

## Electrocatalytic Oxidation of Small Carbohydrate Fuels at Pt–Sn Modified Electrodes

María J. González,<sup>†</sup> Christopher T. Hable, and Mark S. Wrighton\*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The electrocatalytic oxidations of water-soluble alcohols and diols and some other small organic molecules (MeOH, EtOH, 2-fluoroethanol, 2,2-difluoroethanol, 2,2,2-trifluoroethanol, CH<sub>2</sub>(OH)<sub>2</sub>, ethylene glycol, *n*-PrOH, *i*-PrOH, 1,4-butanediol, 1,3-propanediol, 1,2-propanediol, *t*-BuOH, neopentyl alcohol, benzyl alcohol, 2-Me-1-PrOH, formic acid, acetaldehyde, acetic acid, propionaldehyde, propionic acid, acetone, glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid, oxalic acid) have been compared in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> at C and Au electrodes modified with an electrodeposited Pt–Sn catalyst at low (−0.1 to 0.5 V vs SCE) potentials. The Pt–Sn catalyst is electrochemically deposited and forms as a smooth deposit on Au electrodes. At a catalyst loading of ~0.5 mg/cm<sup>2</sup> the electrodeposition of the Pt–Sn catalyst results in formation of adherent ~0.8 μm size particles on C electrodes. In general, for organic molecules containing only C, H, and O with two or more carbon atoms, the presence of H atoms on both the α- and β-carbon results in a relatively negative potential for onset of catalytic current (usually between −0.1 and −0.2 V vs SCE) at Pt–Sn compared to Pt alone. Of the alcohols and diols studied, formaldehyde (which exists in aqueous solutions as the hydrated form, CH<sub>2</sub>(OH)<sub>2</sub>) shows the highest electrocatalytic currents at the Pt–Sn catalyst. The ultimate product, via HCOOH, is CO<sub>2</sub>. EtOH is oxidized only to acetic acid on Pt–Sn electrodes. The EtOH and *n*-PrOH oxidation yields, determined by exhaustive electrolysis, are 4 e<sup>−</sup> per molecule, while *i*-PrOH yields only 2 e<sup>−</sup> per molecule. We confirmed the generation of acetic acid, propionic acid, and acetone as the final products for the oxidations of EtOH, *n*-PrOH, and *i*-PrOH, respectively, by <sup>13</sup>C NMR and/or GCMS. The electron yield of the oxidation of ethylene glycol at Pt–Sn surfaces is only 4 e<sup>−</sup> per molecule instead of the value of 8 e<sup>−</sup> per molecule expected for the oxidation of ethylene glycol to oxalic acid. Glycolic acid (CHOCOOH) is the oxidation product by GCMS. This substance is not electrocatalytically oxidized on Pt–Sn at potentials negative of ~+0.4 V vs SCE in comparison to the −0.1 V vs SCE onset for ethylene glycol oxidation. MeOH, the molecule with the highest electron yield on Pt–Sn (6 e<sup>−</sup> per molecule), unfortunately shows the most positive potential onset for oxidation among the group of alcohols compared in this study, while the two intermediates along the path of oxidation to CO<sub>2</sub>, formaldehyde, and formic acid are oxidized on Pt–Sn at very negative potentials compared to MeOH. Thus, the conversion of MeOH to formaldehyde is the efficiency-determining step in the oxidation of MeOH to CO<sub>2</sub>.

## Introduction

Studies of the electrocatalysis for the oxidation of organic molecules are of importance in connection with efforts to find alternative fuels to H<sub>2</sub> in the anodic compartment of fuel cells. H<sub>2</sub> is an environmentally desirable anodic fuel, considering that only water results from the coupling of its oxidation to the reduction of O<sub>2</sub>. However, H<sub>2</sub> gas is difficult to handle relative to liquid fuels such as alcohols which yield CO<sub>2</sub> upon complete oxidation.

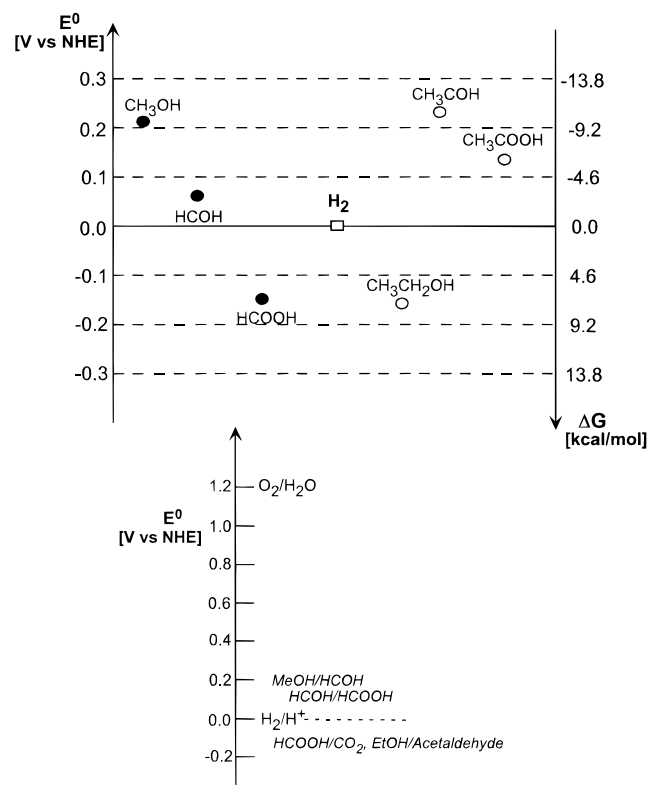
To replace H<sub>2</sub> in fuel cells, one has to look for a fuel with several characteristics. Reasonable requirements for a fuel are the following: availability, low to no toxicity, facility to store and handle safely, and high energy density. Small hydrocarbons and carbohydrates comply with most of these characteristics. On a volume basis, liquid fuels, like MeOH, are energy-rich.<sup>1</sup> Also, the existence of liquid fuel networks for handling, distribution, and storage (e.g., gasoline networks) would make the liquid fuel supply easier, in particular for electric vehicle-

