 and C2, Pt and IrO_2 were made as a mixed catalyst layer, whereas for other BCLs, Pt and IrO_2 were divided to form individual catalyst layers, a Pt catalyst layer and an IrO_2 catalyst layer, respectively. The spraying sequences of the Pt catalyst and IrO_2 catalyst layers also varied as shown in Fig. 1. Four groups of BCLs, C1 and C2, C3 and C4, C5 and C6 and C7 and C8, had the same loading and were prepared from the same inks but differed in the locations of Pt and IrO_2 layers. The BCL that applied Pt onto the GDL was named BCL1, while the BCL that applied Pt onto the membrane was named BCL2, so that C1, C3, C5 and C7 were of the type BCL1, but C2, C4, C6 and C8 were of the type BCL2. The Nafion content was 22 wt.% and the electrocatalyst loading was 0.5 mg cm^{-2} Pt and 0.5 mg cm^{-2} IrO_2 for all bifunctional catalyst layers.

GDL sprayed with only one pure Pt layer or pure IrO_2 layer were also prepared as comparisons to the other BCLs and were named GDL-Pt and GDL-IrO_2, respectively. Membranes sprayed with a pure Pt or IrO_2 layer were also prepared and named M-Pt and M-IrO_2,

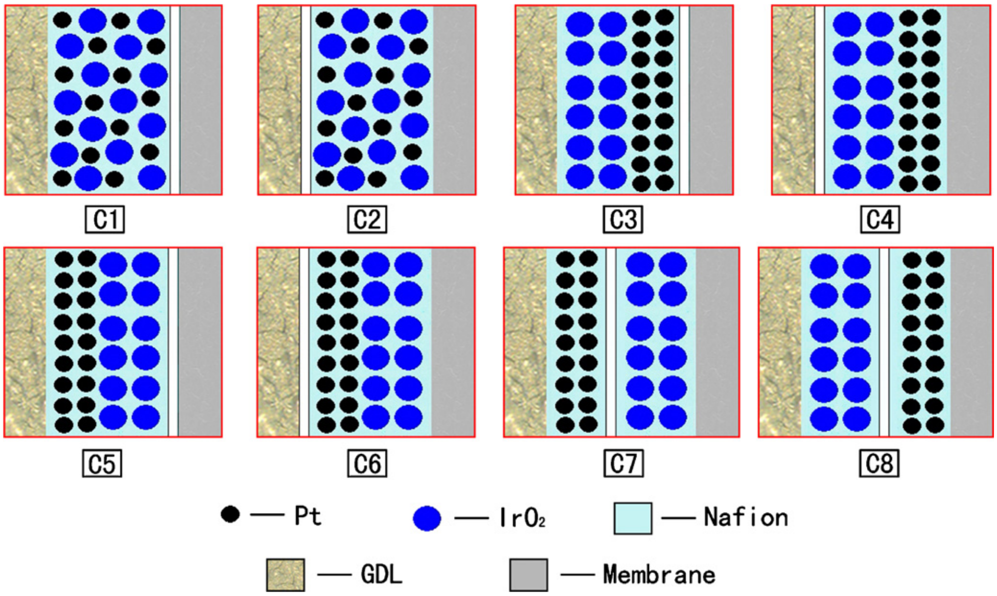

Fig. 1. Schematic diagram of different bifunctional catalyst layers for URFCs. The four groups of BCLs, C1 and C2, C3 and C4, C5 and C6, C7 and C8, were the same electrode structure and catalyst loading; C1, C3, C5 and C7 sprayed Pt onto the gas diffusion layer (BCL1) while others applied Pt onto the membrane (BCL2).