



Short communication

Electro-oxidation of 2-propanol and acetone over platinum, platinum–ruthenium, and ruthenium nanoparticles in alkaline electrolytes

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ABSTRACT

The voltammetric and chronoamperometric electro-oxidations of 2-propanol and acetone were carried out in base over Pt, Pt–Ru, and Ru nanoparticle electro-catalysts. A low-potential current maximum occurs during chronoamperometric electro-oxidations attributed to a reversible 2-propanol/acetone redox couple. The potential of this current maximum becomes more negative with increasing Ru content.

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1. Introduction

We report the electro-oxidation of 2-propanol and acetone over unsupported Pt, Ru, and Pt–Ru nanoparticle catalysts in alkaline electrolytes. Direct alcohol fuel cells (DAFCs) are an attractive method to power portable electronics because alcohols are readily available, they are relatively simple to store and transport, and they commonly have volumetric and mass-specific energy densities that exceed benchmark NiMH and lithium-ion batteries [1]. Direct methanol fuel cells (DMFCs) are the most studied type of DAFCs because methanol is readily available, it is structurally simple, and it has promising electrochemical activity [2]. There are two major challenges that must be overcome before DMFCs can be adopted for widespread use. One challenge is that carbon monoxide, or a related species, is an intermediate in the electro-oxidation of methanol. This intermediate poisons DMFC anode electro-catalysts, and high loadings are typically required to operate DMFCs near room temperature. Another challenge is methanol crossover from the anode to the cathode of the DMFC. Methanol poisons most cathode electro-catalysts, and high loadings are also required in the cathodes of room temperature DMFCs.

Several research groups, including our own, have reported the use of 2-propanol in DAFCs [3–5]. The potential advantages to the

use of 2-propanol as fuel are its relatively low toxicity, it is less prone to anode poisoning at low potentials, and it is less prone to crossover and cathode poisoning. For example, we recently reported the performance of a DAFC that was operated on 2-propanol and methanol as fuels [3]. The 2-propanol cell voltage was ~ 220 mV higher than methanol for current densities ranging from zero up to ~ 200 mA cm⁻². The 2-propanol cell voltages became erratic, however, at current densities higher than ~ 200 mA cm⁻². Similar observations were reported by Qi and Kaufman [4]. The erratic cell voltages at higher current densities were caused by anode poisoning at higher potentials. The mechanism for the electro-oxidation of 2-propanol over Pt in acid is widely studied [6–11]. Acetone is the major product at low potentials and its formation does not involve strongly adsorbed intermediates. The formation of carbon dioxide commences at high potentials, and proceeds through unidentified, strongly adsorbed intermediates. In acidic electrolytes, the onset potential for 1-propanol over Pt is typically between those of 2-propanol and methanol. The major oxidation products are propanal and propanoic acid [5].

We also recently studied the electro-oxidation of 2-propanol over blacked Pt gauzes in alkaline electrolytes [12]. We discovered a low-potential current maximum that occurs during potentiostatic electro-oxidations of 2-propanol in base. The current maximum was significant, no such maximum occurred for the electro-oxidation of methanol, and it likely arose from the rapid electro-oxidation of 2-propanol to acetone. We now report on the electro-oxidation of 2-propanol in alkaline electrolytes over Pt,

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Pt–Ru, and reduced Ru unsupported nanoparticle electro-catalysts. The aims of this study are gain information about the electrochemical behavior of these systems, and to identify potential anode electro-catalyst for evaluation in prototype 2-propanol DAFCs.

2. Experimental

Nitrogen (Praxair, prepurified), hydrogen (Praxair, prepurified), NaOH (Alfa Aesar, 99.99% semiconductor grade), H₂SO₄ (EMD, ACS Grade), Pt black (Johnson Matthey, HiSPEC™ 1000), and Pt–Ru (Johnson Matthey, 50:50 at.%, HiSPEC™ 6000) were used as-received from the supplier. Ru black (Johnson Matthey) was reduced with hydrogen (1 atm) at 60 °C. The reduced catalyst was stored under nitrogen until use, where it was exposed to air at 0 °C prior to fabrication of the working electrode. Water from an in-house distilled water line was distilled once, then distilled again from alkaline KMnO₄ (Fisher Scientific) before use. 2-Propanol (Fisher Scientific, suitable for electronic use) and acetone (Caledon, ACS grade) was freshly distilled before experiments.