fuel cell applications. Another important attribute that makes small organic molecules suitable fuels for fuel cells is that, based on the thermodynamics for their oxidation, they are oxidizable at potentials close to that of the H<sup>+</sup>/H<sub>2</sub> couple.<sup>2</sup> The free energy values for the 2e<sup>−</sup> oxidation of most small carbohydrates are within 0.2 V of H<sup>+</sup>/H<sub>2</sub>, Figure 1. Consequently, it should be possible to obtain a 1 to 1.2 V difference by coupling the oxidation of these fuels with the reduction of O<sub>2</sub>.

In this article we report a comparison of electrocatalytic oxidations of a series of simple carbohydrates at Pt–Sn modified electrodes at low (−0.1 to 0.5 V vs SCE) potentials. We have determined reactivities, electron yields, and product distributions at low potentials because, in a fuel cell, reactivity at low potentials will translate to high output voltage from the cell. This type of study is feasible when catalysts such as Pt–Sn are used, which activate C–H bonds and accomplish oxidation more efficiently than bare Pt at low potentials. The oxidation of small organic molecules, including MeOH,<sup>3–25,80–84,88</sup> formaldehyde,<sup>3–5,26</sup> formic acid,<sup>3–5,10,17,27–29</sup> carbon monoxide,<sup>4,30–32,85–87</sup> EtOH,<sup>21,24,33–35</sup> acetaldehyde,<sup>33,36</sup> *n*-PrOH,<sup>24,37</sup> *i*-PrOH,<sup>24,25,38,39</sup> BuOH,<sup>24</sup> ethylene glycol,<sup>40–47</sup> glyoxal,<sup>42</sup> glyoxylic acid,<sup>5,48</sup> and oxalic acid<sup>41</sup> has been studied at Pt electrodes and Pt modified

\* Author to whom correspondence should be addressed at Washington University in St. Louis, St. Louis, MO 63130.

<sup>†</sup> Current address: Eastman Kodak Co., 1669 Lake Ave., B. 59, Rochester, NY 14650-1707.



**Figure 1.** Equilibrium potentials and free energies for the 2  $e^-$  oxidation of some organic molecules.

with Sn. However, different methods of electrode preparation were used, and a comparison of the reactivity of various molecules on Pt–Sn has not been made on identically prepared electrodes. Here we have compared the electrocatalytic oxidation of several organic molecules at reproducibly prepared electrodes.

We have used electrochemical co-deposition as the method for preparing electrodes modified with the binary catalyst Pt–Sn. The electrochemical oxidation of MeOH on co-deposited Pt–Sn has been previously studied and has been shown to be superior to electrodeposited Pt alone.<sup>3,6,7,14</sup> The oxidation of EtOH has been studied for Pt substrates with adsorbed Sn atoms.<sup>33</sup> However, the use of electrodeposited catalysts, with the possibility of generating small catalyst particles, is more compatible with use in a fuel cell. In addition, the co-deposition method allows dispersion of catalyst particles into high surface area catalyst support materials.<sup>9,14,49–57</sup> Catalyst particles have been deposited onto a variety of support materials including polymer electrolytes,<sup>9</sup> redox polymers,<sup>49–53</sup> and conducting polymers.<sup>14,21,54–58</sup> Conducting polymers such as polyaniline offer promising properties for catalyst support materials, including high conductivity<sup>59,60</sup> and high surface area.<sup>61,62</sup> We have previously studied the oxidation of MeOH and EtOH on polyaniline supported Pt–Sn or Pt–Ru catalyst particles.<sup>14,21</sup> However, in the case of EtOH oxidation on Pt–Sn catalysts, the potential onset of activity occurs at sufficiently negative potentials that the current for EtOH oxidation is limited by the resistivity of polyaniline, particularly in the region of  $-0.2$  to  $0.0$  V vs SCE where polyaniline is in a reduced and insulating state.<sup>59</sup> The high resistance of the polymer limiting the catalysis can be avoided by growing thinner polymer films for support of the same catalyst loading used in our previous work. Electrical conductivity may thus be preserved while still having some dispersion of the catalyst in the polyaniline matrix. In this study, we have electro co-deposited Pt–Sn particles onto

bare C, Au, and Pt, and onto polyaniline (thin films) derivatized substrates. Electrocatalytic behavior toward a given fuel on catalysts with the same loading of Pt–Sn was similar when different substrates and dispersion media were used.

