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Preparation and characterization of bifunctional graphitized carbon-supported Pt composite electrode for unitized regenerative fuel cell

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ABSTRACT

A bifunctional graphitized carbon-supported Pt oxygen electrode with montmorillonite-assisted dispersion was synthesized using an ultrasonic mixed technique process. By comparison, the graphitized carbon-supports obtain the optimal crystal quality with decreasing I_D/I_G ratio from 1.43 to 0.81 and narrow the peak linewidth from 186 to 84 cm^{-1}. Both Raman and the selected area diffraction analysis illustrate that the amorphous carbon tends to decrease via high-temperature graphite annealing so that the number of active C atoms will be reduced to improve oxidation resistance. From the CV measurements, the 20 wt.% Pt/graphite produces the highest specific charge transfer due to helpful montmorillonite assisted dispersion, whereas Pt size can only aggregate to grow bigger with an increase the Pt/graphite concentration. The polarization test of URFC presents the optimal performance in both the water electrolysis and fuel cell modes, with cell potentials of 1.6 V and 0.6 V at 100 mA cm^{-2}, respectively; it exhibits an optimized energy conversion efficiency of 37.5%, which is better than a Pt/C electrocatalyst-coated membrane due to its having more mass transportation formation and corrosion suppression. By using generated hydrogen to produce electricity, the total energy transfer efficiency of the cell measurement system will reach 50.6%.

1. Introduction

Recently, there has been increased interest in developing catalyst supports for fuel cells, and the field of engineering is using different technologies to study the carbon-based supports, e.g. carbon blacks (Vulcan XC72) [1–3]. Typically, the catalyst supports must provide a high surface area for supporting the active catalyst particles as well as reducing catalyst loading. Additional roles would provide good electronic conductivity, corrosion resistance and low cost [1–4]. However, such a carbon black material is unsuitable for use in unitized regenerative fuel cells (URFC); the high potential (about 1.0 V) at the oxygen electrode during water electrolysis will lead to heavy oxidation/corrosion of carbon blacks with the oxidation rate rising along with the potential [5]. In particular, the corrosion rate will be accelerated since Pt catalysts exist on the surface of the carbon blacks; this will lead to a significant performance loss in the URFC [2]. Note that the oxidation/corrosion of the carbon black affects the electrical contact and increases cell polarization, which subsequently leads to mass transport losses and declining cell stability [1]. Some early studies have reported on the use of carbon substitutes as electrical conductors (e.g. boron carbide (B_4C) and titanium carbide (TiC)) as possible catalyst supports for use in the oxygen electrodes of URFCs [1,6,7]. Several groups have also referred to transition-metal oxides (e.g. IrO_2 or RuO_2) as possible support in catalysis for the bifunctional oxygen electrode [8,9]. Although most of these support materials may show good corrosion resistance for use in URFC, their high cost and complex processes, as demonstrated with the current noble-metal-oxide support, make them less feasible for manufacturing.

In one study, Ferreira-Aparicio et al. preliminarily demonstrated the use of high surface area graphite as an alternative support for proton exchange membrane fuel cell (PEMFC) catalysts. They suggested that the extent of the carbon support graphitization plays an important role in achieving electrochemical and thermal stability, with more graphitic carbons demonstrating increased electrocatalyst stability [10]. Not long ago, Wang et al. also reported on a nanoscale graphite-supported Pt catalyst fabrication employed to improve the rate of carbon corrosion in fuel cells [11]. They found that the improved electrocatalyst not only had high cell performance similar to that of the commercial cell but also provided much better corrosion-resistance than the commercial electrocatalyst did; it could therefore possibly replace the currently used carbon blacks. Although the experimental works emphasized improving PEM fuel cell performance by changing the heat treated prescription, the dependence between support dispersion and graphite-supported Pt catalyst activity, as well as the utility of catalyst materials, has never been previously discussed. In addition, few detailed investigations have explored the round-trip

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energy conversion efficiency of graphite-supported Pt catalysts for URFC.

In the present study, the suitability of high surface area graphitized carbon with montmorillonite-assisted dispersion as a URFC catalyst support is investigated and compared with the use of the popular carbon black (Vulcan XC72). The relationship between montmorillonite modules and the size/displacement distribution of Pt nano-dots has been characterized. Both electroactivities and electrochemical properties were evaluated for the determination of the electrochemical surface area and catalyst utilization. Polarization measurements and round-trip energy conversion efficiency analysis were also used to evaluate the effect of graphitized carbon with montmorillonite-assisted dispersion in preparing a bifunctional oxygen electrode to improve URFC performance.

2. Experimental

2.1. Preparation of graphitized carbon-supported Pt electrocatalyst

Carbon supports purchased from the Cabot Co., Ltd. were first heat-treated at 2250 °C for 60 min in a high-temperature furnace under inert gas protection [12]. Afterwards, the ultrasonic mixed technique of graphitized carbon supports and unmodified natural montmorillonite (Cloisite® Na$^+$) with montmorillonite concentration of 1.5 wt.% were dispersed and prepared as catalyst supports in a procedure similar to one described in a previous study [13,14]. Using the finely dispersed graphitized carbon supports, four kinds of various Pt/graphitized carbon weight ratios of 10, 15, 20 and 30 wt.% were prepared, tested and compared for use as bifunctional oxygen electrode catalysts. By using a sonochemical mixed technique [15] with the addition of $H_2PtCl_6{\cdot}6H_2O$ as a Pt black precursor (Seedchem) on graphitized carbon supports, the loading of the Nafion solution was 5 wt.%.

