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Crumpled rGO-supported Pt-Ir bifunctional catalyst prepared by spray pyrolysis for unitized regenerative fuel cells

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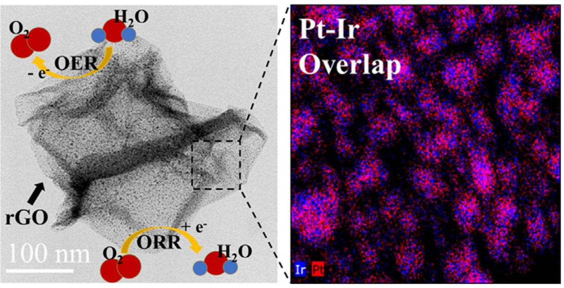
HIGHLIGHTS

- Pt-Ir/rGO was synthesized by a facile spray pyrolysis and following heat-treatment.
- ORR and OER catalytic activities of Pt-Ir/rGO were enhanced by post heat treatment.
- Pt-Ir/rGO_P600 exhibited higher catalytic activities than commercial catalysts.
- Pt-Ir/rGO_P600 showed superior stabilities under reducing and oxidizing conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Three-dimensional (3D) crumpled reduced graphene oxide supported Pt-Ir alloys that served as bifunctional oxygen catalysts for use in untized regenerative fuel cells were synthesized by a facile spray pyrolysis method. Pt-Ir catalysts supported on rGO (Pt-Ir/rGOs) were physically characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA) to observe change in composition by heat treatment, alloying, and morphological transition of the catalysts. Their catalytic activities and stabilities for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) conditions were electrochemically investigated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), potential cycling and hold tests on the rotating disk electrode (RDE). Pt-Ir/rGO with no post heat-treatment (Pt-Ir/rGO_NP) showed a lower activity for ORR and OER although metal nanoparticles decorated on the support are relatively small. However, Pt-Ir/rGO showed remarkably enhanced activity following heat treatment, depending on temperature. Pt-Ir/rGO heat-treated at 600 °C after spray pyrolysis (Pt-Ir/rGO_P600) exhibited a higher activity and stability than a commercially available Pt/C catalyst kept under the ORR condition, and it also revealed a comparable OER activity and durability versus the commercial unsupported Ir catalyst.

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1. Introduction

Hydrogen energy has received exceptional attention for several decades because it is a copious, eco-friendly, and recyclable ($H_2 \leftrightarrow H_2O$) energy source for stationary and automotive applications.

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Specifically, proton exchange membrane (PEM) fuel cell electric vehicles has gained attention as a next-generation vehicle and low-temperature fuel cells as residential power generators are essentially fueled by hydrogen, and fuel-cell power plants that adopt molten carbonate fuel cells or solid oxide fuel cells operating at high temperatures ranging from 600 to 1000 °C use compressed hydrogen gas or hydrogen as a derivative of hydrocarbon prepared through internal and/or external reforming process. The relatively low-quality electricity generated from intermittent renewable energy sources such as solar and wind energy can be stored as hydrogen through water electrolysis and can again produce electricity by fuel cell reactions in energy conversion and storage system [1–6].

A unitized regenerative fuel cell (URFC) that combines PEM-based fuel cell and a water electrolyzer is a promising energy conversion and storage system for using hydrogen. Compared to conventional secondary batteries, URFCs have many advantages, including high specific energy densities relevant to the lower molecular mass of reactants, no self-discharge because of the external supply of fuel and an oxidant as the reactants, and no emission of hazardous products [7–10]. However, they still have several issues, especially at the oxygen electrode. i.e., i) slow reaction rates and high overpotential both for ORR and OER, ii) low stability and reliability of the oxygen electrocatalysts under a rigorously oxidizing environment for an extended URFC operation, iii) high cost of the oxygen electrocatalysts due to the requirement of two different monofunctional electrocatalysts (i.e., ORR and OER catalysts), and high precious metal loading to meet the demands for power density [2,10,11].