## Experimental Section

**Electrochemistry.** Electrochemical experiments were run using a PAR Model 173 potentiostat with a PAR Model 175 programmer. Current–voltage and current–time curves were recorded on a Kipp and Zonen 90B XY or XYY' recorder. Catalyst deposition and cyclic voltammetry were done in a two-compartment cell using a saturated calomel reference electrode (SCE) and a Pt gauze counter electrode. Solutions were deoxygenated with Ar before running the experiments.

**Exhaustive Electrolysis.** In a typical exhaustive electrolysis, the anode potential was set to  $0.35$  V vs SCE for  $20$  h in a small working volume, three-compartment cell. The temperature was kept constant at  $25$  °C and in some cases raised to  $\sim 50$  °C at the end of the experiment to make sure that all fuel had reacted. For these experiments, the catalyst was dispersed onto a high surface area Pt mesh. At approximately  $10$  h of electrolysis, the electrode was taken out of the cell, etched in aqua regia for  $10$  s, and then refreshed by depositing more catalyst onto the mesh. The initial concentration of the fuel was typically  $0.05$  M.

**Materials.** Glassy carbon (GC) electrodes ( $3$  mm diameter) were obtained from Bioanalytical Systems. GC electrodes were polished initially with  $9$  to  $1$   $\mu\text{m}$  diamond paste. Before each experiment electrodes were polished again with  $0.3$  mm alumina or  $1$   $\mu\text{m}$  diamond paste, followed by sonication in EtOH or MeOH. Substrates for scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were either polished GC sheet or  $1$   $\mu\text{m}$  thick  $e^-$  beam evaporated Au or Pt on a Si wafer with a Cr or Ti ( $50$  Å) adhesion layer.  $\text{K}_2\text{PtCl}_6$  (Alfa, Strem),  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (Strem),  $\text{H}_2\text{SO}_4$  (Mallinckrodt), and HPLC grade  $\text{H}_2\text{O}$  (Omnisolve, EM Science) were used as received.

**Product Analysis.** Product analysis of the electrolysis mixtures was performed by solution  $^{13}\text{C}$  NMR spectroscopy using a Bruker AC-250 and/or by gas chromatography–mass spectrometry (GCMS). For the GCMS analyses, product mixtures of exhaustive and short-time electrolyses were used. Analytes were diluted with  $\text{H}_2\text{O}$  to reduce the electrolyte concentration to  $\sim 0.01$  M.

**Electrode Modification.** Au and GC electrodes were modified with binary catalyst particles by cycling the electrodes in a solution containing Pt(IV) and Sn(IV) complexes between  $+0.5$  V and  $-0.3$  V vs SCE at  $50$  mV/s. The Pt–Sn catalyst was deposited from solutions of  $0.5$  M  $\text{H}_2\text{SO}_4$  containing  $\sim 12$  mM  $\text{K}_2\text{PtCl}_6$  and  $\sim 28$  mM  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . From measurements of cathodic charge passed corresponding to reduction of Pt(IV) to Pt(0), we estimated the amount of catalyst deposited onto an electrode as equivalents of Pt(IV) reduced to Pt(0); most studies were done using a catalyst loading of  $\sim 0.5$  mg of Pt per  $\text{cm}^2$  of electrode area.

Previously we have studied the Pt–Sn catalyst deposited from solutions of  $3$  mM  $\text{K}_2\text{PtCl}_6$  with  $7$  mM  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . We have found that increasing the concentration of the Pt and Sn precursors to  $12$  and  $28$  mM, respectively, leads to less variability in the activity of the Pt–Sn catalyst. This may be a result of the increased stability of aqueous solutions of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  at higher concentrations.

In some cases, a thin polyaniline film was first deposited onto the GC before electrodeposition of the Pt–Sn particles for better

adhesion and dispersion of the catalyst. Polyaniline was deposited from 1 M  $\text{H}_2\text{SO}_4$  containing 0.1 M aniline by potential cycling from  $-0.2$  to  $0.9$  V at  $50$  mV/s. Coverages were measured by determining the charge passed corresponding to the oxidation and reduction of the polyaniline in  $0.5$  M  $\text{H}_2\text{SO}_4$  when scanning the working electrode potential between  $-0.2$  and  $+0.9$  V vs SSCE.<sup>59</sup> Typical amounts of charge were  $3 \times 10^{-2}$  to  $7 \times 10^{-2}$  C/cm<sup>2</sup> of electrode area.

**Surface Analysis.** SEM was done on a Hitachi Model S-800 electron microscope. XPS spectra were obtained on a Perkin–Elmer Model PHI-5100 spectrometer using  $\text{MgK}\alpha$  radiation and operating at  $\sim 1 \times 10^{-8}$  Torr. Depth profiles of the samples were obtained by  $\text{Ar}^+$  sputtering. No reduction of  $\text{Sn(IV)}$  in a  $\text{SnO}_2$  control sample was observed by exposure to extensive sputtering (i.e., no reduction of  $\text{Sn(IV)}$  to  $\text{Sn(0)}$  by the ion gun was detected).

