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Original Research

Effect of solvent on Se-modified ruthenium/carbon catalyst for oxygen reduction

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Abstract

Se-modified ruthenium supporting on carbon (Se_x–Ru/C) electrocatalyst was prepared by solvothermal one-step synthesis method. The reaction mechanism was revealed after discussing impact of different solvents (i-propanol and EG) in solvotermal reaction. The result showed that the grain size of Se-modified ruthenium electrocatalyst was as small as 1 to 3 nm and highly dispersed on carbon surface. X-ray photoelectron spectroscopy (XPS) presented that selenium mainly existed in the catalyst in the form of elemental selenium and selenium oxides when the solvent was EG and i-propanol, respectively. The oxygen reduction reaction (ORR) performance was improved by appearance of selenium oxides.

Keywords: Se_x–Ru/C; Solvotermal reaction; Selenium oxides; Oxygen reduction reaction

1. Introduction

For investigating the structure of ruthenium-based catalysts (Ru_xSe_y), Alonso-Vante [1] paid special attention to the distribution of the Se atoms in the particles. Then, they drew cluster model structure of $Ru_{99}Se_{54}$ after comparing Ru_x versus Ru_xSe_y, in which a statistical distribution and an ordered positioning were concluded. Subsequently, Behm found the selenium played a role in surface modification of ruthenium and increased the catalytic stability of ruthenium supported on carbon, so they called the cluster catalysts as selenium-modified ruthenium catalysts [2].

In recent years, the preparation of carbon supported ruthenium catalysts has attracted scientific attention due to the potential application the catalysts as a cathode catalyst in direct methanol fuel cell (DMFC) [3–5]. The structural and chemical features were elucidated, in which carbon supported ruthenium nanoparticles prepared by thermolysis of $Ru_3(CO)_{12}$ in an organic solvent with and without the presence of dissolved selenium [6]. It was shown that the presence of selenium was the decisive factor to significantly improve the catalytic activity and stability compared to unmodified ruthenium nanoparticles. A special selenization in the course of a one-step synthesizing technique resulted in the high ORR activity of the catalysts [7]. However, the catalytic activity was still unsatisfied for commercial application in DMFCs due to undesired catalyst particle aggregation and a shell of amorphous Se-containing byproducts.

A significant leap forward was achieved by introducing a two-step preparation process. Selenium-modified ruthenium catalysts have been synthesized by various methods, using less expensive precursors in more environmentally compatible solvents. Different ruthenium precursors, such as $RuCl_3$, $Ru(NH_3)_6Cl_2$, Ru-oxalate or Ru colloids, and selenium compounds (H_2SeO_3 or $SeCl_4$) have been proposed for the preparation of carbon-supported catalysts [8–10]. The reduction process has been performed with $N(C_8H_{17})_4BEt_3H$, $LiBEt_3H$, or $NaBH_4$ reagents, or heating under hydrogen.

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Selenium-modified ruthenium catalysts have also been demonstrated to have good stability in acids and improved methanol tolerant performance relative to Pt. Good methanol tolerance of Ru_xSe_y, which likely originated from the weak interaction between carbon monoxide and catalyst surface, contributed to the catalyst selectivity toward ORR in the presence of methanol [11]. Additionally, electrochemical investigations using rotating ring-disk have proven that oxygen reduction occurs predominantly via a $4e^-$ path, with the amount of hydrogen peroxide produced not exceeding 6% [12]. These Ru_xSe_y properties make this catalyst attractive to fuel cell cathode applications.

In this paper, selenium-modified ruthenium (Se_x–Ru/C) electrocatalysts were prepared by solvothermal one-step synthesis method using less expensive water-soluble ruthenium chloride and selenious acid as ruthenium and selenium precursors reacted in teflon reaction vessel. The effect of different solvent on ORR activity will be discussed to explore the role of selenium in this electrocatalyst.

