Alcohol electro-oxidation on platinum–ceria/graphene nanosheet in alkaline solutions

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ABSTRACT

Platinum/graphene nanosheet and platinum–ceria/graphene nanosheet are prepared by a one-pot synthesis protocol and examined as electrocatalysts for the oxidation of methanol, ethanol, ethylene glycol, and glycerol in alkaline solutions. The activity of the catalysts is evaluated by cyclic voltammetry, linear sweeping voltammetry, and chronoamperometric tests. It is indicated that the addition of ceria is favorable for the oxidation of the alcohols. The platinum–ceria/graphene nanosheet catalyst exhibits higher current densities and superior durability in comparison with the platinum/graphene nanosheet. Maximum current densities of 1.1, 1.3, 3.2 and 2.5 A mg^{-1} Pt are obtained from the platinum–ceria/graphene nanosheet catalyst for the oxidation of methanol, ethanol, ethylene glycol, and glycerol, respectively. Notably, the current density values for the oxidation of ethylene glycol (3.2 A mg^{-1} Pt) and glycerol (2.5 A mg^{-1} Pt) are among the most active electrocatalysts reported in the literature. The activity of the catalysts in 1 M KOH solution is compared with that in 1 M H$_2$SO$_4$ solution. Both the platinum/graphene nanosheet and platinum–ceria/graphene nanosheet show superior performance in alkaline media.

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Introduction

Direct alcohol fuel cells (DAFCs) using liquid fuels such as methanol, ethanol, ethylene glycol (EG), and glycerol as energy sources, show great application prospect in mobile and portable electronic devices because of the high energy density and easy storage and transport of alcohols [1]. In particular, alkaline DAFCs using anion-exchange membranes as electrolytes have been of great interest because of the faster kinetics of alcohol oxidation and oxygen reduction as compared with those in acidic DAFCs [2]. The utilization of anion-exchange membranes in alkaline DAFCs significantly suppresses alcohol crossover, which is a critical problem of proton exchange membranes in acidic DAFCs [3]. Despite the advantages, the commercialization of alkaline DAFCs is currently impeded by several issues including (i) the slower oxidation kinetics of alcohols as compared with that of hydrogen in hydrogen-fueled polymer electrolyte membrane fuel cells [4], (ii) the incomplete oxidation of alcohols with two or more carbon atoms and (iii) the lack of high-performance alkaline anion-exchange membranes [5]. To address these

issues, numerous work has been devoted to searching for advanced electrocatalysts and anion-exchange membranes [2,5].

So far, Pt is considered as the most active catalyst for alcohol oxidation. Unfortunately, the scarcity and cost of Pt greatly inhibit its massive application in DAFCs. Thus, increasing utilization efficiency of Pt is of paramount importance for the widespread commercialization of DAFCs. To this end, one common strategy is to disperse ultrafine Pt nanoparticles (NPs) in proper supporting materials. The supports affect the physicochemical properties of Pt such as particle sizes, distribution and electronic structures, thereby modifying activity of electrocatalysts. An ideal catalyst support in DAFCs should have a large surface area and excellent conductivity to facilitate the transport of reactants and electrons, and properly interact with Pt NPs to avoid aggregation [6]. Additionally, it should be chemically and electrochemically inert to sustain long-term durability of electrocatalysts [7]. To date, a number of supporting materials such as carbons [8−10], metal oxides [11], carbides [12] and their hybrids were reported in the literature. Among the reported materials, the hybrids of metal oxides and graphene nanosheets (GNSs) are of particular interest because of the significant synergistic effects [13,14], in which the metal oxides promote alcohol oxidation via the so-called bifunctional and electronic effects while the GNSs provide a highway for electron transport and a large surface area to disperse Pt and metal oxide NPs. By delicately engineering the nanostructures, novel Pt-metal oxide/graphene catalysts were prepared and showed excellent activity towards alcohol oxidation [15,16].

