Palladium–copper electrocatalyst for the promotion of the electrochemical oxidation of polyalcohol fuels in the alkaline direct alcohol fuel cell

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ABSTRACT

We demonstrate herein two important features of a $Pd_{87}Cu_{13}/C$ electrocatalyst that indicate it is a more efficient catalyst in alkaline media than Pd/C for the electrochemical oxidation of three polyalcohols: ethylene glycol, propylene glycol, and glycerol. First, we have discovered more efficient behavior in a three electrode electrochemical cell, where the electrochemical oxidation rate of ethylene glycol and propylene glycol was 4 times faster on $Pd_{87}Cu_{13}/C$ than Pd/C. In glycerol, the oxidation rate was 3 times faster in the electrochemical cell. This increase in oxidation rate is due to a combination of the electronic and bifunctional effects. Second, we have found that the $Pd_{87}Cu_{13}/C$ catalyst is also more efficient than Pd/C in an operating alkaline direct liquid fuel cell, although the efficiency gains are smaller than the electrochemical cell. During fuel cell testing, we found that the maximum power density of a propylene glycol fuel cell was 86% greater when the anode catalyst was Pd–Cu/C compared with Pd/C. The maximum power densities of the glycerol and ethylene glycol fuel cells increased by 75% and 32%, respectively. These polyalcohol molecules are of significant interest because they can be made from renewable sources and used to produce power in alkaline direct liquid fuel cells.

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1. Introduction

Recent development of an alkaline anion exchange membrane (AEM) has sparked interest in the efficient utilization of small organic molecules as fuels for direct liquid fuel cells (DLFCs) [1–4]. The alkaline environment of such DLFCs is advantageous for three key reasons [5]. First, electrochemical oxidation of small organic molecules is more efficient in alkaline media since it occurs with lower overpotential. Second, there is no fuel crossover within the fuel cell because the ion transfers through the membrane from cathode to anode. Third, there is no concern with cathode water management since water is produced only at the anode.

The first studies of the AEM in a fuel cell were focused on ethanol due to its availability as a renewable fuel and its limitations in acidic media [6,7]. Since the development of the first alkaline direct ethanol fuel cell (DEFC), other fuels have been explored. Propanol and the polyalcohols ethylene glycol (EG), propylene glycol (PG), and glycerol (G), have all been used as fuels in alkaline DLFCs [8–16]. We recently demonstrated that all of these alcohol fuels can be used in the same DLFC since they all oxidize on a palladium catalyst surface [17]. The most efficient fuel reported to date is potassium formate. The direct formate fuel cell (DFFC) has been demonstrated to produce more than twice the maximum power density (over $300\,mW\,cm^{-2}$) of any of the alcohol fuels [18–22]. In addition, formate has been shown to be the only fuel that is capable of producing continuous power without addition of potassium hydroxide to the fuel stream, since its oxidation reaction rate is not dependent on the pH of the fuel stream [23].

While the polyalcohol fuels are the most energy dense of the aforementioned small organic molecules, they produce less power density in the DLFC than the other alcohols and the formate [17]. However, it is desirable to use these polyalcohols in the DLFC because they can be sourced renewably from cellulosic feedstock (EG and PG) and as a byproduct of biodiesel production (G) [24–28]. Hence, it is imperative that catalysts more efficient than Pd are developed for the electrochemical oxidation of polyalcohols in alkaline media; such catalysts should promote efficient use of these renewable, energy-dense fuels in liquid DLFCs.
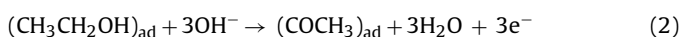
Recently, we demonstrated that the electrochemical oxidation of these polyalcohol fuels became significantly more efficient by the careful addition of small quantities of Sn, Sb, or Pb, at the palladium surface [29]. For example, the oxidation rate of G on Pd–Pb was 23

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times greater than on Pd after 10 min and 7.1 times greater after 12 h. In addition, the electrochemical oxidation of EG on Pd has also been shown recently to be promoted by the addition of Bi or Ni/Zn to the Pd [15,30]. Finally, we developed a $Pd_{87}Cu_{13}$/C catalyst that was shown to increase the electrochemical oxidation rate of ethanol and formate, but this catalyst has not previously been examined for polyalcohols [31].

The enhancement to electrochemical oxidation due to an element being added to Pd has been attributed to the bi-functional effect or the electronic effect (or a combination of both). The bi-functional effect occurs when the additional element directly catalyzes the electrochemical oxidation of the alcohol [5,15,32–34]. For example, the electrochemical oxidation of ethanol occurs on Pd by the following mechanism with the third reaction as the rate determining step [5,35]

$$OH^- \rightarrow OH_{ad} + e^- \tag{1}$$

$$(CH_3CH_2OH)_{ad} + 3OH^- \rightarrow (COCH_3)_{ad} + 3H_2O + 3e^- \tag{2}$$

$$(COCH_3)_{ad} + OH_{ad} \rightarrow CH_3CO_2H \tag{3}$$

Although the elements listed previously (Sn, Sb, Pb, Bi, Ni, Zn) are not known to directly adsorb ethanol, hydroxyls are more readily adsorbed on these non-noble metals than on the noble metal Pd [36]. Therefore, the bi-functional effect could result in a faster electrochemical oxidation rate for ethanol. It is also known that polyalcohol molecules require hydroxyl groups at the surface during oxidation, although their oxidation mechanisms are not as well understood [5].

