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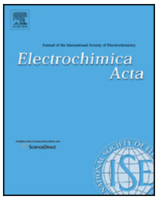

Increased Electrochemical Oxidation Rate of Alcohols in Alkaline Media on Palladium Surfaces Electrochemically Modified by Antimony, Lead, and Tin

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ABSTRACT

Several adatoms (M = Sb, Sn, or Pb) were added to Pd nanoparticles and examined for the electrochemical oxidation of ethanol, 1-propanol, 2-propanol, ethylene glycol, propylene glycol, and glycerol. We observed a significant increase in oxidation rate on Pd-M for each of the adatoms in each of the fuels. For example, the oxidation rate of ethanol was 1.5 times greater on Pd-Pb and Pd-Sn as compared with the oxidation rate on Pd after 10 minutes of oxidation. However, even more notable is the behavior observed by the polyhydric alcohols that exhibit sluggish reaction kinetics even in alkaline media. For example, the oxidation rate of propylene glycol on Pd-Pb was observed to be 21 times greater than the oxidation rate on Pd after 10 minutes, and it was still 7.1 times greater after 12 hours. These results show particular promise for the potential of efficiently oxidizing bulkier and higher energy density alcohols in the alkaline direct liquid fuel cell. All three bimetallic surfaces induced an increase in oxidation rate with all alcohols as compared to the monometallic Pd. Based on analysis of our results, we attribute a significant amount of the increase in oxidation rate to the bifunctional effect and suggest a lesser role is played by the electronic effect.

1. Introduction

Several alcohols are gaining momentum as promising energy carriers for alkaline direct alcohol fuel cells (DAFCs) since the recent development of the alkaline anion exchange membrane (AEM). The alkaline environment of such a fuel cell has several advantages over the acidic environment of a fuel cell employing a proton exchange membrane such as Nafion: reaction kinetics are faster, catalysts are less corroded, alcohol crossover via membrane is minimal, and water management is less complicated [1].

The faster reaction kinetics of an alkaline environment is a key factor that has driven research into the utilization of alcohols for alkaline fuel cells since alcohols containing 2 or 3 carbons generally oxidize poorly in acidic media. Therefore, development of the AEM has inspired several studies of ethanol as the fuel and energy carrier with reports of maximum power densities as high as 185 mW cm^{-2} at 60 °C [1–5]. However, high performance alkaline DAFCs powered by ethylene glycol and C_3 alcohols have been slower to develop because the oxidation rates are more sluggish.

Recently, alkaline DAFCs were powered by ethylene glycol (EG) and glycerol (G) using Pd-(Ni-Zn)/C anode catalyst to achieve maximum power densities of 95 and 119 mW cm^{-2}, respectively, at 80 °C [6]. It should be noted that the maximum power densities were lower when the same fuels were tested with Pd/C anode catalyst, indicating that the Ni and Zn had a promotional effect on the alcohol oxidation rate. While these power densities are significantly lower than that of ethanol, the fuels are attractive because they can be obtained through renewable processes.

Critical to implementation of such fuels in alkaline DAFCs is the development of more efficient oxidation catalysts under benign conditions. Therefore, the purpose of this work is to determine the efficiency of palladium (Pd) catalysts modified by antimony (Sb), tin (Sn), and lead (Pb), using electrochemical surface modification of the Pd. These bimetallic catalyst surfaces have previously been studied for the oxidation of formic acid in an electrochemical cell, in a fuel cell, and using x-ray photoelectron spectroscopy (XPS)

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[7,8]. It was reported that each adatom made the palladium surface more efficient for formic acid oxidation and reduced catalyst poisoning (by CO adsorbate) at intermediate time periods (up to 3 hours of oxidation). The presence of a bimetallic surface leads to the possibility of three effects on the oxidation rate of the fuel.

The *electronic effect* occurs when the adatom alters the electronic nature of the catalytically active atom, in this case palladium, and results in promotion of the fuel oxidation rate [9–13]. The alteration of the electronic nature of the catalyst is identified by a shifting in core level binding energy, which impacts the interaction of key reaction intermediates with the catalyst surface. An upshift in core level Pd 3d binding energy was observed in XPS measurements of Pd-Sb, Pd-Sn, and Pd-Pb nanoparticle surfaces that at least in part contributed to an increase in oxidation rate of formic acid [7,9].

The *steric (or third-body) effect* occurs when the adatom blocks neighboring catalyst sites, preventing formation of strongly-bound poison intermediates [14–17]. In the case of C_1 molecules such as formic acid and methanol, formation of strongly-bound CO is detrimental to the oxidation rate because catalytically active sites are blocked; therefore the steric effect plays an important role during the oxidation of these molecules. It was reported that the adatoms Sb, Sn, and Pb induce a steric effect during formic acid oxidation, at least for a few hours; however, the steric effect is minimized after several hours of oxidation when strongly-bound CO begins to overwhelm the catalyst surface [7]. During the oxidation of the C_2 and C_3 alcohols considered in the present study, strongly-bound CO-like intermediates are not produced in significant quantities because Pd does not promote C-C bond scission under these alkaline, low temperature conditions [6,18]. Therefore, the role of the steric effect in the present study is minimal.

