

Electro-oxidation of 2-propanol on platinum in alkaline electrolytes

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Abstract

The potentiodynamic and potentiostatic electro-oxidations of 2-propanol over rough platinum electrodes were carried out in alkaline electrolytes. A substantive current maximum occurs at low potentials during potentiostatic electro-oxidations of 2-propanol in the presence of base. The magnitude of this current maximum increases as the concentration of either 2-propanol or hydroxide is increased, while increasing the concentration of hydroxide also causes a Nernstian shift in the peak potential to lower values. Experiments were carried out that indicate the high currents observed at low potentials are due to a rapid electro-oxidation of 2-propanol to acetone that proceeds through intermediates that are weakly adsorbed to the platinum surface. The electro-oxidation of acetone commences at potentials higher than the electro-oxidation of 2-propanol to acetone, and it proceeds through strongly adsorbed intermediates.

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1. Introduction

We report the electro-oxidation of 2-propanol over platinum in alkaline electrolytes. Direct alcohol fuel cells (DAFCs) are promising power sources for portable electronic devices because liquid alcohol fuels are easier to store, and they have higher energy densities than hydrogen gas. Direct methanol fuel cells (DMFCs) are the most studied type of alcohol fuel cell because methanol is readily available, it contains no carbon–carbon bonds, and it has promising electrochemical activity [1,2]. The use of methanol in a fuel cell, however, is attended by several challenges that must be overcome before the widespread use of DMFCs can be adopted. Perhaps the most formidable of these challenges is that the electro-oxidation of methanol over noble metal catalysts, typically containing platinum, involves carbon monoxide or related species as intermediates [1–5]. These species bond strongly to electrocatalyst surfaces and cause the electro-oxidation of methanol to self-poison after brief periods of time. This self poisoning causes high overpotentials that start at low current densities, and that greatly reduce the electrochemical efficiency of the DMFC. Platinum-based binary-

[6], ternary- [7], and quaternary- [8] catalysts are being developed to overcome self-poisoning during the electro-oxidation of methanol. The non-platinum components in these catalysts weaken the platinum–carbon monoxide bond [3,9–11], and they act as oxygen transfer electrocatalysts between water and the adsorbed CO to produce CO₂, protons, and electrons [6,12]. Pt–Ru is the most widely used catalyst in prototype DMFCs because it has a promising combination of activity, availability, and operational stability [13–15]. Even using Pt–Ru, however, prohibitively high loadings of anode catalyst (typically 5 mg cm⁻²) are required to overcome the self-poisoning and provide useful performances from DMFCs operating near room temperature.

Related to anode self-poisoning is methanol crossover [16]. Specifically, Nafion™ is typically used as the acidic polymer electrolyte membrane in DMFCs, and Nafion™ is permeable to methanol. This permeability allows facile crossover of methanol from the anode to the cathode of the cell. This crossover is driven by the methanol concentration gradient across the membrane, and by proton transfer from the anode to the cathode of the operating DMFC. Platinum is used as the electrocatalyst in the cathodes of DMFCs. These platinum electrocatalysts are poisoned by methanol crossover, and prohibitively high catalysts loadings (typically 5 mg cm⁻²) are also required at the cathodes of DMFCs to achieve useful levels of performance. Crossover

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can also result in escape of toxic methanol from the DMFC, and it reduces the overall efficiency of the cell.

Several research groups, including our own, have reported the use of 2-propanol as an alternative to methanol in a DAFC [17–19]. 2-Propanol is less toxic than methanol, it is less prone to crossover to the cathode, and it appears not to poison the cathode like methanol does. Further, the electro-oxidation of 2-propanol over platinum containing catalysts occurs at significantly higher currents at low potentials than methanol does in acidic electrolytes. For example, we recently compared the performance of a DAFC operating on methanol and 2-propanol using an acidic NafionTM membrane electrolyte [18]. The cell voltage from open-circuit up to $\sim 200 \text{ mA cm}^{-2}$ was approximately 220 mV higher when it operated with 2-propanol than with methanol. Unfortunately, the cell voltage dropped rapidly and became erratic at higher current densities. We determined that this precipitous drop in cell performance was caused by anode poisoning.