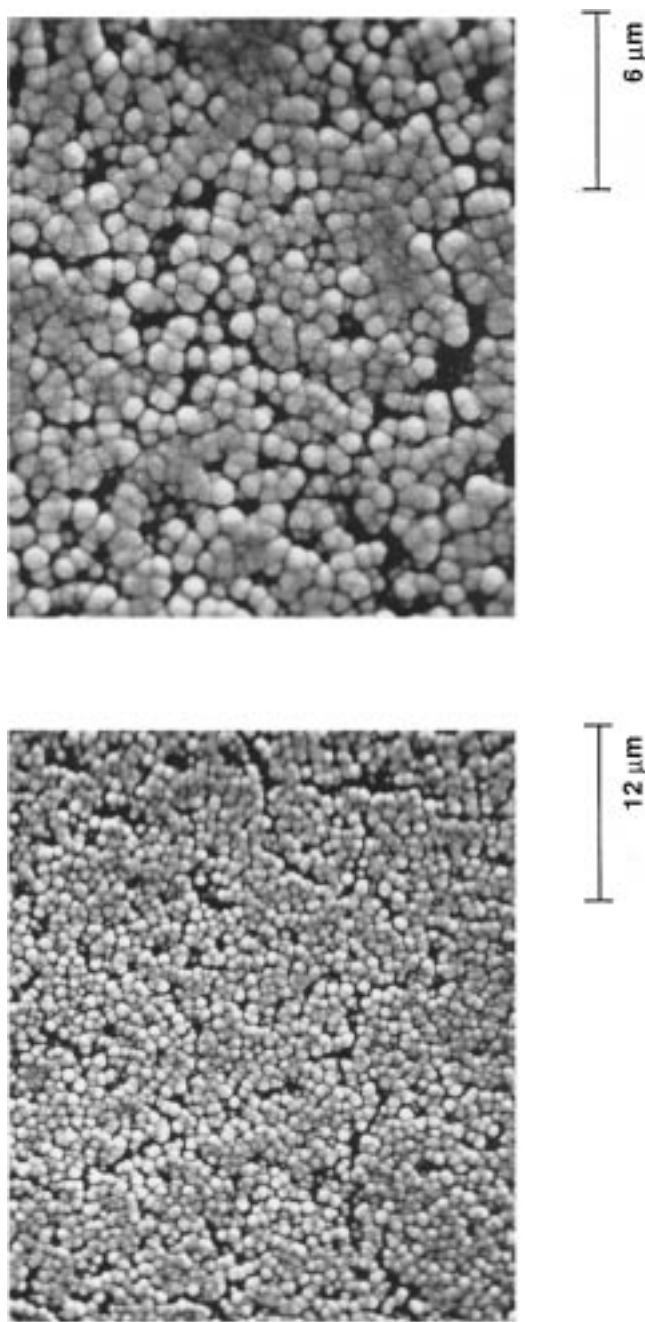
## Results

**Characterization of Catalyst Deposits.** Figure 2 shows SEM micrographs of a Pt–Sn catalyst on a polished GC electrode at a catalyst loading of  $\sim 0.5$  mg/cm<sup>2</sup>. From the SEM micrograph it is clear that the Pt–Sn catalyst deposits as adherent microparticles on the GC substrate. Pt–Sn forms adherent films when deposited onto Au electrodes, and SEM analysis did *not* show the presence of distinct catalyst particles. Some surface roughness could be seen at higher magnification ( $>60000\times$ ) but this roughness is typical of the electron-beam deposited Au substrates. For some experiments the catalyst was dispersed on a thin polyaniline film previously deposited onto GC. Even though there are morphological differences according to the substrate material, at the catalyst loadings studied ( $\sim 0.5$  mg/cm<sup>2</sup>) the choice of substrate did not significantly affect the catalytic activity.

XPS surface analysis of the Pt–Sn catalyst from Figure 2 showed that Sn is present in an oxidized state on the surface, while Pt is fully reduced. The Sn content varied with sample depth. On the surface, the Pt:Sn ratio was approximately 3:1, while in the bulk (after  $\sim 3$  min of  $\text{Ar}^+$  sputtering) the Pt:Sn ratio increased to 9:1.

**Extent of Oxidation of Fuels on Pt–Sn.** By exhaustively oxidizing a given organic fuel and measuring the total oxidation charge one can determine the number of electrons per molecule obtained in the oxidation of that particular fuel. Ideally, all carbohydrates would yield  $\text{CO}_2$ , but unfortunately Pt–Sn is not an effective electrocatalyst for all candidate fuels. However, in the case of MeOH oxidation in  $0.5$  M  $\text{H}_2\text{SO}_4$ , we obtained  $6$  e<sup>−</sup> per molecule, confirming the ultimate oxidation product to be  $\text{CO}_2$ . We also exhaustively oxidized formaldehyde and formic acid in  $0.5$  M  $\text{H}_2\text{SO}_4$ , and we determined the electron yield to be  $4$  e<sup>−</sup> per molecule and  $2$  e<sup>−</sup> per molecule, respectively.  $\text{CO}_2$  was also detected as the product of these electrolyses. The potential used for MeOH, formaldehyde, and formic acid was more negative than  $0.4$  V vs SCE.