2.2. Physical and electrochemical characterization of graphitized carbon-supported Pt electrocatalyst

The Raman spectra of the graphitized carbon supports were measured and compared with a Raman spectrometer using a HeNe laser (632.8 nm excitation wavelength) as the light source. Subsequently, scanning transmission electron microscopy (STEM, Hitachi H-7000) and a single-lens reflex camera (OM, Olympus) were employed to accurately characterize the Pt catalyst and dispersion of the graphitized carbon supports. The average particle size was determined by high-resolution transmission electron microscopy (HRTEM). The software package "DigitalMicrograph^{TM} 3.6.1. by Gatan" was used to determine the average Pt particle size from the real-time HRTEM image [16,17]. Note that the supported Pt particle shape normally assumed to be spherical with a face-centered cubic structure [18]. A large number of particles (360–460) could be examined to obtain the good statistical values. In order to realize the electroactivities and electrochemical properties of the graphitized carbon-supported Pt electrocatalyst, 0.01 ml of catalyst ink was loaded onto a glassy carbon disk electrode (diameter of the active zone was 3 mm). After drying, the electrochemical properties of the physically mixed Pt/graphitized carbon catalysts were analyzed by a cyclic voltammetry (CV) technique through a CHI614D electrochemical analyzer. In order to obtain information concerning electrode activities, glassy carbon disk electrodes coated with Pt/graphitized carbon catalysts were measured in a 1 M H_2SO_4 solution with a 50 mV s^{-1} scanning rate between −0.4 and 1.2 V at room temperature, while a Pt wire served as the counter electrode and an Ag/AgCl served as the reference electrode.

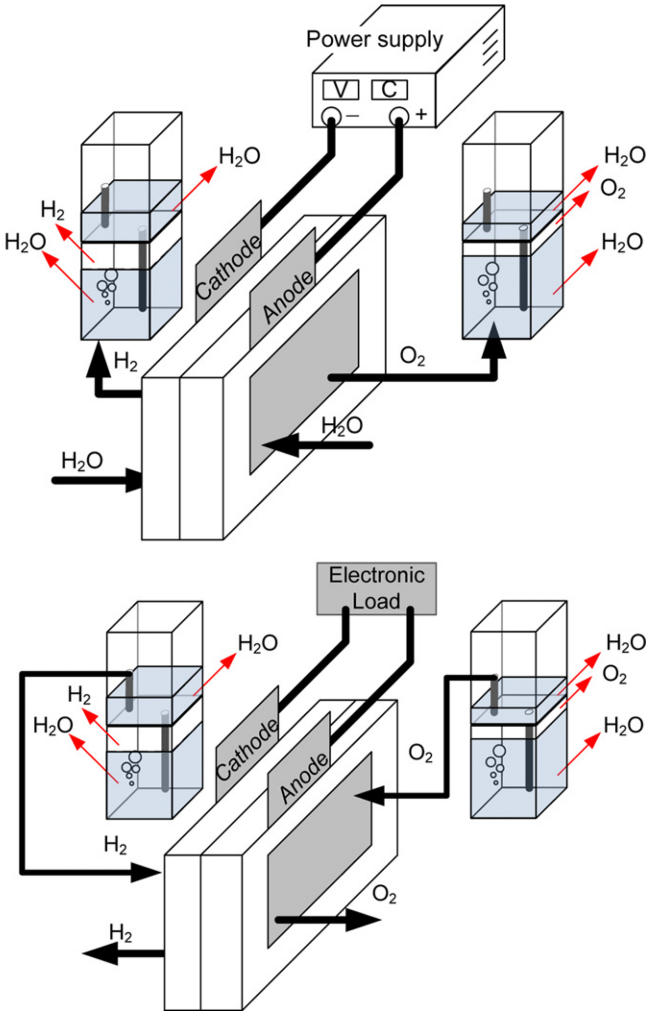

Fig. 1. Schematic operation of a URFC system, (top) PEM electrolyzer and (down) PEM fuel cell.

2.3. Bifunctional membrane electrode assembly (MEA) preparation and unit cell test

To evaluate the round-trip energy conversion efficiency and cell performance of a bifunctional MEA, the maximum charge transferred for hydrogen adsorption obtained from the CV curve of a graphitized carbon-supported Pt electrocatalyst sample was employed in the fabrication of the URFC unit cell. First, the electrocatalyst ink was coated onto both sides of a 9 cm^2 polymer electrolyte membrane (DuPont-Nafion 212), followed by drying at 70 °C. Next the polymer electrolyte membrane was interposed between the two gas diffusion layers (GDLs) using a hot pressing system; the anode/PEM/cathode module was used as the MEA in polarization measurements. Note that the catalyst loading in the electrodes was kept at a constant value of 0.25 mg cm^{-2}. In order to compare the improved performance of their round-trip energy conversion properties, we also prepared a popular carbon black- (Vulcan XC72) based MEA with the same catalyst loading and dispersion method. Subsequently, the MEA was placed in a unit cell, and the cell performance was measured via a cell measurement system; this included the URFC cell, water tanks, DC power supply and electronic loads, as shown in Fig. 1. In the electrolyzer mode, an external power source (DC power supply) provided power directly to the URFC unit cell in order to decompose the water into H_2 and O_2 according the following reaction of $2H_2O + \text{electrical energy} + \text{heat} \rightarrow 2H_2 + O_2$. In the fuel cell mode, the