The mechanism of the electro-oxidation of 2-propanol over platinum in acid electrolytes has been investigated using techniques that include electrochemistry [20–25] and spectroscopic techniques such as Fourier transform infrared spectroscopy [26–28], mass spectrometry [29–32], electron energy loss and Auger spectrometry [33]. Although there are differences between some of the results and interpretations reported in the literature, the following features of the mechanism are in agreement with most of the published observations and conclusions. Acetone and carbon dioxide are the only products observed in solution from the electro-oxidation of 2-propanol. The electro-oxidation to form acetone does not involve strongly adsorbed intermediates such as carbon monoxide, and it commences at lower potentials than the electro-oxidation to form carbon dioxide. The formation of acetone is a surface-structure sensitive reaction, and it is significantly faster than the formation of carbon dioxide at all potentials, even at those greater than 1.0 V versus SHE. Displacement of acetone from the surface by 2-propanol increases the rate of acetone formation and it lowers the rate of carbon dioxide formation. The electro-oxidation of 2-propanol to form carbon dioxide commences at potentials where oxygen-containing species are formed on platinum, and it proceeds through a strongly adsorbed intermediate. The structure of this intermediate is unclear, but some researchers have proposed that it is adsorbed acetone. Carbon monoxide is either not detected, or it is present only in low amounts during the electro-oxidation. The electro-oxidation to form carbon dioxide is less sensitive to surface structure than is the formation of acetone. Based upon these reported observations, we believe that it was the electro-oxidation to form carbon dioxide that poisoned the anode of the 2-propanol DAFC at currents higher than $\sim 200 \text{ mA cm}^{-2}$. It appears from the literature that the window between the commencement potentials for the electro-oxidations to form acetone and carbon dioxide is narrow over platinum electrodes in acidic electrolytes.

Earlier reports have described the electro-oxidation of 2-propanol over platinum in alkaline electrolytes [34–45]. We now report the results from our investigation of this system as

a possible candidate for a DAFC anode. The objectives of this investigation were to increase the current at low potentials for the electro-oxidation to form acetone, and to widen the window between the commencement potentials for formation of acetone and carbon dioxide. Utilizing potentiostatic and potentiodynamic techniques, the nature of the electro-oxidation was investigated and compared to methanol in base, and 2-propanol in acid.

2. Experimental

2.1. General

Nitrogen (Praxair, prepurified), NaOH (Alfa Aesar, 99.99%, semiconductor grade), H₂SO₄ (Alfa Aesar, 99.9999%), H₂O₂ (EM Science, ACS Grade), H₂PtCl₆·6H₂O (Alfa Aesar, 99.9% metal basis), and platinum gauze (Alfa Aesar, $\sim 25 \text{ mm} \times 25 \text{ mm}$, 52 mesh woven from 0.1 mm diameter wire, 99.9% metal basis) were used as received from supplier. The water was deionized, distilled, and distilled again from alkaline KMnO₄ (Fisher Scientific) before use. Methanol (Fisher, ACS grade) was distilled over Mg(OMe)₂, 2-propanol (Fisher Scientific, suitable for electronic use) was freshly distilled, and acetone (Caledon, ACS grade) was distilled over molecular sieves (Caledon, 3A) before use.

Electrochemical experiments were performed in a typical three-electrode glass cell using an EG&G Princeton Applied Research Potentiostat/Galvanostat (model 273) controlled with the supplied EG&G PAR electrochemistry software. Electrolytes were purged with nitrogen for 15 min prior to measurements, and protected by a nitrogen atmosphere at bubbler pressure during experiments. The counter electrode was a blacked platinum gauze behind a 10 μm sintered glass frit, while the working electrode was the same without the glass frit. The preparation of these blacked gauzes is described below. The openings to the electrochemical glass cell were sealed using septa that had been extracted with toluene and punched with holes to fit the electrodes/frit. The electrochemical cell was equipped with a dry ice/acetone condenser to minimize loss of 2-propanol by evaporation. A constant temperature bath (IKA Laborteknik, RCT basic) equipped with a temperature probe/controller (IKA Labortechnik, ETS-D4 fuzzy) was used to maintain the cell temperature at 60 °C. All potentials were recorded versus a reference hydrogen electrode (RHE) made of the alcohol-free electrolyte used for the experiment. All potentials are reported versus SHE, unless stated otherwise.