Extensive studies have been conducted to improve the activity, durability, and the cost-effectiveness of oxygen electrocatalysts in URFCs. There have been two main strategies to obtaining promising oxygen electrocatalysts: the development of a bifunctional catalyst and the introduction of the catalyst support. At the initial stage of URFC development, Pt [1,3,5,12], Pd [13,14], Ir [5], IrO_2 [15], and RuO_2 [8,16] were employed as oxygen electrocatalysts (i.e., oxygen electrode in a dual-layer structure made up of the ORR catalyst and the OER catalyst). Early studies suggested Pt and Pd would be good candidates for ORR catalysts, while Ir, IrO_2, and RuO_2 had attracted favorable attention as OER catalysts [1,3,5,12–16]. However, it has generally been accepted that the Pt catalyst is the most active material toward ORR, whereas the Pd catalyst (not alloyed with Pt) has a relatively low activity and poor stability, especially in a single cell [17,18]. Ir has a superior stability and activity towards OER in acidic media and at rigorously oxidizing environment among transition metals. It is widely utilized as an OER catalyst for water electrolyzer applications [19,20]. Several groups reported that the addition (or alloying) of iridium to platinum improved ORR as well as OER performance [21–23]. Hence, Pt-based or Pt-Ir alloys have been studied as bifunctional catalysts at the oxygen electrode. Chen et al. [21] introduced combinatorial chemistry and examined a variety of single, binary, and ternary catalysts from their library for ORR and OER in acid solution, proposing that $Pt_{4.5}Ru_4Ir_{0.5}$ functioned as a promising bifunctional electrocatalyst. However, the oxidation of metallic ruthenium to RuO_4 that dissolves in the electrolyte for a long-term URFC operation was a big drawback, although the reaction is somewhat suppressed by Ir [22]. Yim et al. [23] prepared bifunctional oxygen electrocatalysts (by physically mixing Pt black and Ir or Ru oxides from its precursor, or electroless deposition of Ir and/or Ru nanoparticles onto Pt black) and compared them to various combinations of the materials mentioned above. According to their study, ORR activity in fuel cell mode of URFCs was observed in the order: Pt black > Pt-Ir > Pt-RuO_x > Pt-Ru ≈ Pt-Ru-Ir > Pt-IrO_x, while the performance in water electrolyzer mode (WE) was higher in the order: Pt-Ir ≈ Pt-IrO_x > Pt-Ru > Pt-Ru-Ir > Pt-RuO_x ≈ Pt black. From their results, Pt-Ir showed a higher activity for both ORR and OER, and a round-trip efficiency during the URFC operation.

The other approach, as mentioned previously, was to adopt catalyst support materials that provided high surface area for the anchoring of metal nanoparticles, show electroconductivity, and are corrosion-resistant at a highly anodic potential greater than 1.5 V (vs. SHE). By and large, Ti-based catalyst supports that includes TiO_2 [24], TiO_2-C [25], TiC [5,26], and TiCN [1,5], and Ir-based materials such as IrO_2 [3,27] and Ir-IrO_2 [10], which serves both OER catalyst and catalyst support for Pt nanoparticles has been proposed for bifunctional oxygen electrocatalyst in URFCs. Carbon-based materials containing porous carbon [28], carbon nanotube [29], graphene [30,31] primarily used for PEM fuel cells offered high surface areas and exhibited good electronic and thermal conductivities. Graphene, among the various carbon materials, is a unique material in that it gives a higher surface area and is flexible and chemically stable. It can be classified into one-dimensional (1D) graphene (i.e., carbon nanotubes, CNTs) and two-dimensional (2D) graphene sheets. There have been many types of studies concerning carbon-metal composites that consist of 1-D CNTs or 2-D graphene and metal (oxide) nanoparticles for electrocatalyst applications [32–34]. However, graphene has intrinsic restrictions of dispersion in the solution that contains metal precursors and restacks with each other sheets due to strong Van der Waals forces during the synthesis of the catalyst, which disrupts its full activity [32,35].

On the other hand, during the preparation of supported electrocatalysts, the formation of metal (oxide) nanoparticles on the surface of the catalyst support is of great importance, since metal nanostructures offer a higher catalytically active area and the catalyst support provides numerous pathways for electrons and even ions that move in the electrolyte (or the ionomer) along the surface of the catalyst [3,36]. To construct such nanostructures from electrocatalysts, many methods of preparation have been introduced, including the polyol method [1,3,5], chemical vapor deposition [37], electrochemical deposition [9], and sputtering [38]. These methods, albeit useful, typically suffer from drawbacks i.e., complicated multistep processes, catalyst poisoning by chemical residues, and poor control over the mean size and size distribution of catalyst particles [12,37]. Spray pyrolysis, as shown in Scheme 1, is a process for preparing particles by forming droplets from a precursor solution and carrying them by a gas into a furnace, where droplets are evaporated and decomposed into solid particles. It is suitable for large-scale production of the powder by ensuring a continuous supply of precursor solutions and synthesis of homogeneous particles, because single particles are formed from single droplets with no agglomeration. Furthermore, this process is capable of tailoring the shape and size of nanocomposite powder as a product by controlling the concentration of the precursor solution, reaction temperature, and flow rate of a carrier gas.

In the present study, to reduce precious metal loading and improve activity and durability, three-dimensional (3D) crumpled reduced graphene oxide (rGO)-supported Pt-Ir alloy (Pt-Ir/rGO) was synthesized as a bifunctional oxygen catalyst in URFCs by spray pyrolysis following heat treatment. Physical characterizations such as XRD, SEM, and TEM were conducted to examine its catalytic properties that are temperature-dependent, as determined following heat treatment. Change in ORR and OER activities and electrochemical surface area (ESA) of the electrocatalyst under the potential cycling and the current response during the potential hold were studied by various electrochemical methods using a rotating disk electrode (RDE).

2. Experimental

2.1. Synthesis of Pt-Ir/rGO

Pt-Ir (50:50 weight ratio) catalyst supported on crumpled rGO

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