Catalyst support effects at the oxygen electrode of unitized regenerative fuel cells

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ABSTRACT

The support effect on PtIr (1:1) catalysts for the oxygen electrode of unitized regenerative fuel cells was investigated by using TiC and TiCN supports, and was compared with carbon supported PtIr catalyst. The electrocatalysts were prepared by the ethylene glycol method, and then heat-treated at 250 °C and 400 °C under helium atmosphere. Physicochemical characterization was carried out by XRD, TEM and X-ray Photoelectron Spectroscopy, meanwhile rotating ring-disk electrode was employed to determine the electrochemical activity and stability. Results revealed that carbon support catalyst treated at 250 °C has the highest activity toward oxygen reduction reaction attributed to its superior electrochemical surface area and the higher support conductivity. However, Ti-support catalysts show an increment of activity toward oxygen reduction reaction as well as of the stability, when catalysts are heat-treated at 400 °C. Moreover, TiCN support leads to a substantial increase toward oxygen reduction activity, and shows better corrosion resistance at anodic potentials (>1.1 V) than TiC support.

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1. Introduction

While fuel cells are becoming recognized as a preferred direct energy conversion device, important roles also exist for fuel cells in traditional and non-traditional energy storage applications. When used as an energy storage device, a polymer electrolyte fuel cell (PEMFC) is combined with a polymer electrolyte water electrolyzer, to create a regenerative fuel cell (RFC) system, which can convert electrical energy to hydrogen, as storable fuel, and then use it in the PEMFC to provide electricity when needed [1–4]. The advantages of these types of cells compared to batteries such as Ni/MH or Li-ions is the nonexistent self-discharge of RFCs and the opportunity to store great quantities of energy that can be converted to electricity. 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 [5]. 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 [6]. Possible applications of a URFC are not only specific for space or military uses, but also for an on-site energy storage system for load leveling of utility grids or for renewable energy such as photovoltaic and wind energy.

In a typical design of a URFC, each electrode is always in contact with the same gas, hydrogen or oxygen, and the electrical polarization of the cell is reversed when the system changes function. Therefore, the electrocatalysts should have a double function (anodic and cathodic) depending on the operation mode, and can be defined as bi-operational electrocatalysts. Nevertheless, it is usual to find this electrocatalysts defined in research works as bifunctional electrocatalysts. In order to improve the round-trip efficiency of the URFC, one key issue is the fabrication of stable and highly active bi-operational oxygen electrode catalysts, which can be used for both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) [7–10] as follows:

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \tag{1}$$
$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^- \tag{2}$$
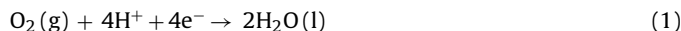
It is well known that the best electrocatalyst for oxygen reduction, platinum (in its reduced form) is not the best catalyst for water oxidation and oxygen evolution. In the other hand, IrO_2 or RuO_2 would be good candidates for oxygen evolution, although are relatively poor candidates as oxygen reduction catalyst. Therefore, mixtures of Pt, Ir, Ru, IrO_2 or RuO_2 were employed as bifunctional oxygen electrode catalysts [7–9,11–20]. However, mixtures of these noble metals are being used directly in the electrode at significantly high catalyst loadings [10,21].

The importance of the support in electrocatalysis is well recognized [22,23]. Typically, the support provides a physical surface for

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dispersion of small metal particles, which is necessary for achieving high surface area. For electrochemical reactions, additional roles of the support are to control wettability and to provide good electronic conductivity. However, carbon black, the catalyst support widely used in fuel cells, is not suitable for URFC due to its corrosion at high voltage especially in water electrolysis mode, as indicated by the following reaction [24,25]:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad (E^\circ = 0.207\,V\,vs.\,NHE\,at\,25\,^\circ C)$$

Some work has been reported on the use of electronically conducting carbon substitutes, including non-precious metal supports such as titanium-based materials in URFCs [26–29]. Chen et al. [26] examined three oxide supports: Ebonex (primarily composed of Ti_4O_7), phase-pure microcrystalline Ti_4O_7 and $Ti_{0.9}Nb_{0.1}O_2$, a doped rutile compound. These supports improved activity, but had short-lived electrochemical stability. The decrease was attributed to loss of electronic conductivity. Sui et al. [28] studied the effect of preparation method of Pt-Ir/TiC electrocatalysts. They found that compared with the electrocatalyst prepared by chemical reduction and deposition, the novel Pt-Ir/TiC electrocatalys prepared by plasma reduction displays the finer particles (<5 nm), relatively uniform distribution on the support TiC surface, and significant improvement in the electrocatalytic activity both for the OER and for the ORR. Recently, Huang et al. [29] studied physical mixtures of Pt/TiO_2 and Ir/TiO_2 electrocatalysts. These mixtures showed 30% higher round-trip energy conversion efficiency than that of unsupported Pt-Ir black.

Research is also being pursued on materials based on transition metal carbide and nitride family for their application in low temperature fuel cells, as described in a review by Ham and Lee [30]. Titanium carbides and nitrides are well-known for its high melting point, high resistance to oxidation and corrosion, good thermal and electrical conductivity. But behavior of these materials cyclic/high potentials, highly acidic conditions (pH < 1), which are the typical conditional variables of an electrocatalyst material in a URFC, has not been reported in the literature.