2.2. Preparation of electrodes

The working and counter electrodes were prepared by first cleaning a platinum gauze with 1% H₂O₂, followed by blacking in 2 wt.% H₂PtCl₆·6H₂O in 1 M HCl at 50 mV versus SHE for 3 h with stirring. The real surface area of the working electrode was measured daily using the charge under the cathodic hydrogen region of potentiodynamic sweeps recorded in 1 M H₂SO₄ [46].

2.3. Potentiodynamic electro-oxidations

Potentiodynamic electro-oxidations were performed using the three electrode setup described in the previous section. The parameters and conditions used are described in the text and figure captions.

2.4. Potentiostatic electro-oxidations

The potentiostatic electro-oxidations were performed using the three electrode setup described previously. The working electrode was conditioned at 1.2 V versus RHE for 60 s, then at -0.1 V for 60 s, followed by a jump to the desired potential. The electrode was held at the desired potentials for 15 min, unless stated otherwise. The measurements are not IR compensated.

3. Results and discussion

Fig. 1 shows the stabilized voltammogram of a blacked platinum gauze obtained in the presence of 2-propanol in 0.5 M NaOH electrolyte at 60°C . The figure also shows the voltammogram obtained without 2-propanol. All currents reported in this paper are normalized to the real surface area of the platinum electrode measured before the experiment was run. The potentiodynamic response in the absence of 2-propanol is typical of polycrystalline platinum in NaOH [47]. The hydride region of the stabilized voltammogram obtained in the presence of 2-propanol retains elements of structure that are present in its absence. This similarity in structure indicates that the hydride region is not significantly poisoned by repeated sweeps with 2-propanol in alkaline electrolyte over the period of these experiments. This interpretation is consistent with the radioactive indicator experiments reported by Kazarinov and Dolidze [39,40,43], and with early mechanistic proposals [34,45,46] for the electro-oxidation of 2-propanol in alkaline electrolytes. The currents in the hydride regions of the anodic and cathodic sweeps are higher, however, in the presence of 2-propanol. This increase of current in the hydride region shows that the electro-oxidation of 2-propanol

occurs at these low potentials. There is also a significant, rapid increase in current for the electro-oxidation of 2-propanol in the cathodic sweeps that occurs when the oxides are electro-reduced from the surface. This rapid increase in current during the cathodic sweep shows that surface oxides impede the electro-oxidation. This property is a well-known phenomenon for most reported electro-oxidations of alcohols over platinum in acidic or basic electrolytes.

Fig. 2 shows the stabilized voltammograms obtained with 1, 2, 3, and 4 M solutions of 2-propanol in 1 M NaOH [41]. Attempts to use higher concentrations of 2-propanol were prevented by the formation of biphasic electrolyte mixtures. Increasing the concentration of 2-propanol resulted in an increase in current in the hydride-, double layer-, and oxide regions of the voltammograms. The shapes of the voltammograms did not change significantly upon increasing the 2-propanol concentration. A second electro-oxidation peak did appear, however, centered at ~ 100 mV in the cathodic sweeps when the concentration of 2-propanol was increased from 1 to 2 M or higher. The origins of this new peak are unclear at this time.

Fig. 3 shows the stabilized voltammograms obtained in 0.5, 1, and 3 M solutions of NaOH in 1 M 2-propanol. Increasing the hydroxide concentration from 0.5 to 1 M decreased the current for the electro-oxidation in the oxide region of the voltammogram. Increasing the concentration from 1 to 3 M decreased the current further, and it shifted the current maxima in the cathodic and anodic sweeps by approximately -100 and -150 mV, respectively. Increasing the hydroxide concentration did not change the current in the hydride region to the extent that it decreased the current in the oxide region of the voltammogram. Increasing the hydroxide concentration did, however, change the relative peak heights in the hydride region of the anodic sweeps. Specifically the second oxidation peak at lower potentials increased relative to the first peak at high NaOH concentrations. These differences in response to hydroxide concentration indicate that the electro-oxidation of 2-propanol in the hydride region occurs by a different mechanism than the electro-oxidation in the oxide region. Potentiostatic electro-oxidations

