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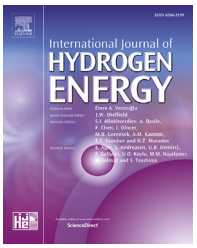

Effect of noble metal species and compositions on manganese dioxide-modified carbon nanotubes for enhancement of alcohol oxidation

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ABSTRACT

By integrating the effects of alloying, chemical composition and support, a series of mono- and bi-metallic catalyst nanoparticles electrodeposited on α-manganese dioxide (MnO_2)-modified carbon nanotube (CNT) supports were synthesized to improve the efficiency of direct alcohol fuel cells. Small and dispersed nanoparticles on the CNT/MnO_2 surfaces with high electrochemically active surface area (ECSA) were successfully obtained in this work. The support materials were characterized by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD), while the as-prepared catalysts were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) and chronoamperometry (CA) were used to study the activity and stability of the catalysts, respectively. The results showed that a combination of Pt, Pd, Au and MnO_2 on the CNTs significantly affected the topography of the composite catalyst surfaces, and their electrochemical measurements showed excellent electrocatalytic activity toward the reaction. For methanol and ethanol oxidation in acid solution, CNT/MnO_2/1M3Pt (M = Pd or Au) catalysts revealed greater activity improvement compared to the other prepared catalysts. For the bimetallic CNT/MnO_2/xMyPt catalysts, the values of the forward peak current (I_f)) and the ratio of the forward peak current to the reverse peak current (I_f/I_b) were higher, while their onset potentials (E_o) were lower compared to those of the monometallic CNT/MnO_2/4Pt catalyst. Moreover, CO oxidation on these bimetallic catalysts was also confirmed to be poisoning resistant. These results indicate that our prepared catalyst showed excellent electrocatalytic performance, reliability, and stability. The catalytic activity improvement was based upon the unique integrated structural and functional properties and the synergistic effect of different compositions in the catalyst system.

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Introduction

Direct alcohol fuel cells are remarkable electrochemical devices for clean and renewable power generation [1–4]. These fuel cells show the advantages of high energy density and low carbon emission and do not require an external reformer [2,3]. Moreover, the fuel source is liquid at ambient conditions, making it easy to store and transport and leading to more convenient use in practical applications. Recently, the fabrication of metal catalysts loaded on carbon materials has been intensely investigated to improve the performance of these fuel cells.

Loading of co-catalysts or secondary metals can modify the catalyst electronic structure, providing an opportunity to tune and develop their catalytic properties for several applications [4–7]. Most importantly, second-metal catalysts offer enhanced adsorption of H, O and OH species for the reduction of CO to perform electrochemical oxidation of alcohol [4,8–10]. However, numerous challenges to alloyed catalyst development, such as slow kinetics, unsatisfying catalytic activity and low catalyst stability, must still be overcome. To improve the performance of Pt-based catalysts, their alloys with various morphologies and metal compositions have been studied. The incorporation of a second element such as Pd, Au, Ni, Ru, Rh, Sn, and Cu has been reported to alter the electronic structure and chemical environment of Pt [11–17]. Among these additive metals, noble metals provide Pt-based catalysts with the most promising activity and stability.

In addition to the active metals, catalyst support is also a significant component because it intensely affects the production of active species. Lately, carbon-based materials such as carbon black, carbon nanotubes, graphene and its derivatives have attracted considerable attention as electrocatalyst supports in low-temperature fuel cell applications [18–20]. These carbons help increase the dispersion and stability of the metal catalysts and thereby enhance the electrocatalytic performance. Among these carbon materials, carbon nanotubes (CNT) have been shown to be promising candidates due to their unique properties such as large surface area, great mechanical strength and elasticity, exceptional electrical and thermal conductivity and ease of modification. They also afford high reactant mass transport and provide accessibility through high catalyst surface area for electron transfer [20–22]. Furthermore, the oxygen-containing groups (epoxy, hydroxyl, and carboxyl groups) on the CNT surface can support the poisoning-tolerant catalyst in a fuel cell [19–22].

Modification of carbon with metal oxide is another option for support development. Compared to various transition metal oxides, manganese oxides (MnO_2) with several crystallographic structures and morphologies have attracted strong attention due to their superior properties such as multiple valences, high activity and specific capacitance. These properties make manganese oxides widely used in catalysis applications [18,19,22,23]. Manganese oxides have been extensively studied in alcohol oxidation reactions due to their strong oxidizing property toward small organic molecules, excellent proton conductivity and good recyclability arising from a synergistic effect between the active metal component and the oxide [23–25]. MnO_2 was found to enhance CO tolerance due to the action of the Mn^{4+}/Mn^{3+} redox pair and the existence of labile oxygen, showing high promoting and anti-poisoning activities for alcohol electrooxidation [23–26].

To obtain commercially viable fuel cells, an intense effort has been dedicated to the design of electrocatalysts with low cost and high performance. Although Pt-based catalysts are usually recognized as the best catalysts for alcohol oxidation and have been intensively explored for the anodic fuel cell catalysis, the very high cost of Pt and the fact that it is easily poisoned by carbonaceous intermediates produced in electrocatalytic processes have largely limited their practical application [25,27,28]. In addition, the incorporation of bimetallic xMyPt could improve CO tolerance in Pt catalysts by changing the electronic band structure of Pt and modifying the strength of surface adsorption [14,17,29–31].

A structurally controlled CNT@SnO_2/Pt catalyst was prepared using an ethylene glycol reduction method [31]. It exhibited higher catalytic activity for ethanol electrooxidation than that of CNT/Pt. The structure of the CNT@SnO_2//Pt catalyst and a large amount of OH_{ads} increased the synergetic interaction between Pt and SnO_2. This result suggests that CNT@SnO_2 core-shell composites with a thin shell are good candidates as a catalyst support and second catalyst for ethanol oxidation.

The CNT/MnO_x/Pt catalyst was successfully prepared by the microwave-assisted polyol method reported [28,29,32]. While Mn in the CNT/MnO_x/Pt catalyst is found in several valence states, namely Mn^{3+}, Mn^{4+} and Mn^{5+}, its main valence state is Mn(V), which can dramatically enhance the exchange rate of H^+ ions. The existence of MnO_x in the CNT/MnO_x/Pt catalyst not only produces uniformly small Pt nanoparticles but also enhances proton conductivity, promotes the dehydrogenation of ethanol oxidation, eliminates adsorbed intermediates to discharge the Pt active sites and increases Pt utilization via the synergistic effect between Pt and MnO_x.

Moreover, Huang et al. successfully used MnO_x, Pt and Pb on CNT for the fabrication of a CNT/MnO_x/PtPb catalyst [8]. The existence of Mn^{4+}, Mn^{5+}, Pb^{2+} and Pt^0 species and partial alloying between Pt and Pb were found. Methanol oxidation with this catalyst demonstrated higher specific activity and somewhat lower onset potential than on CNT/Pt catalysts. The addition of Pb resulted in enhanced activity toward the oxidation of intermediate species, while dehydrogenation in methanol oxidation processes was noticeably enhanced by using CNT/MnO_x as a support [8,29,30].

In this work, a series of mono- and bi-metallic (Pt, Pd and Au) catalysts on MnO_2-modified CNT supports were prepared. The activity and stability of these electrocatalysts were determined by cyclic voltammetry (CV) and chronoamperometry (CA), respectively. The prepared catalyst-modified electrode demonstrated effective and stable performance in the oxidation of methanol and ethanol. Catalyst characterization was also carried out to elucidate the structure-activity relationship.

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