In similar experiments, we studied the oxidation of EtOH, *n*-PrOH, *i*-PrOH, and the  $2$  e<sup>−</sup> oxidation products of these molecules. It has been shown,<sup>33</sup> and our studies confirm, that the initial product of EtOH oxidation at Pt–Sn electrodes is acetaldehyde. However, Sn adatoms also enhance the catalytic activity of Pt for the oxidation of acetaldehyde.<sup>36</sup> Figure 3 shows cyclic voltammograms for the oxidation of EtOH, acetaldehyde, and acetic acid on Pt–Sn electrodes. EtOH and acetaldehyde are both oxidizable at relatively negative potentials on surfaces modified by Pt–Sn electrodeposits, but acetic acid is practically inert on Pt–Sn. Product analysis shows acetic acid to be the ultimate product from oxidation of EtOH at



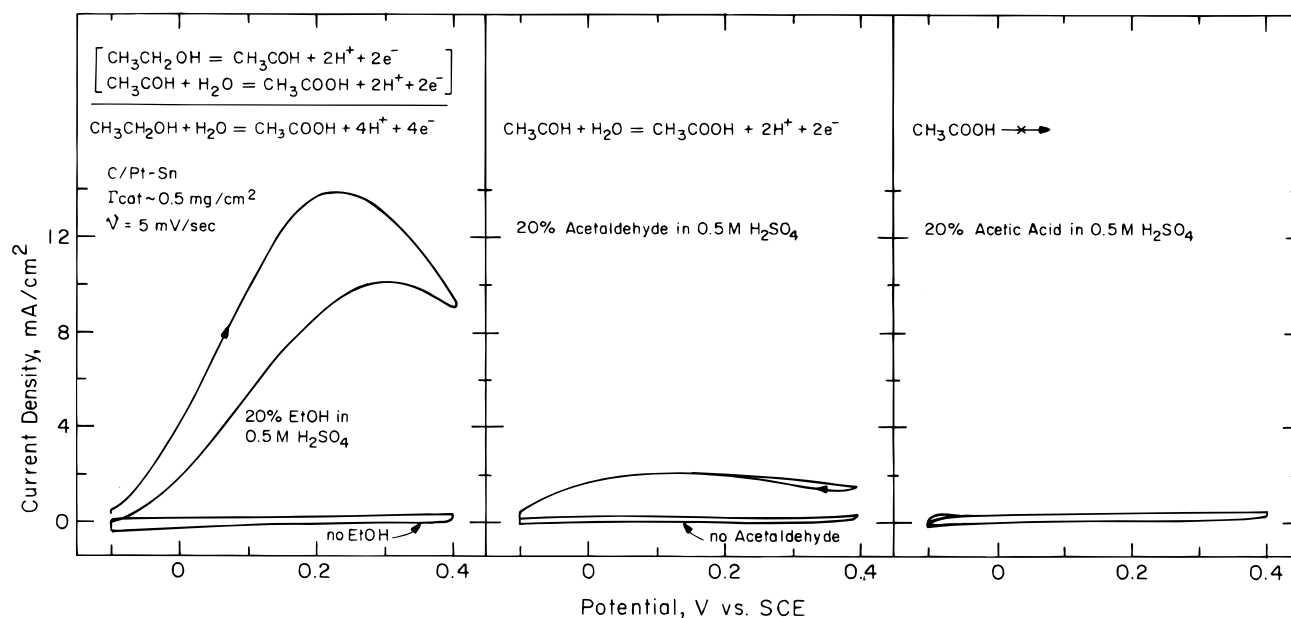
**Figure 2.** SEM micrographs of Pt–Sn catalyst deposited on a glassy carbon electrode. The catalyst loading is about  $0.5$  mg/cm<sup>2</sup>. The catalyst was deposited from  $0.5$  M  $\text{H}_2\text{SO}_4$  containing  $12$  mM  $\text{K}_2\text{PtCl}_6$  and  $28$  mM  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ .

potentials negative of  $0.5$  V vs SCE. Unfortunately, Pt–Sn catalysts do not activate C–C bonds at potentials lower than  $0.5$  V vs SCE, at room temperature. Thus, though EtOH could ideally provide  $12$  e<sup>−</sup> per molecule we find that the reaction stops at the stage of a  $4$  e<sup>−</sup> oxidation.

