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Strategic synthesis of platinum@ionic liquid/carbon cathodic electrocatalyst with high activity and methanol tolerance for the oxygen reduction reaction

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ABSTRACT

Improving the electrocatalytic activity and methanol tolerance of cathodic Pt electrocatalyst for the oxygen reduction reaction (ORR) is very important for accelerating commercial viability of direct methanol fuel cells. In this work, the highly dispersed Vulcan XC-72 carbon supported 1-butyl-3-methylimidazolium chloride (BmimCl) ionic liquid modified Pt nanoparticles (Pt@BmimCl/XC-72) composites are synthesized successfully by simple NaBH₄ reduction method in the presence of BmimCl ionic liquid. In the method, the interaction between BmimCl ionic liquid and K₂PtCl₄ results in the generation of ultrafine BmimCl-Pt^{II} complex precipitate, which is responsible for the well dispersion and small particle size of final Pt@BmimCl/XC-72 composites. During the synthesis, the Pt nanoparticles are modified by BmimCl simultaneously due to the strong N-heterocycle-Pt interaction. The as-prepared Pt@BmimCl/XC-72 composites exhibit significantly improved activity and selectivity for the ORR in the presence of methanol in acidic media compared to Pt/XC-72 composites prepared by general NaBH₄ reduction method.

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Introduction

Direct methanol fuel cell (DMFCs), as highly promising alternative energy sources to fossil fuels, are receiving much more attention due to the high energy density, high energy conversion efficiency, low pollutant emission, and simple device fabrication [1–12]. So far, Pt is still the most efficient electrocatalyst for the oxygen reduction reaction (ORR) in the acidic

media [13–17]. However, its high cost, sluggish kinetics for the ORR, and easy poisoning by CO_{ads} intermediates generated in the methanol oxidation reaction (MOR) process due to the methanol crossover problem still hinder the commercialization of DMFCs. Fortunately, some strategies have been developed to improve the ORR selectivity of Pt electrocatalysts, including alloying Pt with a second atoms [18–20], isolating Pt atoms [21], and constructing porous nanoshell on Pt surface [22,23]. By preventing the adsorption of alcohol

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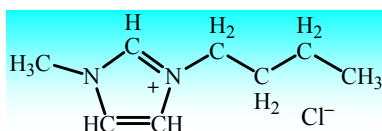
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molecules [18–21] and blocking the access of alcohol molecules [22,23], these advanced Pt electrocatalysts show the excellent selectivity for the ORR.

At present, Vulcan XC-72 carbon, a commercial carbon nanomaterial, has been widely used as a support to synthesize Pt/carbon composites due to its big surface area, high specific conductivity, and low double layer charging, which effectively reduce the dosage of precious Pt metal and enhance the electrocatalytic activity of Pt nanoparticles [24–26]. It has been accepted that the high-quality Pt/carbon composites with well-monodispersity and small particle size are the effectively cathodic electrocatalyst for DMFCs. However, the Pt/carbon composites also have excellent electrocatalytic activity for the MOR. Thus, cathodic Pt/carbon composites still suffer from CO_{ads} poisoning problem due to the methanol crossover.

Recently, many excellent works have demonstrated the electrocatalytic activity and selectivity not only depend on surface structure (such as particle size and crystallographic plane) of noble metal nanoparticles but also on interface structure of noble metal nanoparticles. Effective interface control over noble metal nanoparticles (i.e., modifying the metal surface with appropriate organic ligands) can effectively improve their electrocatalytic activity and selectivity due to electronic effect, steric effect, or their combination [27–38]. For example, calix [4] arene modified Pt nanoparticles could electrocatalyze selectively hydrogen oxidation reaction in the presence of oxygen due to strong ensemble effects [28,29]. Polyethyleneimine modified Pt nanocubes improved the ORR kinetics due to the electronic effect [37]. The experimental results confirm the chemical functionalization of Pt nanocrystals is effective method for improving the activity and selectivity of Pt nanocrystals.

In recent years, the room temperature ionic liquids have been widely used to synthesize Pt nanocrystals due to big dynamic viscosity, high thermal stability, and good electrochemical stability [39–44]. However, the effect of interface structure of Pt@ionic liquid on the ORR selectivity is rarely investigated [36,38]. In this work, we report a simple precipitation–reduction method to synthesize the high-quality Pt/carbon composites with well-monodispersity and small particle size by using NaBH_4 as reducing agent and 1-butyl-3-methylimidazolium chloride (BmimCl, Scheme 1) ionic liquid as precipitant and modifying molecule. Herein, BmimCl ionic liquid is selected because of its bargain price (2.5 g s^{-1}) and particular coordination ability for Pt^{II} precursor. The as-prepared Vulcan XC-72 carbon supported BmimCl modified Pt nanoparticles (Pt@BmimCl/XC-72) composites show improved electrocatalytic activity and methanol tolerance for the ORR compared to Vulcan XC-72 carbon supported Pt nanoparticles (Pt/XC-72) composites in the acidic media.



Scheme 1 – The molecular structure of BmimCl ionic liquid.

Experimental

Reagents and chemicals

Vulcan XC-72 carbon was obtained from Cabot Company (Boston, USA). 1-butyl-3-methylimidazolium chloride (BmimCl, Scheme 1) ionic liquid was purchased from Shanghai Chengjie Chemical Co., Ltd (Shanghai, China). Other reagents were of analytical reagent grade and used without further purification.

Synthesis of Pt@BmimCl/XC-72 and Pt/XC-72 composites

In a typical procedure, 1.0 mL of 0.048 M K_2PtCl_4 , 37.4 mg of Vulcan XC-72 carbon were added into 9.6 mL of 0.5 M BmimCl aqueous solution. After sonicating for 30 min, the resulting mixture was heated to 80°C for 12 h under continuous stirring conditions. After cooling, 10 mL of fresh prepared 0.5 M NaBH_4 solution was added into the mixture. The reaction was carried out at room temperature for one night. Finally, Vulcan XC-72 carbon supported BmimCl ionic liquid modified Pt nanoparticles (Pt@BmimCl/XC-72) composites were collected by centrifugation and dried for 12 h at 60°C . For comparison, the XC-72 carbon supported Pt nanoparticles (Pt/XC-72) composites were also prepared in the absence of BmimCl ionic liquid under the same experimental conditions.

Physical characterizations

Transmission electron microscopy (TEM) images of the samples were recorded JEOL JEM-2100F microscope (Hitachi, Tokyo, Japan) operating at 200 kV. X-ray diffraction (XRD) measurements were performed on a Model D/max-rC diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 electron spectroscopy (Thermo VG Scientific, Waltham, USA). The binding energy for C1s peak at 284.6 eV was used as an internal reference to calibrate the binding energy of sample. Element maps images were made in JSM-2010 scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) device. The metal loading on XC-72 carbon was measured by X Series 2 inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo Scientific, Waltham, USA). Thermogravimetric analyses (TGA) measurement was performed on a thermogravimetric analyzer (TA Q600SDT, Inc. New Castle, USA) under air atmosphere.

Electrochemical instruments

The electrochemical measurements were conducted on a computer-controlled CHI 660 D electrochemical analyzer with a Gamry RDE710 rotating disk electrode at 30°C using a conventional three-electrode system. A catalyst modified glassy carbon electrode as a working electrode, a saturated calomel electrode as a reference electrode, and a Pt wire as an auxiliary electrode. All potentials reported in this work refer to the reversible hydrogen electrode (RHE). The catalyst modified glassy carbon working electrode was prepared according to

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