Synergetic effect of palladium–ruthenium nanostructures for ethanol electrooxidation in alkaline media

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HIGHLIGHTS

- Bi-phase Pd_xRu_{1-x}/C nanoparticles were prepared by a polyol method.
- $Pd_{99}Ru_1$/C nanoparticles have six times higher mass activity compared to Pd/C.
- $Pd_{50}Ru_{50}$/C lowers onset EOR potential by 290 mV compared to Pd/C.
- Improved EOR on Pd_xRu_{1-x}/C is correlated to the synergetic effect of the surface oxides.

GRAPHICAL ABSTRACT
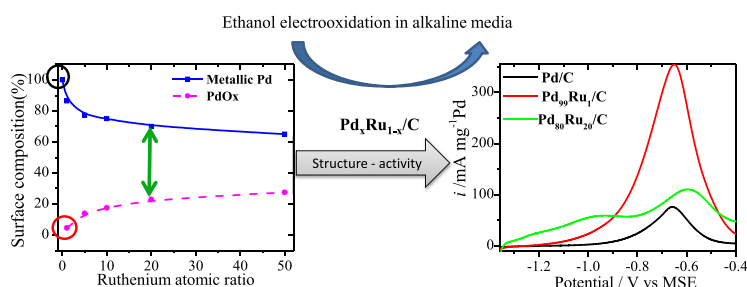
Ethanol electrooxidation in alkaline media

ABSTRACT

Palladium–ruthenium nanoparticles supported on carbon Pd_xRu_{1-x}/C (x = 1, 0.99, 0.95, 0.90, 0.80, 0.50) were prepared using a polyol method for ethanol electrooxidation in alkaline media. The resulting bimetallic catalysts were found to be primarily a mix of Pd metal, Ru oxides and Pd oxides. Their electrocatalytic activity towards ethanol oxidation reaction (EOR) in 1M KOH was studied using cyclic voltammetry and chronoamperometry techniques. Addition of 1–10 at.% Ru to Pd not only lowers the onset oxidation potential for EOR but also produces higher current densities at lower potentials compared to Pd by itself. Thus, $Pd_{90}Ru_{10}$/C and $Pd_{99}Ru_1$/C provide the current densities of up to six times those of Pd/C at −0.96 V and −0.67 V vs MSE, respectively. The current density at different potentials was found to be dependent on the surface composition of Pd_xRu_{1-x}/C nanostructures. $Pd_{90}Ru_{10}$/C catalyst with more surface oxides was found to be active at lower potential compared to $Pd_{99}Ru_1$/C with less surface oxides, which is active at higher potentials. The steady-state current densities of the two best catalysts, $Pd_{90}Ru_{10}$/C and $Pd_{99}Ru_1$/C, showed minimal surface deactivation from EOR intermediates/products during chronoamperometry.

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1. Introduction

Direct alcohol fuel cells (DAFCs) that operate in alkaline media are an emerging technology starting to receive research attention as alternative electrical power sources due to the tremendous progress in the development of anion exchange solid electrolytes [1–6]. The advantages of using alcohols as fuel are mainly due to their

high volumetric energy density. Additionally, their storage and transportation are cheaper than hydrogen fuel and alcohols can be easily obtained from renewable biomass [6,7] By operating in alkaline media instead of acidic media DAFCs have low corrosiveness and permits the use of non-noble metal electro-catalysts such as nickel, cobalt, copper, molybdenum and iron [7,8] thus decreasing significantly the cost. However, there are some challenges hindering the full commercialization of DAFCs which need to be addressed and are the subject of recent reviews [1,6,9]. The main challenges for DAFCs are: i) the much slower oxidation kinetics of alcohols compared to hydrogen fueled *polymer electrolyte membrane fuel cells* (PEMFCs) and ii) the incomplete oxidation of alcohols with two or more carbon atoms [1] Therefore, research efforts are geared towards designing and developing efficient electrocatalyst to increase electrical performance of DAFCs. Among the alcohols studied most are methanol, ethanol, ethylene glycol, propanol and glycerol of which ethanol is the most promising and non-toxic candidate [7]. The state-of-the-art catalysts are able to partially oxidize ethanol to acetaldehyde and/or acetate ions, giving a maximum of four electrons. This partial oxidation of ethanol translates to the energy density output which is three times lower compared to what would be obtained if CO_2 was the final product in which twelve electrons are exchanged. Therefore, design and implementation of highly active and stable electrocatalyst for ethanol electrooxidation is required.

Palladium has been shown as a promising electrocatalyst for ethanol oxidation in alkaline media [9]. Efforts in combining Pd with a second metal that can be either noble, e.g., Ru, Au, Rh or non-noble metals such as Fe, Co, Ni, Cu and Mo have been shown to improve not only the catalytic activity but also reduce the cost of the *membrane electrode assemblies* (MEAs) [8,10–13]. Ruthenium is known as a good promoter for alcohol oxidation and was recently reported to enhance ethanol oxidation on Pt in alkaline media yielding CO_2 as the major final product [14]. Recently, the interest for bimetallic Pd–Ru catalyst systems for ethanol oxidation reaction (EOR) in alkaline media has attracted the attention of various research groups [7,15–19].