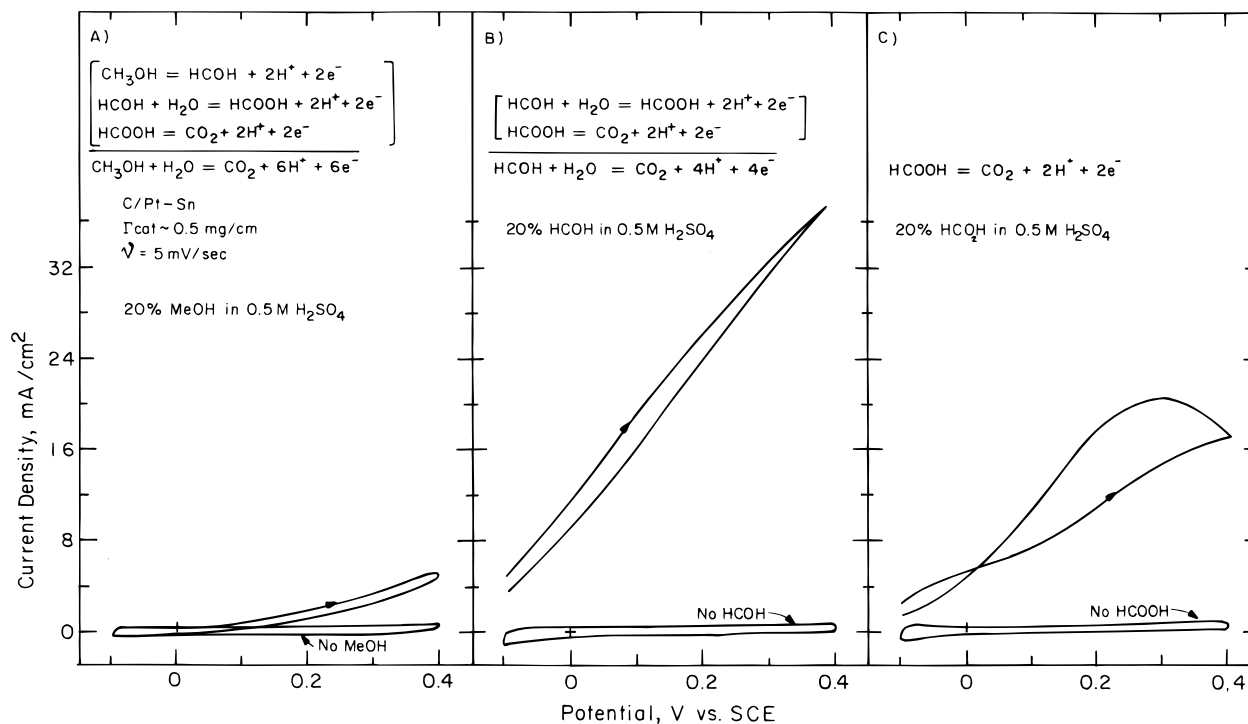
*n*-PrOH is oxidized to propionic acid on Pt–Sn surfaces at potentials negative of  $0.5$  V vs SCE. Like EtOH and acetaldehyde, both *n*-PrOH and propionaldehyde are oxidized at relatively negative potentials on Pt–Sn catalysts. Propionic acid, like acetic acid, is inert at negative potentials. Accordingly, *n*-PrOH yields  $4$  e<sup>−</sup> per molecule, with the ultimate product being propionic acid. Production of propionic acid as the result of *n*-PrOH oxidation was confirmed by  $^{13}\text{C}$  NMR.

In the case of *i*-PrOH, only  $2$  e<sup>−</sup> per molecule are obtained from its exhaustive electrolysis. This means that *i*-PrOH





**Figure 3.** Cyclic voltammograms for the oxidation of EtOH, acetaldehyde, and acetic acid on Pt-Sn. The current-voltage curves were recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and then with 20 vol % of fuel added. The scan rate is 5 mV/s.



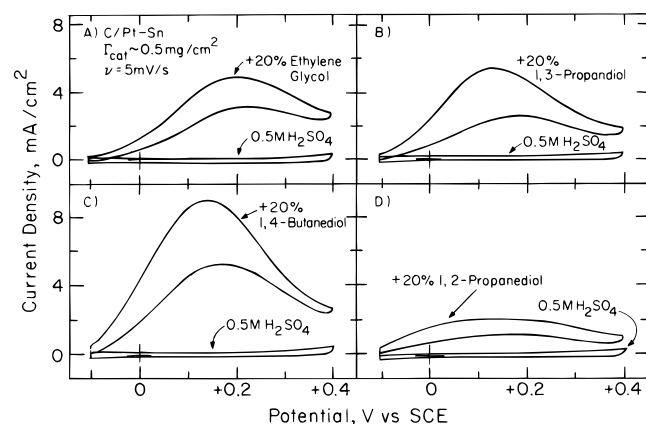
**Figure 4.** Cyclic voltammograms showing the oxidation of MeOH, formaldehyde, and formic acid on Pt-Sn electrodes. The current-voltage curves were recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and then with 20 vol % of fuel added. In the case of formaldehyde, a commercial 40% aqueous solution of formaldehyde was 1:1 diluted with 1 M H<sub>2</sub>SO<sub>4</sub>. The scan rate is 5 mV/s.

oxidation stops at the production of acetone. Acetone is indeed inert on Pt-Sn electrodes, and it was found as the only product of the oxidation of *i*-PrOH by GCMS. For the alcohols MeOH, EtOH, *n*-PrOH, and *i*-PrOH, only MeOH is oxidized at negative potentials to CO<sub>2</sub> at Pt-Sn catalysts. This means that only MeOH delivers its theoretical electron yield at ambient temperature and at moderate potentials. However, even for MeOH there is a shortcoming of the Pt-Sn catalyst revealed in comparison of oxidation rate vs potential.

Cyclic voltammograms for MeOH, formaldehyde, and formic acid oxidation are shown in Figure 4. It is interesting to note the big differences in the potential onset for oxidation for these

three one-carbon molecules. Formaldehyde is oxidized most readily on Pt-Sn surfaces. MeOH, on the other hand, is the least reactive among the three molecules in the path to CO<sub>2</sub> formation. Hence, the first 2 e<sup>-</sup> oxidation, the conversion of MeOH to formaldehyde, is the efficiency-determining step in the oxidation of MeOH to CO<sub>2</sub>. A more negative onset for oxidation means a higher fuel cell output voltage. Thus, a MeOH-based fuel cell employing a Pt-Sn catalyst would be limited by the inefficient conversion of MeOH to formaldehyde.