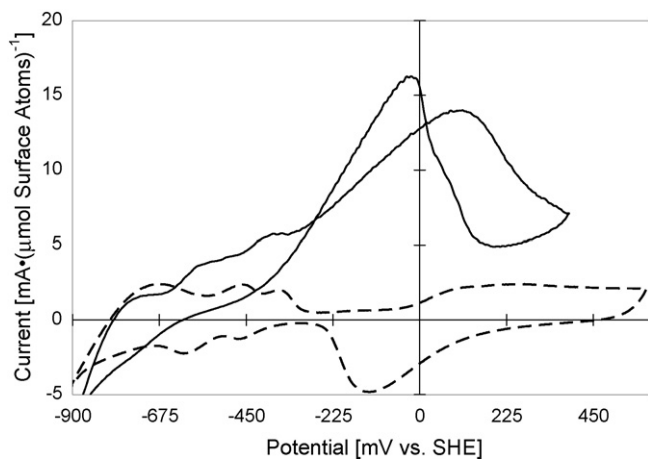


Fig. 1. Stabilized cyclic voltammograms of a blacked platinum gauze in 0.5 M NaOH (---), and 1 M 2-propanol in 0.5 M NaOH (—). $T = 60^\circ\text{C}$, sweep rate = 5 mV s^{-1} .

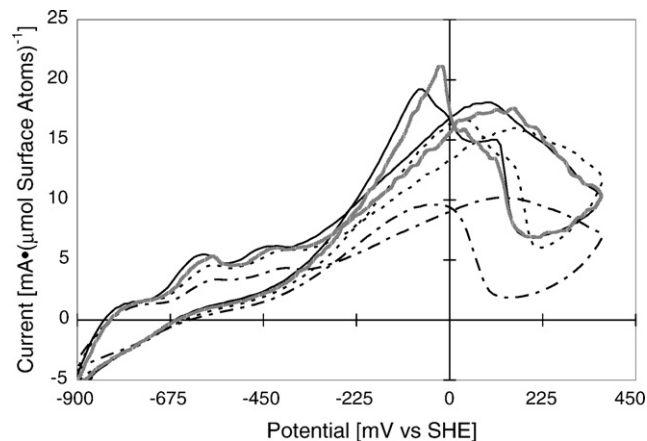


Fig. 2. Stabilized cyclic voltammograms of a blacked platinum gauze in 1 M NaOH (---), 2 M (---), 3 M (⋯), and 4 M (—) 2-propanol in 1 M NaOH. $T = 60^\circ\text{C}$, sweep rate = 5 mV s^{-1} .

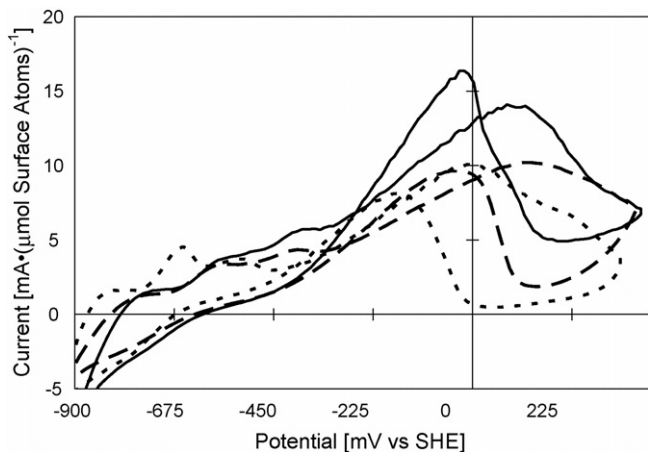


Fig. 3. Stabilized cyclic voltammograms of a blacked platinum gauze in 1 M 2-propanol in 0.5 M (—), 1 M (---), and 3 M (---) NaOH. RHE's were prepared with the corresponding NaOH electrolyte. $T = 60^\circ\text{C}$, and sweep rate = 5 mV s^{-1} .

of 2-propanol were carried out over platinum in base to further investigate this system under conditions that better approximate an operating fuel cell.