Electrochemical experiments were performed using the setup described previously [9]. All potentials are reported versus the normal hydrogen electrode (NHE), unless stated otherwise. The working electrode was a Pt foil with an adsorbed layer of nanoparticle catalyst. The foil was cleaned in solutions of Aqua Regia (3:1 HCl:HNO₃) for 15 min, Piranha (5:1 H₂SO₄:H₂O₂) for 15 min, before rinsing and drying in an oven at 100 °C. The electro-catalyst was suspended in water by sonicating 2.5 mg of electro-catalyst in 2 mL of water for 1 h. A 200 μL aliquot of the suspension was dropped on a Pt foil by a glass syringe, and allowed to dry in air to give a physically adsorbed layer of ~0.25 mg of catalyst.

All current densities reported are normalized to the real electro-catalyst surface areas. For Pt, the charge transferred from the cathodic formation of an adsorbed hydrogen (H_{ad}) monolayer in 1 M H₂SO₄ was used to approximate the number of active site assuming an H_{ad} efficiency of 77% [13]. In the cases of Ru and Pt–Ru, a layer of carbon monoxide was adsorbed onto the electro-catalyst in 1 M H₂SO₄ at 75 mV (Pt–Ru), and 100 mV (Ru) for 25 min. The electrolyte was purged with nitrogen while maintaining the electrode at its adsorption potential, followed by sweeping anodically [14].

Before potential cycling and chronoamperometry, the electrode was conditioned at –50 mV versus RHE for 2 min. Potential limits were chosen as to avoid irreversible catalyst oxidation, and are outlined in the text. Potential sweeps were conducted at 50 mV s^{–1}. Potential step experiments were held for 15 min before returning to OCV. The electrolyte was not stirred. The measurements are not *iR* compensated.

3. Results and discussion

Fig. 1 shows the stabilized voltammogram of 4 M 2-propanol in 1 M NaOH at 60 °C over the Pt nanoparticles. All experiments with 2-propanol were carried out under these conditions. All currents are normalized to the electrode's real area determined by hydrogen adsorption or carbon monoxide stripping, as detailed in the experimental section. All potentials are reported versus the normal hydrogen electrode (NHE). The onset potential for electro-oxidation of 2-propanol was –690 mV. The current then increased to a high maximum at –60 mV. Acetone is the product of 2-propanol electro-oxidation at low potentials over Pt in acid [1,5–10] as well as over oxide-covered nickel, silver, copper, and cobalt electrodes in 1 M KOH [15]. It is likely that a similar reaction occurs over Pt in base at low potentials. Further, the calculated E° for the 2-propanol/acetone redox couple is –697 mV [16], a value close to the

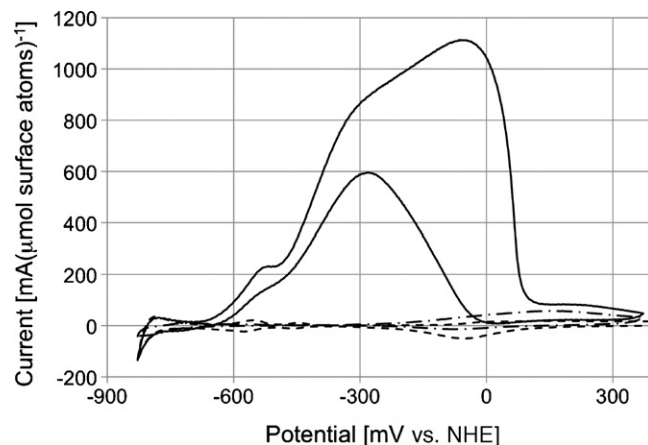


Fig. 1. Stabilized voltammogram of Pt nanoparticles in 1 M NaOH (---), 4 M 2-propanol/1 M NaOH (—), and 1 M acetone/1 M NaOH (-·-·-) electrolytes. All experiments were run at $T=60\text{ }^\circ\text{C}$ and $n=50\text{ mV s}^{-1}$.

onset potential (–690 mV). The current maximum occurs near the onset for surface oxide formation, thus surface oxides hinder the electro-oxidation, a result typical for alcohols in acidic and alkaline electrolytes. Fig. 1 also shows the stabilized voltammogram for acetone over Pt. All acetone experiments were carried out under the same conditions as those for 2-propanol, except [acetone] = 1 M. Pt is substantially less active towards acetone electro-oxidation than 2-propanol. There is a reductive shoulder at –800 mV in the cathodic sweeps that is likely due to the reduction of acetone to 2-propanol.