In the present study, we investigate the support effect on PtIr electrocatalysts for ORR and OER. TiC and TiCN have been studied and evaluated as titanium-based supports materials for URFC systems, and the results have been compared with catalyst supported on carbon black. In addition, the electrocatalysts thus obtained were heat-treated in a tube furnace at 250 °C and 400 °C under helium atmosphere looking for a higher interaction between catalyst particles and the supports. We demonstrated that heat treatment at 400 °C is necessary to improve the activity of the Ti-supported catalysts.

2. Experimental

2.1. Catalysts synthesis

The supported PtIr electrocatalysts were prepared by the ethylene glycol method (EGM) [31]. Ethylene glycol (>99%, Sigma–Aldrich) was used as solvent and reducing agent. Appropriate amounts of metal precursors ($IrCl_3$, Johnson Matthey, and $PtCl_4$, Alfa Aesar) were employed to obtain nominal metal loading of 20 wt.% with a Pt:Ir atomic ratio of 1:1 on the support material, Carbon Vulcan XC-72R (Cabot, Surface area (SA): 230 m^2/g), TiC (Sigma–Aldrich, SA: 23 m^2/g) and TiCN ($TiC_{0.7}N_{0.3}$ Sigma–Aldrich, SA: 22 m^2/g). Ir black (Johnson Matthey) was used for comparison XRD.

The metal precursors were dissolved in ethylene glycol under sonication and added into a suspension of the support in the same solvent. Then, the pH was adjusted to 11 and the temperature increased to 160 °C under a N_2 flow. After 3 h, the pH was adjusted

to 2 and the catalysts were washed with acetone and later rinsed with water and dried at 80 °C. Finally, a thermal treatment was carried out under He flow (80 mL/min) during 1 h at a 250 or 400 °C depending on the catalyst desired. Therefore, six catalysts were obtained and named as PtIr/C-250, PtIr/C-400, PtIr/TiC-250, PtIr/TiC-400, PtIr/TiCN-250 and PtIr/TiCN-400. Additionally, Pt/C-250 (20 wt.%) was obtained using the same preparation method.

2.2. Physicochemical characterization

Metal loading was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), with a Perkin-Elmer Optima 3300 DV spectrometer.

X-ray diffraction profiles of the powder catalysts were obtained on a PANalytical X'Pert Pro X-ray diffractometer with a Cu Kα source. Bragg's angles ranging from 2° to 90° were recorded at a scan rate of 0.04° per second.

A JEOL 2100F microscope operating at an accelerating voltage of 200 kV was used to obtain transmission electronic microscope (TEM) images, which were utilized to evaluate the morphology and particle size of the catalysts. The average particle diameter of each catalyst was calculated measuring the diameter of at least 300 metallic particles. With a coupled EDX analyzer (INCA x-sight from Oxford Instruments), semiquantitative chemical compositions were obtained.

Samples were examined by X-ray photoelectron spectroscopy (XPS), performed with a SPECS customized system for surface analysis equipped with a non-monochromatic X-ray source XR 50 and a hemispherical energy analyzer PHOIBOS 150. X-ray MgKα line (1253.6 eV) was used as excitation (operating at 100 W/10 kV), and the highest transmission mode of the lenses was used for the detector. Samples were stuck with a double-sided adhesive copper tape on sample holders, and were placed first in the pre-treatment chamber at room temperature for 1 h before being transferred to the analysis chamber. The instrument operated typically at pressures ca. 8×10^{-9} mbar in the analysis chamber. The XPS data were signal averaged for an enough number of scans to get a good signal/noise ratio, at increments of 0.1 eV and fixed pass energy of 25 eV. The binding energies (BE) were calibrated relative to the C 1s peak at 284.6 eV to take into account charge effects. The areas of the peaks were calculated from fitting of the experimental spectra using gaussian/lorentzian combined shapes, after the elimination of background noise upon use of Shirley-type curves. The surface atomic contents of the different components were calculated from such fittings, taking into account corresponding atomic sensitivity factors.

2.3. Electrochemical measurements

All measurements were carried out in a three-electrode cell at room temperature controlled by an Autolab PGSTAT302N potentiostat-galvanostat. A carbon row was used as a counter electrode, while the reference electrode was a reversible hydrogen electrode (RHE) in the supporting electrolyte (H_2SO_4 0.5 M, Merck, p.a.). All potentials are referred to this electrode. A rotating ring-disk electrode (RRDE) composed of Pt ring and glassy carbon disk (geometrical area = 0.196 cm^2) was used. The working electrode consisted in a catalyst suspension (20 μL) dried onto the glassy carbon disk under Ar atmosphere. The suspension was prepared by stirring 2 mg of catalyst with 30 μL of Nafion® (5%, Sigma–Aldrich) and 1 mL of water (Milli-Q, Millipore). N_2 (99.99%, Air Liquide) was used to deoxygenate all solutions and O_2 (99.995%, Air Liquide) to dose measurements related to oxygen reduction reaction (ORR).

Before electrochemical experiments, an activation step was carried out cycling between 0.05 and 0.9 V at a scan rate of 0.2 V s^{-1} until the acquisition of a stable voltammogram was obtained.