Methanol tolerant core-shell RuFeSe@Pt/C catalyst for oxygen reduction reaction

Haili Gao [a,*], Shijun Liao [b,**], Yong Zhang [a], Lizhen Wang [a], Linsen Zhang [a]

[a] Department of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450001, PR China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, PR China

ARTICLE INFO

ABSTRACT

Pt decorated RuFeSe/C catalyst is prepared by reduction of Pt precursor on pre-formed RuFeSe/C for oxygen reduction reaction (ORR). The catalyst is characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The catalyst particles are found to disperse on the carbon support with an average particle size of 2.8 nm. Physical characterizations and electrochemical tests confirm that Pt is deposited on the surfaces of RuFeSe particles and RuFeSe@Pt/C catalyst has a core-shell structure. The as-prepared catalyst has high durability and shows high ORR activity through a four-electron transfer process. RuFeSe@Pt/C exhibits 1.3-fold greater specific activity and 1.4-fold greater mass activity for ORR than Pt/C. More importantly, it has excellent tolerance to methanol. Consequently, RuFeSe@Pt/C may be used as fine cathode catalyst in direct methanol fuel cells (DMFCs).

Introduction

In order to meet the growing energy demand and reduce environmental pollution, scientists have paid more attention to fuel cells (FCs). Direct methanol fuel cells (DMFCs) have developed greatly [1–3] owing to the easy fuel handling and storage, environmental friendliness, high energy efficiency, and so on. Despite this, there still exist some problems, such as resource scarcity and high cost of Pt catalyst, the comparably sluggish kinetics of the oxygen reduction reaction (ORR), and methanol crossover from anode to cathode through polymer electrolyte membrane [4] which decreases the fuel cell efficiency [5].

At present, there are mainly two approaches to solve such problems: development of new proton-conducting membranes and synthesis of methanol-tolerant cathode catalysts. The latter has become one of the research hotspots in DMFCs and has drawn the attentions of scientists and engineers. Up to now, many non-Pt catalysts have been studied, such as Pd-M alloys (M = Fe, Co, Ni, Mo, et al.) [6–9], Pd–TiO₂ [10], Fe–N–C [1], Ru-based (RuSe or RuMSe) [11] catalysts, and so on. These catalysts have excellent methanol tolerance, but unfortunately, the activities of these catalysts for ORR are lower than

that of Pt, and the long-term stabilities are far from satisfactory [12].

In addition, preparation of Pt-based alloys and construction of core@shell structure are regarded as effective methods to reduce Pt loading and improve utilization efficiency. Especially in recent years core-shell nanostructures have attracted wide attention due to the unique physical and chemical properties [13]. By proper choice of the composition, the activity of Pt shell for ORR can be improved through structural effect and electronic effect [14]. So far, Core-shell structured PdFe@Pt, PdPb@Pt, Au@Pt, Pd (111)@Pt, Cu@Pt [15—18] nanomaterials have been successfully prepared.

In the present paper, a core-shell structural RuFeSe@Pt/C cathode catalyst with high ORR activity and excellent methanol tolerance was prepared by using a three-stage method. There are several reasons why we choose RuFeSe as core. First of all, the resource of Ru is four times abundant than that of Pt but the price of Ru is just one nineteenth of Pt, according to the latest price on line (http://hq.smm.cn/gjs). Secondly, Ru-based materials have been reported as cathodic catalysts but their ORR catalytic activities are lower than those of Pt. Finally, in our previous work, we have successfully prepared a series of core-shell structured catalysts [19—21], and the as-prepared catalysts showed improved catalytic activities and high utilization of noble metal. In addition, Woo and co-workers [22] prepared PtRuFeSe/C catalyst and $Pt_{50}Ru_{10}Fe_{20}Se_{10}$ showed higher methanol tolerance and ORR activity than Pt/C. It is reported that the addition of Se to the Ru-catalysts can reduce the particle size [23] and protect the surface of Ru from oxidation [24], which can enhance the ORR activity. Moreover the addition of a second transition metal (Mo, W, Fe, or Cr) to the RuSe catalysts also increases the ORR activity because of electron localization in metalclusters [25]. Therefore preparation of core-shell structural RuFeSe@Pt/C catalyst and evaluation of catalytic performance for ORR are worth studying.