The as-received unsupported Ru was reduced under hydrogen flow at 60 °C prior to use. Fig. 2 shows the voltammogram of the reduced Ru nanoparticles, the voltammogram for 2-propanol, and the voltammogram for acetone. The upper limit of the sweeps was set to –75 mV, a value slightly above the equilibrium potential for the formation of Ru₂O₃ ($E^\circ = -0.330\text{ V}$) [17]. The activity of Ru towards 2-propanol is substantially lower than Pt. We note, however, that Ru has some activity towards 2-propanol in the hydride region of the anodic sweep, lower than the onset potential over Pt. The activity of Ru towards acetone electro-oxidation is very low. There are, however, strong reductive currents between –830 and –740 mV in the anodic and cathodic sweeps for acetone. These currents are far higher than those over Pt, showing that Ru is quite active towards the reduction of acetone at low potentials. The likely product of the reduction is 2-propanol.

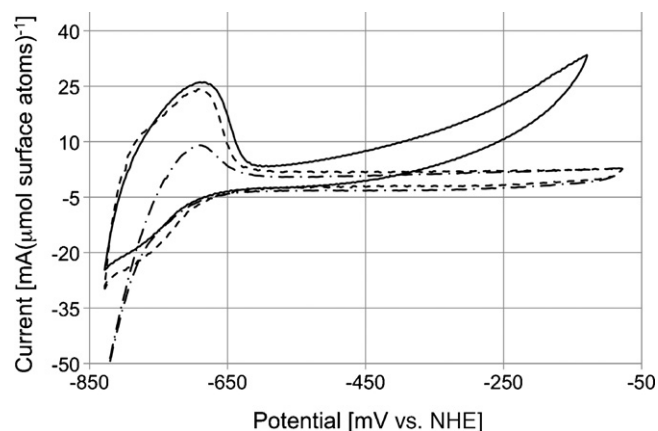


Fig. 2. Stabilized voltammogram of Ru nanoparticles in 1 M NaOH (---), 4 M 2-propanol/1 M NaOH (—), and 1 M acetone/1 M NaOH (-·-·-) electrolytes.

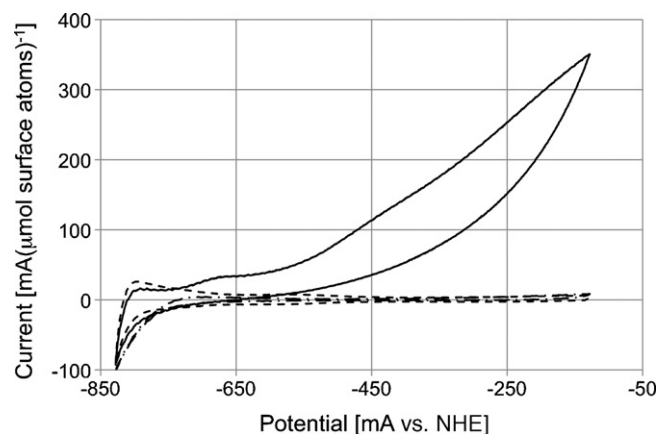


Fig. 3. Stabilized voltammogram of Pt-Ru nanoparticles in 1 M NaOH (---), 4 M 2-propanol/1 M NaOH (—), and 1 M acetone/1 M NaOH (- - - -) electrolytes.

Fig. 3 shows the baseline, 2-propanol, and acetone voltammograms over unsupported Pt-Ru in 1 M NaOH. The onset potential for 2-propanol in the anodic sweep is -740 mV, consistent with the calculated 2-propanol/acetone equilibrium potential, and lower than the onset potential over Pt. At potentials greater than -500 mV, Pt-Ru is $3\times$ more active than Ru, but $1/3$ as active as Pt. As was the case for Ru, Pt-Ru is very active towards the reduction of acetone at low potentials in both the anodic and cathodic sweeps. The normalized current for this reduction is larger than Pt or Ru, thus, the combination of these elements is more active than its individual components. Pt-Ru has low activity towards the electro-oxidation of acetone.