Fig. 4 shows the current versus time plots for potentiostatic electro-oxidations of 2-propanol carried out in 1 M NaOH at various potentials. The platinum was conditioned before each electro-oxidation by holding the potential at 1.2 V versus RHE for 1 min, then at -0.1 V for 1 min, followed by a jump to the desired potential. After the jump to the desired potential, there typically occurred an initial, rapid decrease in current followed by a region of more stable currents that decreased slowly during the remainder of the electro-oxidation. The electro-oxidation of 2-propanol occurred even at -730 mV . Further, comparison of the stabilized current at increasing potentials reveals an unexpected and substantive current maximum that occurred at low potentials. Fig. 5 shows a plot of the stabilized current measured at 15 min versus potential that shows the large current maximum centered at approximately -660 mV , and ranging from approximately -730 to -580 mV . To the best of our knowledge, no such a maximum in stabilized current at low potentials has been

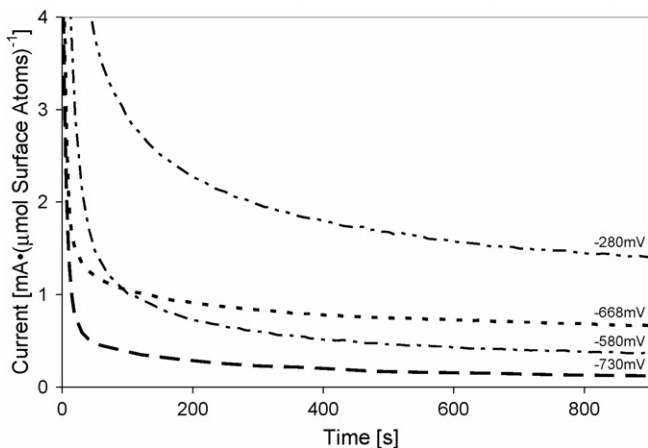


Fig. 4. Current vs. time plot for the electro-oxidation of 1 M 2-propanol in 1 M NaOH over a blacked platinum gauze at -730 mV (---), -668 mV (---), -580 mV (---), and -280 mV (---) vs. SHE. $T = 60^\circ\text{C}$.

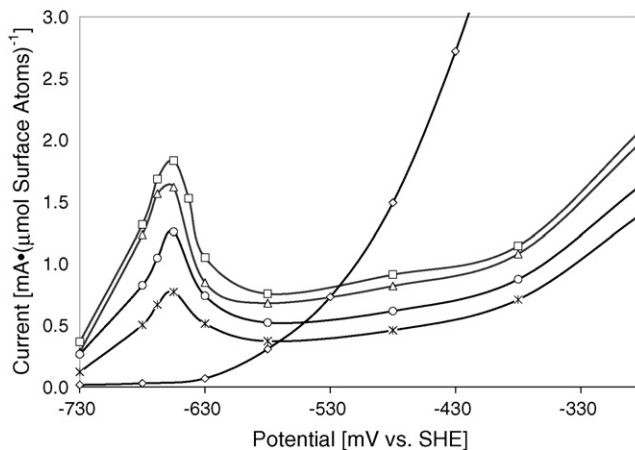


Fig. 5. Current at the end of a 15 min electro-oxidation vs. potential for 1 M (×), 2 M (○), 3 M (△), and 4 M (□) 2-propanol in 1 M NaOH over a blacked platinum gauze. 1 M methanol (◇) in 1 M NaOH is supplied for comparison. $T = 60^\circ\text{C}$.

reported previously for the potentiostatic electro-oxidation of an alcohol over a platinum-based catalyst. For comparison, Fig. 5 also shows a plot of stabilized current versus potential for the electro-oxidation of methanol under identical conditions. As is typical for alcohols, the electro-oxidation of methanol produces only negligible stabilized currents at low potentials.

The maximum in current for the electro-oxidation of 2-propanol at low potentials confirms the evidence from the potentiodynamic experiments that at least two mechanisms operate in basic electrolytes. One mechanism predominates at low potentials, while the other, or perhaps both, mechanisms operate at higher potentials. Fig. 5 also shows plots of the stabilized current versus potential in 1, 2, 3, and 4 M 2-propanol. Increasing the concentration of 2-propanol from 1 to 4 M increased the current maximum at low potentials by a factor of ~ 2.4 . This substantial increase in current shows that the electro-oxidation at potentials below, or near the current maximum is not limited by saturation kinetics over this concentration range of 2-propanol. That the electro-oxidation is not limited by saturation kinetics in 2-propanol at low potentials, and that the low-potential current maximum is quite large, both show that 2-propanol and the intermediates involved in its electro-oxidation in this potential range do not strongly poison platinum. As would be expected if different mechanisms were in operation, the increases in current with the concentration of 2-propanol were less at higher potentials than they were at low potentials.

