



Short communication

Development of porous Pt/IrO₂/carbon paper electrocatalysts with enhanced mass transport as oxygen electrodes in unitized regenerative fuel cells



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ARTICLE INFO

Article history:

Received 25 November 2015

Received in revised form 25 December 2015

Accepted 7 January 2016

Available online 12 January 2016

Keywords:

Unitized regenerative fuel cell

Oxygen electrode

Platinum

Iridium oxide

ABSTRACT

The oxygen electrodes in unitized regenerative fuel cells (URFC) must have high activities towards oxygen reduction reaction (ORR) as well as oxygen evolution reaction (OER), thus requiring high loading of noble metal electrocatalysts. In this study, porous Pt/IrO₂/carbon paper (CP) electrocatalysts were developed to reduce the metal loading. The Pt/IrO₂/CP electrodes were fabricated by sequential formation of IrO₂ layers (loading 0.1 mg cm⁻²) and porous Pt layers (0–0.3 mg cm⁻²) on CP substrates by electrodeposition and spraying techniques, respectively. The fuel cell (FC) performances increased linearly up to 0.69 A cm⁻² with increasing Pt loading (up to ~0.3 mg cm⁻²) at 0.6 V, whereas the water electrolysis (WE) activity was highest at Pt loading of 0.2 mg cm⁻². The current densities in the FC and WE modes and round-trip efficiency of the developed Pt/IrO₂/CP electrodes with the oxygen electrocatalysts loadings of 0.3 and 0.4 mg cm⁻² were higher or comparable to previously reported values with higher loading (1.5–4.0 mg cm⁻²). These high performances with low loading are probably due to the facile oxygen and water transport through well-developed macropores originating from the open CP structures, providing effective utilization of the IrO₂ and Pt electrocatalysts towards OER and ORR, respectively.

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1. Introduction

Renewable energy sources, such as solar power and wind power, have attracted increasing interest as alternatives to conventional systems based on fossil fuels. As the electricity generation by these renewable sources is highly dependent on weather conditions, energy storage systems that can store extra electricity are required for ensuring stable electricity supply to consumers [1]. Regenerative fuel cells (RFCs), which enable bidirectional conversion between electricity and hydrogen, is considered a promising candidate for electrochemical energy storage. Since the energy capacity of an RFC-based system can be

increased independent of its power, capital cost to expand its energy capacity is lower than that of a Li battery and is thereby expected to be suitable for large-scale applications [2].

The RFCs can be classified as unitized regenerative fuel cells (URFC) and discrete regenerative fuel cells (DRFC) [3]. The URFCs, having integrated fuel cell (FC) and a water electrolyzer (WE) units, are expected to reduce the capital cost; the DRFCs, having separated FC and WE units, have lower technical barriers as they can utilize commercially available FC and WE devices. However, generally high loadings of noble metal electrocatalysts are required for URFCs, which increases the system cost. Since the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) for the URFC are sluggish, Pt and Ir (or IrO₂) electrocatalysts that provide high ORR and OER activities, respectively, have been used together in mixture [4–6] or double-layer form [7,8]. In addition, bifunctional electrocatalysts of a Pt–Ir alloy [9] and (RuO₂–IrO₂)/Pt [10] have also been investigated. For these studies, high electrocatalyst loading (1.5–4.0 mg cm⁻²) with 50%–85% Pt content, typically providing current densities above 0.7 A cm⁻² @ 0.6 V (FC) and 1 A cm⁻² @ 1.7 V (WE). There have been

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studies to lower the loading of noble metal electrocatalysts, but the corresponding WE and FC performances were not satisfactory [11,12].

In this study, we developed a novel electrocatalyst of porous Pt/IrO₂/carbon paper (CP) as an oxygen electrode of URFC. For this, the IrO₂ layer was electrodeposited on the CP and then the porous Pt layers were sprayed, with the total electrocatalyst loading controlled up to 0.4 mg cm⁻². As the Pt/IrO₂/CP electrocatalyst has an open structure with macropores, originated from the CP substrates, the mass transport of oxygen and water should be highly enhanced compared to conventional film-structured electrodes. Using the Pt/IrO₂/CP as oxygen electrodes, single-cell tests were performed in both FC and WE modes to demonstrate high URFC performance with decreased oxygen electrocatalyst loading (0.1–0.4 mg cm⁻²), focusing on the effect of Pt loading on FC performances, which is lower compared to the WE mode [4,5,7–11].

2. Experimental

According to the procedure in our previous study [13], IrO₂ electrodes were prepared by electrodeposition at a deposition voltage of 0.7 V, using TGPH-090 CP (Toray Inc.) as substrates. The fabricated IrO₂/CP, on which the IrO₂ loading was controlled to be 0.1 mg cm⁻², was designated as IP0. Pt electrocatalyst ink was prepared by mixing Pt black powder (Johnson Matthey), 5 wt.% Nafion dispersion (Dupont), 1,2-propanol (J.T. Baker), and deionized water; the mixture was sprayed onto IP0 to form porous Pt layers. The Pt loadings were controlled to be 0.1 mg cm⁻² (IP1), 0.2 mg cm⁻² (IP2), and 0.3 mg cm⁻² (IP3). As hydrogen electrodes, Pt/C (46.3 wt.%, TKK) layers (0.4 mg cm⁻²) on bare CP (10 BC, SGL Ltd.) were fabricated by spraying a dispersion of Pt/C and Nafion ionomers in 1,2-propanol/deionized water mixture. The microstructures and compositions of the thus-prepared electrodes were analyzed by scanning electron microscopy (SEM; Inspect F50, Field Emission Inc.) and electron-probe micro-analysis (EPMA; JXA-8500F, JEOL), respectively. Samples for cross-sectional images were prepared by focused ion beam (FIB; Nova 600, FEI) technique. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses were performed using a Dmax2500/Server (Rigaku) and ESCA 2000 (Thermo), respectively.