Chen et al. and Sun et al. have compared the performance of Pd–Ru and Pt–Ru and showed that Pd–Ru in alkaline media is almost four times better for EOR than Pt-Ru [7,20]. Yi et al. studied porous Pd–Ru nanoparticles supported on titanium prepared by hydrothermal method [15]. They reported that $Pd_{87}Ru_{13}$ showed the best catalytic activity towards EOR in alkaline media in means of current density and onset potentials. They suggested that the "bifunctional mechanism" and the large surface area of $Pd_{87}Ru_{13}$ are playing a critical role in the overall catalytic performance. Anindita et al. investigated nanostructured Pd–Ru nanoparticles supported on carbon synthesized using sodium borohydride reduction method [16]. They prepared Pd-0.5wt% C and Pd-0.5wt% C-x wt. % Ru where x was 1, 5, 10, 20, and 50. They found that when the ruthenium content is 20 wt% electrocatalytic activity for EOR in alkaline media increases considerably. Bagchi et al. studied the electrocatalytic activity of an electrodeposited Pd–Ru catalyst supported on nickel for EOR in alkaline media [17,19]. They observed that the amount of loading and the composition of the catalyst have a superimposed effect on ethanol electrocatalytic activity. The thinner the electrodeposit film, the greater was the peak current per unit mass of deposit due to greater roughness factor arising from small size of the crystallites. Correia et al. studied EOR using Pd–Ru bimetallic complexes [18]. Although, they found increased current density at high potentials, no improvement was observed on onset potential for the reaction. In the recent work by Liang Ma et al. [21], authors reported EOR on Pd–Ru supported on carbon prepared by impregnation method with Ru content ranging between 20 and 50%. Liang Ma et al. showed that

Pd–Ru system not only performs well in half-cell tests but also gave 1.8 times higher power density compared to Pd/C in prototype fuel cell assemblies. They showed that the best performing catalyst has composition of 25% Ru and that the PdRu/C catalysts are promising materials for ethanol oxidation in alkaline environment.

Despite all these studies on Pd–Ru catalyst system for EOR in alkaline media [7,11–15] and the observed promotional effect of Ru on Pd electrocatalytic activity, several key points still remain to be understood and clarified. Among them, the role and effect of Ru both bulk and surface content. Similarly, the effects of surface structure modifications on the catalytic activity of bimetallic Pd–Ru nanoparticles for EOR in alkaline media are not yet fully understood.

In the current work, we show the correlation of the surface-structure-composition-activity of Pd_xRu_{1-x} (where x = 1, 0.99, 0.95, 0.90, 0.80 and 0.50) for ethanol electrooxidation in alkaline media. The nanoparticles were prepared using a polyol method and then supported on carbon. The NPs were characterized by scanning transmission electron microspectroscopy (STEM), X-ray diffraction (XRD) techniques and X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity was investigated using cyclic voltammetry (CV) and chronoamperometry (CA) techniques.

2. Experimental

2.1. Materials

The following materials: Palladium chloride ($PdCl_2$) anhydrous (*Fisher*), Ruthenium (III) chloride ($RuCl_3$) 99.99% anhydrous (*Alfa Aeser*), Ethylene glycol (EG) (*Fisher*), Potassium hydroxide (KOH) 85% (*EMD*), Sodium hydroxide (NaOH) ACS grade (*EM Science*), carbon black (C) Vulcan XC-72R (*Cabot*), Nitrogen gas (N_2) 99.9% (*Linde*), carbon monoxide (1000 ppm CO in He) (*Linde*), Nafion perfluorinated ion-exchange resin 5 wt.% solution in lower aliphatic alcohols/H_2O mix containing 15–20% water from (*Aldrich*), and Ethanol 99.9% (*Fisher*), were used as received.

2.2. Catalyst preparation

The Pd_xRu_{1-x}/C nanoparticles were prepared using a polyol method reported earlier [22,23]. In a typical synthesis, 0.25 g of the metal precursor salts ($PdCl_2$ and $RuCl_3$) were separately dissolved in 50 mL of EG. Then appropriate amounts of the two salt solutions were mixed to prepare Pd_xRu_{1-x} (x = 1, 0.99, 0.90, 0.95, 0.80, 0.50 and 0). The solution pH was adjusted to 8 by adding 0.06 M NaOH in EG. The mixture was homogenized by stirring for 30 min at room temperature before refluxed at 160° for 2 h. To the resulting colloidal NPs, appropriate amount of carbon black was added to obtain supported catalysts of 20 wt% loading. The mixture was stirred for 48 h so as to achieve high dispersion and complete deposit of Pd–Ru nanoparticles. The supported catalysts were thoroughly washed and rinsed five times with de-ionized water (18 Ω cm) to remove EG and salt ions through vacuum filtration and dried in the oven at 100 °C for 4 h.

2.3. Physical characterization

2.3.1. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) equipped with energy-dispersive X-ray spectroscopy (EDX)

The FEI Titan3 80–300 microscope equipped with a CEOS aberration corrector for the probe forming lens and a monochromatic field-emission gun was used to acquire HAADF-STEM images of the nanoparticles supported on carbon samples. The HAADF-STEM was operated at 300 k eV. The specimens were prepared by sonicating