Fig. 6 shows plots of the stabilized current after 15 min versus potential for potentiostatic electro-oxidations of 1 M 2-propanol in 0.5, 1, and 3 M solutions of NaOH. The current maximum at low potentials undergoes a Nernst shift to more negative potentials relative to SHE as the concentration of NaOH is increased. The size of the current maximum also increased with the concentration of NaOH. Increasing the concentration of NaOH from 0.5 to 3 M increased the low-potential current maximum by a factor of ~ 1.6 . The current in the potential range from approximately -600 to -375 mV also increased with increasing NaOH concentration, but to a lesser extent than the current increased at the low-potential maximum. Conversely, the currents at potentials

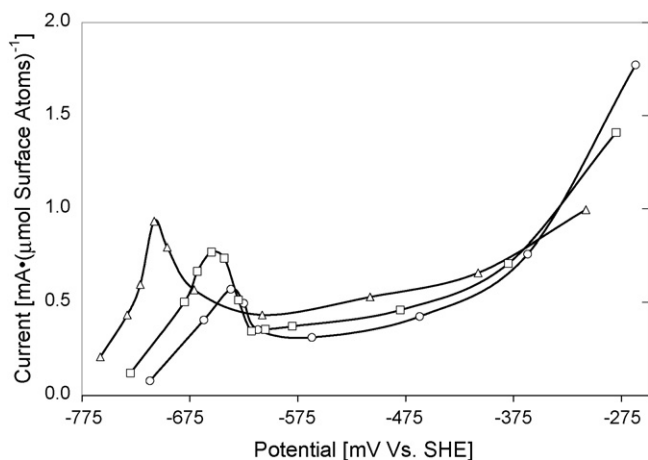
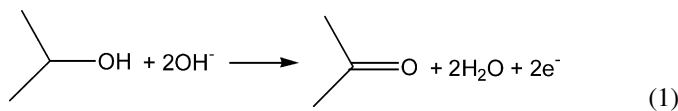


Fig. 6. Current at the end of a 15 min electro-oxidation vs. potential for 1 M 2-propanol in 0.5 M (○), 1 M (□), and 3 M (△) NaOH over a blacked platinum gauze. RHE's were prepared with the corresponding NaOH electrolyte and had potentials of: 0.5 M, $E = -812$ mV; 1 M, $E = -830$ mV; 3 M, $E = -858$ mV vs. SHE. $T = 60^\circ\text{C}$.

greater than -375 mV decreased with increasing NaOH concentration. This behavior is also consistent with one mechanism operating for the electro-oxidation of 2-propanol at low potentials, with another mechanism, or combination of mechanisms operating at high potentials. We propose that the mechanism up to the current maximum at low potentials involves the electro-oxidation of 2-propanol to acetone (Eq. (1)). Taking into



consideration the reported observations made in acid [26,27,29–32] and in base [34,42,45,46] electrolytes, it is reasonable to assume that the electro-oxidation of 2-propanol to acetone proceeds at high currents because it does not involve strongly adsorbed intermediates that poison the platinum surface. We propose that the current drop after the low-potential current maximum is caused by the onset of acetone oxidation. Taking into consideration the reported observations made in acid [26,27,29–32] and in base [42] electrolytes, the electro-oxidation of acetone in base appears to proceed through strongly adsorbed intermediates. We investigated this possibility by carrying out the potentiostatic electro-oxidation of acetone over platinum in base.

Fig. 7 shows plots of the stabilized current versus potential for the potentiostatic electro-oxidations of 1 M 2-propanol and 1 M acetone under identical conditions in 1 M NaOH. Comparison of the plots at low potentials shows that negligible currents are produced by the electro-oxidation of acetone up to the low-potential current maximum for the electro-oxidation of 2-propanol. The low-potential current maximum for the 2-propanol electro-oxidation, and the onset of acetone electro-oxidation occur at nearly the same potential. This coincidence in potentials is further, strong evidence that the electro-oxidation of acetone proceeds through strongly adsorbed intermediates that impede the rapid electro-oxidation of 2-propanol to acetone at