**Extent of Oxidation of Diols on Pt-Sn Catalysts.** Figure 5 shows the current voltage curves for oxidation of a series of water-soluble diols. In 5a-c, as the number of methylene



**Figure 5.** Oxidation of water-soluble diols at Pt-Sn. The current-voltage curves were recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and then with 20 vol % of the diol added. The scan rate is 5 mV/s.

groups between the alcohol groups is increased, a slight increase in the peak current at  $\sim +0.15$  V vs SCE occurs. In all cases the activity of Pt-Sn modified electrodes for oxidation of the diols is enhanced compared to oxidation at Pt alone. It is interesting to note that formaldehyde, which is hydrated in aqueous solutions to form the diol, methylene glycol, shows the highest rate of oxidation at low overpotentials. The oxidation of 1,2-propanediol, Figure 5d, results in significantly lower currents than 1,3-propanediol at higher overpotentials, but again the onset for oxidation occurs negative of  $-0.1$  V vs SCE and for both molecules the potential for onset of oxidation is lower than on Pt alone.<sup>63,64</sup>

The simplest diol (besides hydrated formaldehyde or methylene glycol), ethylene glycol, offers appealing features for use as fuel in a fuel cell. The oxidation of ethylene glycol at Pt electrodes in aqueous acid has been studied extensively at smooth Pt surfaces,<sup>44–46,65,66</sup> platinized-Pt,<sup>41,67,68</sup> and on Pt surfaces with adatoms.<sup>40–42,66,69,70</sup> Sn adatoms on Pt have been shown to enhance the rate of electrochemical oxidation of ethylene glycol in acidic electrolytes.<sup>40,41</sup> The oxidation of the alcohols studied is thermally activated on Pt-Sn. This fact is significant because fuel cells should be operated near or above 100 °C for the purpose of H<sub>2</sub>O discharge. One important feature which makes ethylene glycol a particularly appealing fuel is that its boiling point is above 100 °C so that H<sub>2</sub>O could be discharged from the cell without evaporation of the fuel. Ethylene glycol is readily available, cheap, and relatively nontoxic. The low onset for oxidation currents should result in correspondingly high cell voltages, even without C–C bond cleavage. Ethylene glycol could deliver 8 e<sup>−</sup> per molecule if conversion to oxalic acid were achieved (eq 1), as might be expected from our findings of converting EtOH and *n*-PrOH to acetic acid and propionic acid, respectively.



The Pt-Sn catalyst offers no benefit over Pt alone with respect to C–C bond oxidation which, for oxalic acid, occurs positive of +0.558 V vs SCE at Pt-Sn and Pt surfaces.<sup>71</sup> We evaluated the activity of Pt-Sn catalysts toward the oxidation of the possible intermediates in the conversion of ethylene glycol to oxalic acid, along the pathway depicted in Scheme 1. The current-voltage curves corresponding to the oxidation of each molecule are shown for comparison. Not all of the intermediates in the stepwise oxidation of ethylene glycol are reactive at Pt-Sn surfaces. Both ethylene glycol and glycolaldehyde are fairly