Core-shell structural RuFeSe@Pt/C catalyst was synthesized via deposition of Pt on the surfaces of preformed RuFeSe core by a three-stage approach. The core-shell structure of the catalyst was confirmed by Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electrochemical measurement. RuFeSe@Pt/C possesses higher ORR activity and methanol tolerance than Pt/C due to the special structure. In addition, the core-shell structural RuFeSe@Pt/C catalyst exhibits good durability.

Experimental

Catalyst preparation

RuFeSe/C catalyst was prepared from inorganic precursor by impregnation-reduction method. A typical preparation of this catalyst would consist of the following steps: Vulcan XC-72 carbon (Cabot Corp., denoted as C) was pretreated in 30% H_2O_2 and 10% HNO_3 solution at 80 °C. Then 83.3 mg $RuCl_3 \cdot 3H_2O$ and 77.1 mg $Fe(NO_3)_3$ were dissolved in small amount of aqueous solution, followed by addition of 200 mg pre-treated carbon. The mixture was allowed for water evaporation at 70 °C in an oil bath. After being dried at 60 °C in

vacuum for 12 h, the solid was grinded and heated in a tube furnace under hydrogen atmosphere at 200 °C for 2 h. Afterwards, appropriate amounts of H_2SeO_3 solution (0.041 mol L^{-1}) was added dropwise to the RuFe/C, followed by heat treatment at 200 °C in a H_2 atmosphere for 2 h. The metal loading was 20 wt.% and the atomic ratio of Ru:Fe:Se = 1:1:0.3.

RuFeSe@Pt/C catalyst was prepared by an organic colloid method. 150.0 mg $H_2PtCl_6 \cdot 6H_2O$ and 206.8 mg sodium citrate were dissolved in 20 mL ethylene glycol (EG) and a homogeneous solution was formed. The as-prepared RuFeSe/C was then poured into the solution (~18 wt.% of Pt loading). After ultrasonic treatment, the pH of the mixture was adjusted to >10 by drop-wise addition of KOH/EG solution under intensive stirring. The black slurry was then poured into a Teflon-lined autoclave and conditioned at 120 °C for 6 h, followed by filtering, washing with deionized water and vacuum drying at 60 °C. For comparison, 20 wt.% Pt/C was also prepared following a similar procedure except that C was added instead of RuFeSe/C.

Catalysts characterization

The surface morphology and average particle size of the catalysts were assessed from transmission electron microscopy (TEM, JEM 2010HR) from JEOL instrument. The atomic composition of the catalyst was determined by the energy dispersive spectrometer (EDS) technique coupled to a TEM. The phase structure was analysed through X-ray powder diffraction (XRD) using a Shimadzu XD-3A (Japan) diffractometer. The X-ray photoelectron spectroscopy (XPS) measurement was carried out on a PerkinElmer PHI1600 system (PerkinElmer, USA) with Mg Ka X-ray radiation.

Electrochemical measurements

The electrochemical performances of the samples were measured in a conventional three-electrode test cell, using an IVIUM electrochemical workstation (Netherlands). The reference and counter electrodes were an Ag/AgCl (saturated KCl) electrode and a platinum wire, respectively. The working
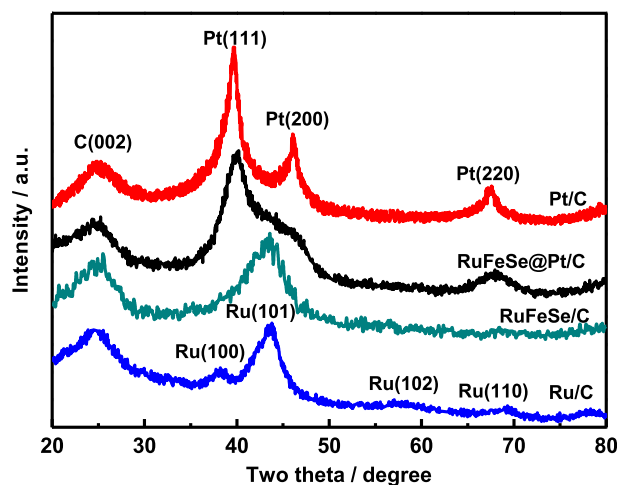

Fig. 1 — X-ray diffraction patterns of Ru/C, RuFeSe/C, Pt/C and RuFeSe@Pt/C catalysts.