The electronic effect occurs when the electronic structure of the Pd is modified by the presence of some other metal with a different d-orbital filling [37,38]. The resulting shift in Pd binding energy and d-band center changes the interaction of the Pd with the small organic molecule that is being oxidized [39,40]. When the changes to the Pd electronic structure are favorable, the reaction rate on the Pd is increased. It is difficult to distinguish between these two effects, although the reaction mechanisms offer some clues. For example, the electrochemical oxidation of formate occurs on a Pd surface by the following mechanism [21]:

$$HCOO^- \rightarrow H_{ad} + CO_2{}^-{}_{ad} \tag{4}$$

$$H_{ad} + OH^- \rightarrow H_2O + e^- \tag{5}$$

$$CO_2{}^-{}_{ad} \rightarrow CO_2 + e^- \tag{6}$$

which does not required the adsorption of a hydroxyl. Therefore, we did not expect the bi-functional effect to play a significant role in the electrochemical oxidation of formate, while it may play a significant role in the electrochemical oxidation of alcohols [31].

We previously reported physical and chemical characterization results on Pd/C and $Pd_{87}Cu_{13}$/C made by wet synthesis using sodium hypophosphite reducing agent and used in this work [31]. We found that the particle size was 4.7 ± 0.9 nm for the Pd/C and 5.0 ± 1.2 nm for the Pd–Cu/C. We identified a slight shift in the X-ray diffraction pattern indicating compression of the lattice due to alloying of Cu with Pd. Using these catalysts, we found an increase in the electrochemical oxidation rates of ethanol and formate in alkaline media. We attributed this to a combination of the electronic and bi-functional effects in ethanol and the electronic effect in formate. With respect to the electronic effect, we determined that there was an upshift in Pd $3d_{5/2}$ binding energy for Pd–Cu/C compared with Pd/C; this was a result of Pd valence electrons moving toward Cu. Since electrochemical oxidation of ethanol requires adsorbed hydroxyl in the rate determining step (Eq. (3)), we expected that its oxidation would be more influenced by the bifunctional effect, whereby the presence of Cu makes hydroxyl adsorption more favorable [5,31,35,36].

In the present work, we compare the electrochemical oxidation rates of the three polyalcohols (EG, PG, and G) on $Pd_{87}Cu_{13}$/C to their oxidation rates on Pd/C in an electrochemical cell. We then expand on this work to demonstrate the behavior of this Pd–Cu/C catalyst in an operating alkaline DLFC using each of the 3 polyalcohols.

2. Experimental

2.1. Catalyst synthesis

Each catalyst was prepared using metal salt reduction synthesis as described in our previous work [31]. In summary, sodium hypophosphite was used to reduce palladium and copper aqueous salts on activated Vulcan carbon. The solution was stirred, and sodium hydroxide and polyvinyl alcohol were added to control particle size. Proper atomic ratios of Pd and Cu precursors were used to produce $Pd_{87}Cu_{13}$/C and Pd/C. These catalysts were previously characterized using transmission electron microscopy, carbon analysis, elemental analysis, and X-ray diffraction [31].

2.2. Electrochemical analysis

Electrochemical measurements were performed using a PAR263A potentiostat in a custom-designed, three-electrode electrochemical cell. Catalyst ink was prepared using the carbon supported nanoparticles, AS-4 binder (Tokuyama, 15 wt% of final ink mass), and water. After sonication, a drop of this ink was dried onto a gold disk working electrode. The gold disk was rotated at 2000 rpm to remove gases produced during oxidation. The counter electrode was a platinum mesh (Alfa Aesar), and the reference electrode was a saturated calomel electrode (SCE, CH Instruments). Chronoamperometry was performed at -0.4 V vs SCE in each of the polyalcohols (1 M polyalcohol + 1 M KOH) for 3 h, where the polyalcohol is either ethylene glycol, propylene glycol, or glycerol (Fisher). Cyclic voltammetry was also performed in 1 M glycerol + 1 M KOH at 30 mV s^{-1}. Cyclic voltammetry measurements of the catalysts were also performed using data from the first sweep in acid solution prior to oxidation of Cu (i.e., 1 M H_2SO_4) to estimate their electrochemically active surface areas [41]. Once a catalyst was examined in the acid solution, it was not used again in the polyalcohol due to leaching of copper from the nanoparticles.

2.3. Fuel cell analysis

Fuel cell measurements were performed using a DC load box (BK Precision, 8500), a custom-designed active fuel cell with a 4 cm^2 electrode area, and the fuel cell heated to 60 °C. The membrane electrode assembly (MEA) was an alkaline AEM (Tokuyama, A201) spray painted with 2 mg cm^{-2} Pd/C or $Pd_{87}Cu_{13}$/C total metal loading at the anode, platinum black (Alfa Aesar, high surface area) at the cathode, and carbon cloth diffusion layers (Fuel Cell Stores) at both electrodes. Prior to spray painting, the catalyst inks were prepared with 6 parts catalyst, water (cathode) or isopropanol (anode), and 1 part alkaline ionomer (Tokuyama, 5 wt% AS-4). During operation, the fuel stream was 1 M alcohol plus 2 M KOH at a flow rate of 1 mL min^{-1} for voltage current (VI) tests and 0.2 mL min^{-1} for constant current (CC) tests. The oxidant was pure, humidified oxygen at 100 sccm. During VI experiments, the voltage was stepped from open circuit to 0.1 V. The CC experiments were run at 25 mA cm^{-2}. Each fuel was run through the same membrane electrode assembly, since all fuels oxidize readily on the same Pd/Pt or Pd–Cu/Pt combination of anode/cathode catalysts [17].