Membrane electrode assemblies (MEA) were fabricated by placing an oxygen electrode (IP0–IP4) and a hydrogen electrode on either side of N212 membranes (DuPont Co.). The URFC single cells (active area: 6.25 cm²) were prepared by assembling the MEA with graphite bipolar plates (CNL energy). For FC test, fully humidified H₂ (100 mL min⁻¹) and O₂ (100 mL min⁻¹) were supplied to the hydrogen and oxygen electrodes, respectively, and polarization curve was obtained with increasing current density from 0 to 1.2 A cm⁻². For WE operation, deionized water (15 mL min⁻¹) was fed to the oxygen electrode of the single cell, and polarization curves were obtained over 1.35–1.8 V, with a stepwise increase at intervals of 0.05 V (HCP-803, Biologics Ltd.). The durability was analyzed by potential cycling between 1.35 and 1.80 V at a scan rate of 5 mV s⁻¹ in the WE mode. By switching between FC and WE modes, URFC operation was carried out at 0.3 A cm⁻² [4,6]. The cell temperature was 80 °C.

3. Results and discussion

The SEM image of electrode IP2 shows open structure originated from the CP substrate, randomly crossed carbon fibers in the CP (Fig. 1a). The inter-fiber spaces, which should facilitate mass transport during FC and WE operation, were as large as ~100 μm and were hardly blocked by the porous Pt layers. The Pt layers sprayed on the IrO₂-coated CP shows a highly porous structure having sub-micrometer-sized pores (Fig. 1b). Cross-sectional image of a fiber indicated that porous Pt layers covered IrO₂/CP with a thickness of a few micrometers (Fig. 1c), while EPMA element mapping shows a thin IrO₂ film on the carbon fiber (Fig. 1d).

The XRD pattern of IP0 shows diffraction peaks at 26.5°, 42.4°, and 54.7°, which correspond to the (002), (100), and (004) planes of graphite (PDF#: 65-6212, hexagonal structure), respectively [14,15] (Fig. 1e). The absence of the diffraction peak of IrO₂ could be attributed to its amorphous nature, based on the TEM analysis (not shown). The XRD patterns of IP1, IP2, and IP3 show additional peaks at 39.8°, 46.2°, and 67.7°, corresponding to the (111), (200), and (220) planes of Pt (JCPDS#: 65-2868, FCC structure), respectively [16].

The XPS analysis shows that, with increased Pt loading, Ir 4f peaks significantly decreased in intensity while the Pt 4f peaks increased

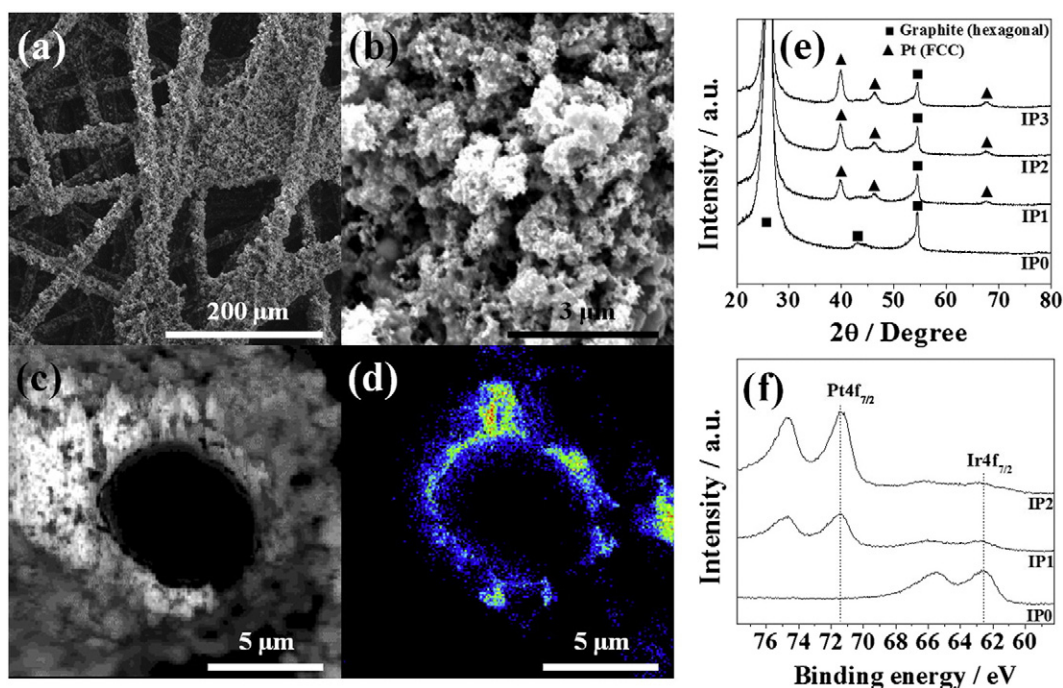


Fig. 1. (a) and (b) SEM images of porous Pt/IrO₂/CP electrode (IP2) surfaces. (c) Cross-sectional image and (d) Ir-mapping image of a porous Pt/IrO₂ electrocatalysts coated carbon fiber. (e) XRD pattern and (f) Pt 4f and Ir 4f X-ray photoelectron spectra of the porous Pt/IrO₂/CP electrodes.

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