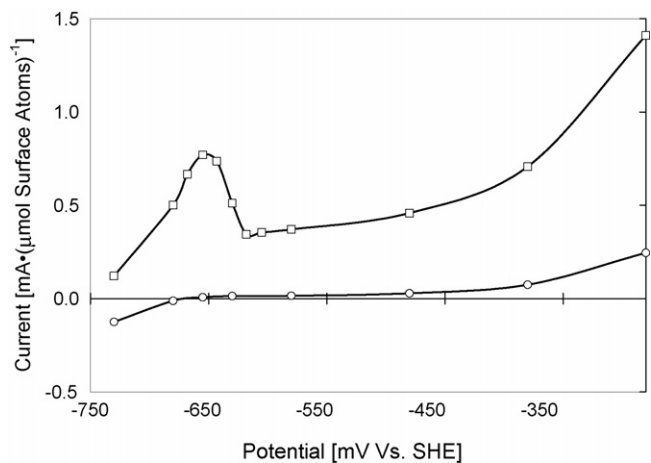


Fig. 7. Current at the end of a 15 min electro-oxidation vs. potential for 1 M 2-propanol (□), and 1 M acetone (○) in 1 M NaOH over a blacked platinum gauze. $T = 60^\circ\text{C}$.

low potentials. The cathodic current that occurs in 1 M acetone at potentials below approximately -660 mV is likely due to the electro-reduction of acetone, perhaps to produce 2-propanol.

Gradual declines after the initial, rapid decrease in current are often observed during potentiostatic electro-oxidations of alcohols over platinum-based electrocatalysts in acid. Fig. 8 shows the current versus time plots we obtained for the potentiostatic electro-oxidation of 2-propanol carried out over a 3 h period at -680 , -530 , and -330 mV in 1 M NaOH. The current at -680 mV, below the low-potential current maximum observed after 15 min (Fig. 5) was the most stable of the potentials studied. The current at -530 mV, a potential after the low-potential current maximum, was lower than the current at -680 mV over most of the oxidation, and it drifted downwards faster as well. The decline of the current over the last hour of the electro-oxidation at -330 mV was the fastest of the potentials studied. In fact, the current for the electro-oxidation at this higher potential drifted downward to a value below the current at -680 mV by the end of the 3 h period, despite the 350 mV difference between these two applied potentials. This behavior is consistent with the

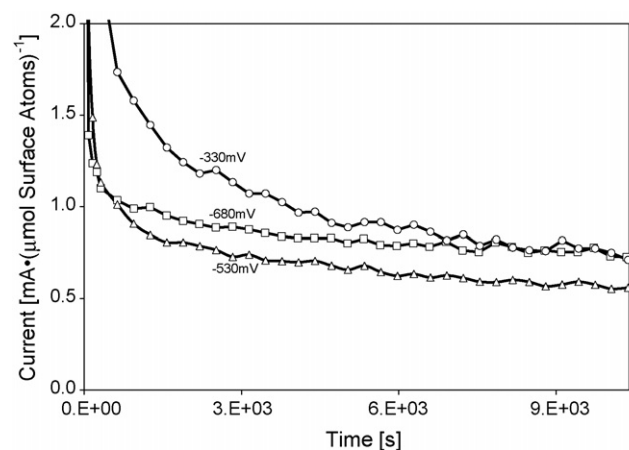


Fig. 8. Current vs. time plot for the electro-oxidation of 4 M 2-propanol in 1 M NaOH over a blacked platinum gauze at -680 mV (□), -530 mV (△), and -330 mV (○) vs SHE. $T = 60^\circ\text{C}$.