Chronoamperometry was performed to investigate the activity of these electro-catalysts under conditions that are more representative of an operating fuel cell. Before each experiment, the electrodes were conditioned for 2 min at -878 mV to reduce the surface and form a monolayer of H_{ad} . The electrode was then stepped to the desired potential, and held for 15 min without stirring. Fig. 4 shows the current recorded at 15 min versus applied potential for 2-propanol over the catalysts. A low-potential current maximum was observed for all three catalysts. The magnitude of the current maximum is slightly less for Ru than Pt, but it occurs at 130 mV lower in potential. To the best of our knowledge, this is the highest potentiostatic current density reported near the H_2/H^+ redox couple for an alcohol/catalyst system. The magnitude of the current maximum is approximately $3\times$ higher over

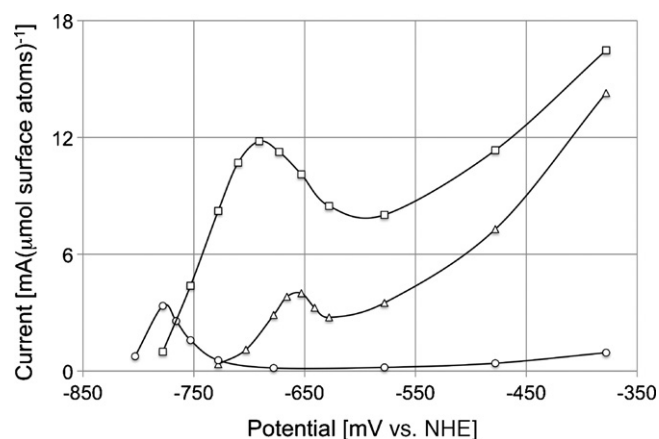


Fig. 4. Sampled-current voltammogram of 4 M 2-propanol/1 M NaOH over Pt (triangle), Ru (circle), and Pt-Ru (square) electro-catalysts.

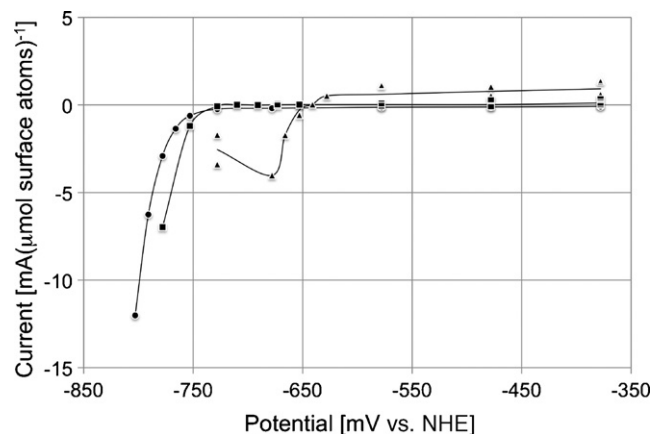


Fig. 5. Sampled-current voltammogram of 1 M acetone/1 M NaOH over Pt (triangle), Ru (circle), and Pt-Ru (square) electro-catalysts.

Pt-Ru than it is over either Pt or Ru. Confirming the cooperative effect between these elements observed during the potentiodynamic experiments. The potential of the current maximum over Pt-Ru occurs at -690 mV, a value between the maximums for Ru and Pt. Pt-Ru is the most active of these catalysts at high potentials.

Fig. 5 shows the current at 15 min plotted versus potential for acetone over the three catalysts. All three catalysts possess poor activity towards the electro-oxidation of acetone. Ru and Pt-Ru are highly active towards acetone reduction at low potentials, with Pt-Ru being more active than Ru. This result, combined with those from 2-propanol electro-oxidation, shows that a highly reversible, low-potential 2-propanol/acetone redox couple exists over Pt-Ru electro-catalysts in alkaline electrolytes.

4. Conclusions

The results of this study show there is a cooperative effect between Pt and Ru towards the electro-oxidation of 2-propanol at the low potentials required for an efficient DAFC. The Pt-Ru catalyst had the most favorable combination of onset potential current magnitude at low potentials [8]. There is a low-potential current maximum for the oxidation of 2-propanol for all three catalysts. The Ru-containing catalysts are highly active towards the electro-reduction of acetone at low potentials. A reversible 2-propanol/acetone redox couple thereby occurs over the Pt-Ru electro-catalyst. Studies on prototype alkaline DAFCs using 2-propanol and related alcohols as fuel are underway in these laboratories to determine if the results reported in this paper apply to regenerative fuel cell systems.

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