



TiC supported Pt–Ir electrocatalyst prepared by a plasma process for the oxygen electrode in unitized regenerative fuel cells

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ABSTRACT

Unitized regenerative fuel cells (URFCs) have become more attractive for some time due to its potentially wide energy storage application such as in fields of space and renewable energy. In this study, TiC supported Pt–Ir electrocatalysts (Pt–Ir/TiC) for oxygen electrode in URFCs were synthesized, respectively, by chemical reduction process and plasma reduction process. Their physical and electrochemical properties are characterized and compared using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), cyclic voltammogram (CV), potentiostatic technique, and electrochemical impedance spectroscopy (EIS). The results from XRD, XPS and TEM demonstrate that the plasma process gives a finer metal crystals and higher metal dispersion on the TiC support. The CV, polarization, potentiostatic and EIS results show that the Pt–Ir/TiC electrocatalyst prepared by the plasma reduction process is obviously more active than that by the chemical reduction process, in agreement with the above metal-dispersion observations. The plasma process is a promising way for the preparation of supported electrocatalysts.

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1. Introduction

Hydrogen as an energy storage medium, which stores electrical energy by splitting water into hydrogen and oxygen, is preferably connected to a renewable energy source, such as solar or wind energy. Unitized regenerative fuel cells (URFCs), using hydrogen as the medium, is a compact energy storage unit where the water electrolyser (WE) and the fuel cell (FC) are combined into one unit and only one of the two modes can be operated at one time [1]. In the WE mode, hydrogen and oxygen are generated by splitting water using electrical power. In the FC mode, the hydrogen and oxygen or air are combined to generate water and give off electricity. Compared with conventional secondary batteries (for example, lead acid and Li-ion batteries) as storage systems, URFCs have many advantages in long-term energy storage, including high energy density, high durability and low environmental impact. They can be applied in many different areas, such as high-altitude long-endurance airship, hybrid energy-storage/propulsion systems for spacecraft, energy storage for remote (off-grid) power sources, and peak shaving for on-grid applications [2].

One of the most difficult challenges in the development of the URFCs is to improve the performance of their oxygen electrodes,

and more specifically, to improve the performance of the bifunctional electrocatalysts for the oxygen electrodes [3].

To date, typical bifunctional electrocatalysts for oxygen redox reaction of URFC include Pt–Ir, Pt–Ru–Ir, Pt–IrO₂ and Pt–IrO₂–RuO₂. Most of the above described bifunctional oxygen electrode electrocatalysts are obtained by mixing an efficient electrocatalyst for oxygen reduction – Pt black, and an efficient electrocatalyst for oxygen evolution – Ir or IrO₂ or IrO₂–RuO₂, which may result in a slightly decreased performance in either the oxidation or the reduction reaction (depending on catalyst composition) and thus a lower bifunctional performance of the oxygen–electrode electrocatalysts. The electrocatalyst compositions need to be optimized for a given system application. Yim et al. [3] optimized Pt–Ir electrocatalyst for URFC and concluded that Pt–Ir catalyst with 1 wt.% Ir revealed the highest URFC efficiency. Grigoriev et al. [4] recently suggested anodic bifunctional electrocatalytic structures for URFCs based on proton exchange membrane (PEM) technology. Among various Pt–Ir compositions, the best URFC performances were reported to be obtained with two adjacent porous layers, of which the first layer was made of Ir (50 wt.%) in direct contact with the polymer membrane and the second layer was made of Pt (50 wt.%) and coated over the first one.

Several factors influence the electrocatalytic activity of the catalysts for the oxygen evolution reaction, including the crystal-field stabilization energy, mixed and doped oxides, catalyst dispersion, crystallinity, and crystallite size [5]. IrO₂/Pt can be prepared by

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deposition of the colloid precursor $\text{Ir}(\text{OH})_3(\text{H}_2\text{O})_3$ on Pt black. Ioroi et al. [6] reported that the catalytic performance of the deposited IrO_2/Pt is better than that of mixed IrO_2/Pt because it is relatively easy to maintain the conduction path of electrons along Pt agglomerates in the deposited IrO_2/Pt catalyst, while the electron conduction path tends to be hindered by IrO_2 agglomerates in the mixed IrO_2/Pt catalysts.

On the contrast, Yao et al. [7] reported that platinum nanoparticles deposited on the surface of IrO_2 by chemical reduction, compared to the mixture of Pt and IrO_2 , showed distinct behaviors in the oxygen reduction reaction (ORR) and in the oxygen evolution reaction (OER). As a bifunctional electrocatalyst for oxygen electrode, IrO_2 -supported Pt exhibits slightly lower ORR activity but markedly higher OER activity than the mixture of Pt and IrO_2 . They explained it by the downshift of the d-band center energy through the d-band coupling, therefore resulting in a weaker O_2 molecule adsorption on Pt catalysts supported by IrO_2 . Zhang et al. [8] synthesize a bifunctional $\text{RuO}_2\text{-IrO}_2/\text{Pt}$ electrocatalyst for the URFC by colloid deposition. URFC with the deposited $\text{RuO}_2\text{-IrO}_2/\text{Pt}$ showed better performance than that of URFC with mixed $\text{RuO}_2\text{-IrO}_2/\text{Pt}$ catalyst. Cyclic performance of URFC with deposited $\text{RuO}_2\text{-IrO}_2/\text{Pt}$ was reported very stable during 10 cyclic tests.

To reduce the loading of the noble metals, supports are used in the bifunctional electrocatalysts. Chen et al. [9] examined three oxide supports: Ebonex (primarily composed of Ti_4O_7), phasepure microcrystalline Ti_4O_7 and $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$, a doped rutile compound. These supports improve activity, but have short-lived electrochemical stability. We [10] reported recently that the catalytic activity of the Ir/TiC for the OER is significantly higher than that of the unsupported Ir catalyst. The TiC support is chemically and electrochemically stable in the whole range of experimental potentials.