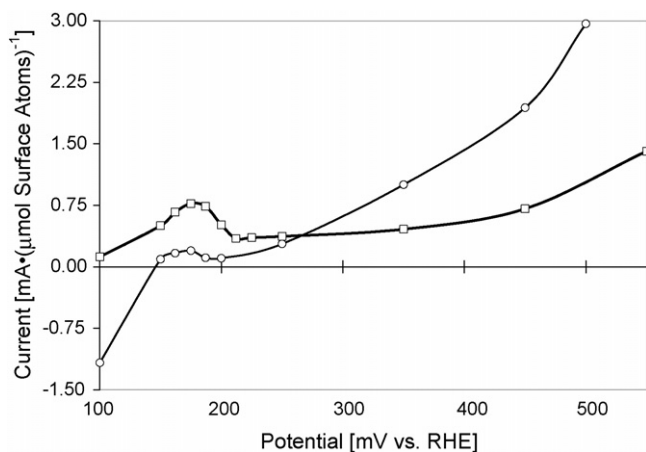


Fig. 9. Current at the end of a 15 min electro-oxidation vs. potential for 1 M 2-propanol in 1 M NaOH (\square), and 0.5 M H_2SO_4 (\circ) over a blacked platinum gauze. RHE electrolytes are 1 M NaOH ($E = -830$ mV vs. SHE), or 0.5 M H_2SO_4 ($E = 0$ mV vs. SHE). $T = 60^\circ\text{C}$.

change in mechanism proposed previously that involves a rapid electro-oxidation of 2-propanol to acetone at low potentials, and a slower electro-oxidation of acetone that occurs at higher potentials through an intermediate or intermediates that bind strongly to the platinum surface.

Fig. 9 shows the current at 15 min plotted versus potential for the potentiostatic electro-oxidation of 2-propanol in 0.5 M H_2SO_4 and in 1 M NaOH. The potentials are plotted versus the reference hydrogen electrodes prepared with the corresponding electrolytes. The electro-oxidation kinetics of 2-propanol in acid are faster at potentials higher than ~ 260 mV and up to the maximum potential used for this experiment, 550 mV. The electro-oxidation kinetics in base, however, are substantially faster at low potentials, ranging from 100 through 260 mV. There was only a small current maximum at low potentials in acid. These observations are consistent with the decreased electrode polarization during the electro-oxidation of 2-propanol over platinum in alkaline versus acidic electrolytes reported by Rao and Roy [45]. The cathodic current observed in acid at potentials below 150 mV is likely due to the electro-reduction of 2-propanol in acid to generate water and propane, as reported by others [29]. Such an electro-reduction is not possible in alkaline media.

4. Conclusion

The potentiostatic electro-oxidation of 2-propanol over platinum in base occurs with a large current maximum at low potentials. In comparison, current densities of 0.8 mA ($\mu\text{mol surface atoms}$) $^{-1}$ were obtained at low potentials using 2-propanol in base, whereas 2-propanol in acid, and methanol in base solutions provided only 0.2 and 0.05 mA ($\mu\text{mol surface atoms}$) $^{-1}$ respectively under comparable conditions and potentials. To the best of our knowledge, such a low-potential current maximum as with 2-propanol in base has not been observed previously. We suspect that similar behavior will occur during the electro-oxidation of other secondary alcohols over platinum in base.

The evidence obtained during this investigation indicates that two or more mechanisms are in operation for this electro-oxidation. At low potentials, the electro-oxidation produces acetone at high currents without strongly adsorbed intermediates. At higher potentials, the electro-oxidation of acetone commences via formation of strongly adsorbed intermediates that impede the electro-oxidations. Detailed mechanistic experiments are required to confirm these suppositions.

As we reported previously [18], the cell voltage from open-circuit up to ~ 200 mA cm^{-2} of an acid electrolyte (NafionTM) DAFC was ~ 220 mV higher when it operated on 2-propanol than methanol. Unfortunately, the 2-propanol cell voltage dropped rapidly and became erratic at current densities higher than ~ 200 mA cm^{-2} . Despite this drop at high currents, the higher cell voltage up to ~ 200 mA cm^{-2} resulted in an electrical efficiency at peak power operating on 2-propanol that was nearly twice (60% versus 32%) that of the cell operating on methanol. The peak power of the 2-propanol cell was $\sim 75\%$ that of the methanol cell. The results obtained from the present investigation hold promise that an alkaline-based, 2-propanol DAFC will operate at high cell voltages over larger current ranges than did the acid-based DAFC. Other potential advantages of such an alkaline, 2-propanol DAFC include: (1) that formation of carbon monoxide and carbonate would be minimized at high currents and cell voltages [48–50]; (2) that anion flow from the cathode to the anode would impede 2-propanol crossover; (3) that such a system can, in principle be made regenerative by hydrogenating the acetone to produce 2-propanol [51]. Studies of prototype, alkaline DAFCs operating on 2-propanol and other secondary alcohols are under way in these laboratories to determine the extent that these potential advantages are offered by such systems.

Acknowledgements

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