2. Experimental

2.1. Se_x–Ru/C catalysts preparation

Se_x–Ru/C catalysts were prepared using ruthenium trichloride ($RuCl_3 \cdot nH_2O$, Purity 99%, Special Grade Reagent) and selenious acid (H_2SeO_3, purity 99%, special grade reagent) as the ruthenium and selenium precursors, using a Teflon reaction vessel. Typically, 0.6 mmol of $RuCl_3 \cdot nH_2O$, 0.2 mmol of H_2SeO_3, 95.6 mg carbon substrate and 11 mL of i-propanol or EG were added into Teflon reaction vessel with inner volume of 25 mL. The sealed Teflon reaction vessel was fixed on the rotatable metal rod in reaction oven and kept at constant temperature of 150 °C for 10 h. After cooling, washing and drying, the as prepared catalyst was calcined at 300 °C for 2 h in normal tube furnace with argon and hydrogen flow. The final product was named as Se_x–Ru/C, in which x meant the molar ratio of selenium to ruthenium and here $x \approx 0.3$.

2.2. Physical characterization test

The catalyst powder was characterized by X-ray powder diffraction (XRD) to determine the catalyst structure and particle size estimation under a Rigaku Ultima IV X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å). Specific scan parameters are tube voltage of 40 kV, tube current of 800 mA, step angle of 0.02, and scan rate of 2°/min. The specific surface area was measured by BEL SORP-max ($P/P_0 = 0.1$–0.3 atm) produced by BEL JAPAN, INC. Pressure of 0.1–0.3 atm N_2 at liquid nitrogen (JEOL Ltd.) temperature (relative pressure: P/P_0) was calculated by BET method specific surface area of the sample from N_2 (Tosa Sanso CO., LTD) adsorption. High-resolution transmission electron microscopy (HRTEM) was used to examine the morphology and microstructure of the products on Hitachi H9500 instrument working at 200 kV.

2.3. Preparation of electrode

The suspension, which was comprised of relevant electrocatalyst, ethanol (purity 99.5%, Sophisticated analysis) and a small amount of 0.5 wt% Nafion (Toyota Motor Corporation) as a binder, was dripped on the glassy surface of glass carbon electrode (GC, HR2-D1-GC5, Hokuto Denko) by injector after ultrasonic mixing in ultrasonic cleaning machine (5510J-MT, Branson UL Trasonics Corporation) for 15 min. The mass density of target electrocatalyst films cast on the GC was 10 μg cm^{-2}.

2.4. Electrochemical test

Cyclic voltammetry (CV) curves and oxygen reduction reaction (ORR) curves were tested by rotating disk electrode (RDE) equipment (HD HOKUTO DENKO) which was comprised of an Automatic Polarization System HZ-5000, a Dynamic Electrode Controller HR-300 and a Dynamic Electrode HR-301. Three-electrode system included a glassy carbon (HR2-D1-GC5) working electrode, a RHE (HS-250C) reference electrode and a platinum counter electrode. O_2-saturated 0.1 M $HClO_4$ was utilized to test RDE data at 27 °C with 1600 rpm by collecting cyclic voltammograms at 15 mV s^{-1}.

3. Results and discussion

Fig. 1 shows the XRD patterns of Se_x–Ru/C catalysts prepared in different solvents before and after calcination at 300 °C in Ar and H_2 flow. Six obvious diffraction peaks in all catalysts before calcination corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) were attributed to characteristics of hcp Ru metal (JCPDS powder diffraction data file no. 06-0663). The grain growth or some organic compounds being removed by heat treatment in Ar and H_2 flow resulted in the higher peak intensity in the patterns after

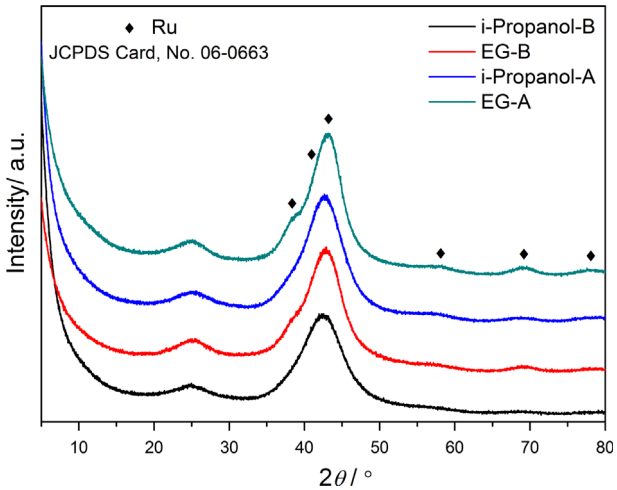

Fig. 1. Powder XRD patterns of Se_x–Ru/C catalysts prepared in different solvents, in which "B" represented before calcination and "A" represented after calcination.