Finally, the *bi-functional effect* occurs when the adatom directly catalyzes the oxidation of the fuel [1,6,19–21]. The adatoms Sb, Sn, and Pb, are not known to *directly* adsorb or oxidize the organic molecules in the present study, but they are each expected to adsorb hydroxyl molecules more readily than palladium does. Therefore, if adsorbed hydroxyl is a key reactant in the reaction mechanism, then its surface adsorption will be facilitated by the presence of the non-noble adatom. For example, ethanol oxidation is proposed to occur according to the following mechanism on a Pd surface [1,22]:

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

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

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

In this mechanism, the rate determining step is step 3, which is dependent both on surface concentration of adsorbed acyl *and* adsorbed hydroxyl. Therefore, since the adatom more readily adsorbs hydroxyl, one would expect that the rate limiting step proceeds by adsorbing an acyl group on Pd and a hydroxyl group on the adatom. This bifunctional effect would be expected to play a role during the oxidation of any molecule on Pd which requires adsorption of hydroxyl to proceed.

In the present work, we use the exact same method of metal adsorption that Haan and Masel used previously [7,8]. Therefore, we know the extent of binding energy shift induced on the Pd by each adatom. The purpose of this present work is to expand this knowledge to the application of alcohol oxidation in alkaline media. We expect that the electronic effect and bifunctional effects will play a role in promoting the oxidation rate of these alcohols, but we do not expect the steric effect to play a significant role since strongly-adsorbed intermediates have not been observed during oxidation of these molecules on Pd [1]. Understanding the role of the electronic effect and bifunctional effects during the oxidation of these alcohols in alkaline media will inform the development of more efficient catalysts in hope that several or all of these alcohols could be used in efficient alkaline DAFCs.

2. Experimental

2.1. Electrochemical surface modification and alcohol oxidation

A standard three-electrode electrochemical cell was used with a Princeton Applied Research potentiostat (Model 263 A), a saturated calomel reference electrode (CH Instruments), and a platinum mesh counter electrode (Alfa Aesar). The working electrode was an ink made by mixing palladium black (99.9%, Alfa Aesar) with Nafion binder (Ion Power, Inc.), directly painted onto small strips of carbon paper (Toray).

Voltammograms of the Pd catalyst were performed in 1 M H_2SO_4 before and after deposition of the adatom to determine the surface area of the catalyst using hydrogen adsorption/desorption peaks [8,23,24]. Chronoamperometry in the various fuels was performed before and after adsorption of the adatoms on the palladium. Chronoamperometry was performed at a potential of -0.4 V vs SCE (relevant to fuel cell anode oxidation potential) in all fuels and on all catalysts for 10 minutes or 12 hours. The fuel (ethanol, 1-propanol, 2-propanol, ethylene glycol, propylene glycol, or glycerol) was combined with 1 M KOH electrolyte to facilitate electrochemical measurements. Voltammetry was also performed in these fuels; however, significant differences were not observed between the fuels due to the high fuel concentration, so representative voltammograms are shown. The adatom adsorption was performed using the same technique previously established by Haan and Masel: the potential was held at 0.45 V versus SCE in a solution of each respective adatom/electrolyte: 2 mM Sb_2O_3 and 0.5 M $HClO_4$, 2 mM $Pb(NO)_2$ and 0.5 M $HClO_4$, or 2 mM SnO and 0.5 M $HClO_4$ [7]. Before each experiment, the electrochemical cells were degased in a constant flow of argon for at least 15 minutes.

2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS-165 with a monochromatized AlKα X-ray anode (1486.6 eV). The spectrometer was calibrated against the Au $4f_{7/2}$ peak at 84.0 eV and the Ag $3d_{5/2}$ peak at 368.3 eV. For the XPS measurements, the samples were further cleaned by Ar^+ sputtering to remove the remaining precursor compounds. The XPS spectra of Pd 3d was analyzed using commercial software (CasaXPS). Furthermore, all spectra were smoothed using the Sawitzki-Golay algorithm with a kernel of 5 pts.

3. Results

3.1. Electrochemical oxidation of monohydric alcohols

Chronoamperometry was performed on Pd black in ethanol for 10 minutes at -0.4 V vs SCE. The catalyst was then modified with the adatom and chronoamperometry was performed on the Pd-M (where M = Sb, Sn, or Pb) for 10 minutes. The purpose of this short oxidation time was to screen all catalyst/alcohol combinations. The adatoms were found by XPS to have the following concentrations when reduced onto the Pd: Sb 12.3 at%, Sn 25.6 at%, or Pb 10.7 at%. In Section 3.3 we discuss the long-term stability of these adatoms. This procedure was repeated several times in ethanol, and it was also repeated in the other monohydric alcohols, 1-propanol and 2-propanol. By way of example, we found that the oxidation rate of ethanol (Fig. 1) at -0.4 V vs SCE increased from 0.15 mA cm^{-2} on Pd black to 0.23 mA cm^{-2} on Pd-Pb, indicating that Pb at the Pd surface increases the oxidation rate of ethanol by 1.5 times in that trial. The