Many conventional methods are used in the electrocatalyst preparation, such as chemical reduction by HCHO, KBH_4 or NaBH_4 , the electrochemical deposition and chemical vapor deposition (CVD) [11–14].

Recently, plasma reduction has attracted more attention. Plasma can enhance or assist deposition of catalytically active compounds on various supports and produce ultrafine catalyst particles [15]. Legrand et al. [16] used the afterglow of a hydrogen microwave plasma for the preparation of zeolite yttrium (Y) supported gold and platinum nanoparticles. Kim et al. [17] reported that a hydrogen atmospheric dielectric-barrier plasma could be used as the reducing agent to prepare supported Pt and Co catalysts. Liu et al. [18–23] had used argon glow discharge plasma at room temperature to prepare Pd, Pt, $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts and noticed these catalysts were reduced during the process of plasma treatment.

In the present study, we prepared two kinds of Pt–Ir/TiC electrocatalysts, respectively, by chemical reduction and plasma reduction processes, and characterized them by physical and electrochemical measurements.

2. Experimental equipment and procedures

2.1. Preparation of the Pt–Ir/TiC electrocatalyst by thermal reduction process

The Pt–Ir/TiC electrocatalyst prepared by thermal reduction was made by chemical reduction and deposition with ultrasonic dispersion described in our early investigation [10]. TiC powder is a commercial product purchased from Fujian Sinocera Advanced Materials Co., Ltd. Its main physical and chemical characteristics are described as follows: TiC purity >99%, cubic structure, surface area $14.41\text{ m}^2\text{ g}^{-1}$, and particle size 100–200 nm. Briefly, the support TiC powders were wetted in de-ionized water containing an appropriate amount of isopropanol to form a suspended phase. The

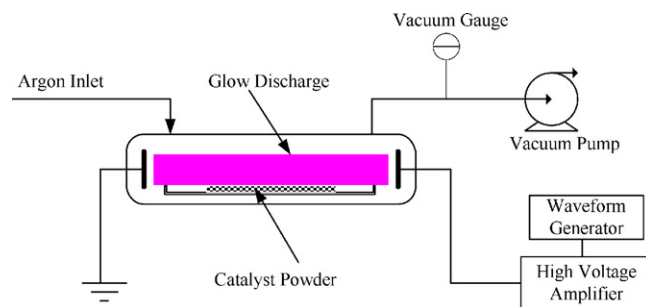


Fig. 1. Schematic setup of glow discharge plasma catalyst reduction.

slurry was dispersed in an ultrasonic reactor for 10 min at room temperature. $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ (analytical grade) and $(\text{NH}_4)_2\text{IrCl}_6$ (Alfa Aesar) were added to the above slurry in the calculated amount for the desired loading. The aqueous solution was subsequently heated to 80°C and stirred under ultrasonic agitation. The reducing agent ($\text{HCHO}:\text{NH}_3:\text{H}_2\text{O} \approx 2:1:21$, weight ratio) was added to the mixture at 80°C over a period of 40 min and the mixture was kept at 80°C under ultrasonic agitation for an hour. After cooling to room temperature, the reduced and precipitated slurry was washed repeatedly with de-ionized water until the content of chlorine anion (Cl^-) in the filtrate was less than 40 ppm. After drying at 80°C for an hour, the filter cake was then set in a tube furnace and annealed at 500°C for 30 min under flowing argon before cooling down to room temperature. The Pt–Ir electrocatalyst loading on the TiC support was 40 wt.%. The sample is labeled as S1.

2.2. Preparation of the Pt–Ir/TiC electrocatalyst by plasma reduction

The novel Pt–Ir/TiC electrocatalyst was prepared by plasma reduction. The TiC powders were first wetted in de-ionized water containing an appropriate amount of isopropanol to form a suspended phase. The slurry was dispersed in an ultrasonic reactor for 10 min at room temperature. $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ (analytical grade) and $(\text{NH}_4)_2\text{IrCl}_6$ (Alfa Aesar) were added to the above slurry in the calculated amount for the desired loading. This aqueous solution was subsequently heated to 80°C and stirred under ultrasonic agitation for 3 h. After drying at 80°C for 15 h, the cake was mashed and followed by plasma reduction. The plasma reduction was conducted using argon glow discharge. Details of the plasma setup were given elsewhere [20–23]. The sample (about 0.4 g), loaded on a quartz boat, was placed in the glow discharge chamber which was a horizontal quartz tube (i.d. 35 mm) with two stainless steel electrodes (o.d. 30 mm). The system was connected to a source of Ar and was evacuated with a vacuum pump. When the argon pressure was adjusted to 50–100 Pa, the glow discharge plasma was generated by applying 900 V to the electrodes using a high voltage amplifier (Trek, 20/20B), with high purity argon (>99.999%) as the plasma-forming gas. The current was in the range of 1–2 mA. The signal input for the high voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett–Packard, 33120A) with a 100 Hz square wave. The plasma reduction lasted for 10 min at each time. Because the plasma reduction is a surface reaction, the sample was stirred using a glass rod after the plasma reduction and reduced several times. Here each sample was reduced 6 times. The gas temperature of plasma was measured by infrared imaging (Iacon, 100PHT), indicating that the reduction was conducted at ambient temperature. The schematic setup of plasma reduction is shown in Fig. 1. The loading of the Pt–Ir electrocatalyst supported on the TiC is the same with the S1, but is labeled as S2.

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