Ceria was widely reported as a promoting component in electrocatalysts for alcohol oxidation [17−30]. For instance, Scibioh et al. [21] synthesized Pt-CeO$_2$/C catalysts with varying contents of ceria for the oxidation of methanol in 1 M H$_2$SO$_4$ and found that a 40 wt. % Pt-9 wt. % CeO$_2$/C catalyst exhibited better activity and stability than unmodified Pt/C catalyst. De Souza et al. [24] also prepared a series of Pt-CeO$_2$/C electrocatalysts for ethanol oxidation in an acidic medium. They found that a Pt-CeO$_2$/C (1:3) catalyst had higher activity than Pt/C and PtRu/C catalysts, which was attributed to the reduced poisoning and maximum utilization of catalyst surface. Xu and Shen [26] studied the oxidation of methanol, ethanol, glycerol and EG on a Pt-CeO$_2$/C catalysts in alkaline media. They found that the addition of CeO$_2$ significantly improved the electrode performance in terms of the reaction activity and poisoning resistance. Ou et al. [28] pointed out that the strong Pt−ceria interaction in Pt−ceria/C catalysts was responsible for the promoting effect of ceria in the oxidation of alcohols. Chu et al. [30] reported a facile approach to prepare Pt/C-CeO$_2$ catalysts by anchoring Pt NPs on carbon coated CeO$_2$ supports, which showed enhanced catalytic performance for methanol oxidation in acidic media due to increased electron conductivity, decreased dissolution-corrosion of CeO$_2$ support, as well as more oxygen-containing species. The authors' group [31−34] also devoted many efforts to exploring the promoting effects of ceria in electrocatalysts. The earlier work mainly focused on the synthesis of the Pt−ceria/carbon nanotube for alcohol oxidation [31−33]. In recent work [34], we prepared platinum−ceria/graphene nanosheet (Pt-CeO$_{2-x}$/GNS) catalysts by assembling Pt NPs in the hybrid of ceria and GNSs. The as-prepared Pt-CeO$_{2-x}$/GNS contained numerous Pt-ceria-GNS interfacial triple junctions, which facilitated the oxidation of alcohols. However, the Pt-CeO$_{2-x}$/GNS showed mediocre durability because of the leaching of cerium (III) ions in acidic media. Since ceria is relatively stable in alkaline solutions [35], it is expected that the durability of the Pt-CeO$_{2-x}$/GNS catalyst could be enhanced in alkaline media. Thus, in this work, we investigated the catalytic performance of the Pt-CeO$_{2-x}$/GNS catalyst in 1 M KOH solution. The oxidation of four alcohols (methanol, ethanol, EG and glycerol) on the catalysts was systematically studied. The objective of this work is to reveal the electrochemical features of oxidation of the four alcohols in alkaline media and illustrate the effects of electrolyte solutions in the catalytic performance of the catalysts. Hopefully, the results reported in this manuscript combined with those reported in our previous work [34] could present a complete study on the Pt-CeO$_{2-x}$/GNS and Pt/GNS catalysts for DAFCs.

Experimental section

Synthesis of catalysts

GNS support was derived from catalytic decomposition of methane and thoroughly purified by acid etching and sedimentation separation [36]. The GNSs consisted of few-layered graphene sheets (<10 layers). The Pt-CeO$_{2-x}$/GNS catalyst was synthesized by the polyol-assisted reduction process as reported in our previous work [34]. Briefly, 100 mg of GNS support, proper amounts of ceria (III) nitrate and H$_2$PtCl$_6$ aqueous solution (8 wt. %) were thoroughly mixed in 100 mL of EG by ultrasonication to form a stable suspension. 1.2 g of NaOH was dissolved in 50 mL of EG and the resulting solution was slowly added into the suspension under vigorous stirring. The reaction was carried out at 180 °C for 30 min. Then, the product was purified and dried to obtain the Pt-CeO$_{2-x}$/GNS catalyst. For comparison, GNS supported Pt catalyst (denoted as Pt/GNS) without addition of ceria was also prepared under identical conditions. The nominal weight percentage of Pt in the catalysts is 40% and that of ceria in the Pt-CeO$_{2-x}$/GNS catalyst is 10%.

Structural characterization

A field emission scanning electron microscope (JEOL 7600) was employed to observe the morphology of the catalysts. For field emission scanning electron microscopy (FESEM) tests, the powered catalyst sample was dispersed in a conductive copper tape and then transferred to the sample holder. The elemental composition of the catalyst was determined by inductively coupled plasma (ICP) analyses. The N$_2$ adsorption−desorption isotherms were obtained using the accelerated and surface area porosimetry system (ASAP 2020, Micromeritics). Before the test, the sample was degassed overnight at 100 °C in a vacuum oven. The surface area was calculated using the Brunauer−Emmett−Teller (BET) method.