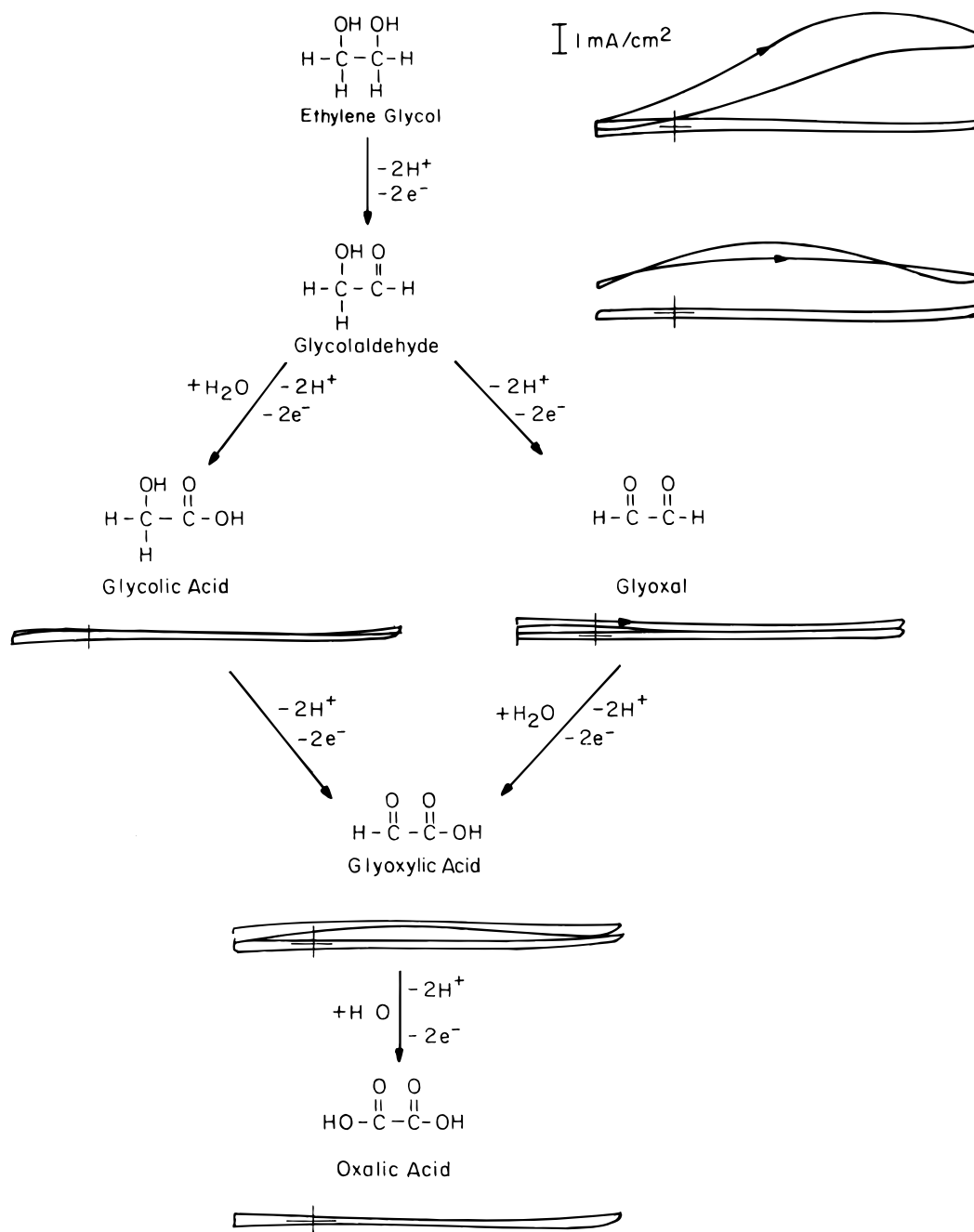
reactive on Pt-Sn. Some reactivity is observed in the case of glyoxal and glyoxylic acid, but glycolic acid and oxalic acid are completely inert at potentials ranging from  $-0.1$  to  $0.5$  V vs SCE. Thermal activation is observed in the oxidation of ethylene glycol, glycolaldehyde, glyoxal, and glyoxylic acid at all potentials. However, there is no increase in the oxidation current at  $E < 0.1$  V for glycolic acid or oxalic acid with temperature. Therefore, if the oxidation of ethylene glycol yields primarily glycolic acid, the reaction will probably stop at this stage, and only 4 e<sup>−</sup> per molecule of ethylene glycol will be obtained, instead of the 8 e<sup>−</sup> per molecule corresponding to the oxidation of ethylene glycol to oxalic acid. Unfortunately, the exhaustive electrolysis of ethylene glycol shows that only 4 e<sup>−</sup> per molecule are produced, and glycolic acid is detected as the main product by GCMS. Consequently, on Pt-Sn surfaces, the aldehyde group on glycolaldehyde is converted faster to acid than the alcohol group to aldehyde at low potentials ( $E < 0.1$  V) and room temperature.

**Comparison of Oxidation Rate vs Potential for Small Carbohydrates.** Study of other alcohols reveals additional information regarding oxidation rate at a given potential. In Figure 6 we show a comparison of the reactivities of primary vs secondary and tertiary alcohols. For EtOH, *n*-PrOH, and *i*-PrOH the onset for oxidation current is more negative than  $-0.1$  V vs SCE, which represents a significant improvement compared to Pt alone.<sup>37,39,69,72</sup> Yet, the currents at all potentials are higher for EtOH and *n*-PrOH than for the secondary alcohol *i*-PrOH. The tertiary alcohol *t*-BuOH is completely inert on Pt-Sn surfaces, as expected from a catalyst system that does not, apparently, activate C–C bonds.

For a series of primary alcohols, the reactivity decreases when the carbon chain length (the “greasy tail” to the alcohol group) is increased from EtOH to *n*-BuOH, Figure 7. However, MeOH is the least reactive molecule at the most negative potentials; even *n*-BuOH shows slightly higher current density than MeOH at potentials negative of 0.1 V vs SCE. The frustrating finding, therefore, is that MeOH, among the primary alcohols studied, is the only one not easily oxidized at a negative potential. The inefficient oxidation of MeOH to formaldehyde is thus the key shortcoming of the Pt-Sn catalyst.

**Effect of Substitution in the Reactivity of Alcohols Containing Two or More Carbon Atoms.** In general, it appears that alcohols with hydrogen atoms on the carbon  $\beta$  to the hydroxyl group can be oxidized at electrodes modified with Pt-Sn at low overpotentials compared to their oxidation on Pt alone. However, the reactivity of EtOH is dramatically decreased by substitution of just one H atom on the carbon  $\beta$  to the hydroxyl group by a F atom when comparing EtOH oxidation vs 2-fluoroethanol oxidation, Figure 8. This result shows that substituents on the  $\beta$ -carbon can dramatically affect the oxidation of alcohols at the Pt-Sn catalyst. The reactivity is practically destroyed by further fluorine substitutions on the same carbon, when evaluating the reactivities of 2,2-difluoroethanol and 2,2,2-trifluoroethanol. The equivalent trend is observed when comparing the reactivity of EtOH with those of 2-chloroethanol and 2-bromoethanol.

The Pt-Sn catalyst is not irreversibly poisoned or damaged by the fluorinated alcohols. The currents for oxidation of 1 M EtOH do decrease by about 50% in the presence of 1 M 2-fluoroethanol (Figure 8). However, the Pt-Sn catalyst showed no decreased activity for EtOH oxidation after being removed from aqueous solutions containing fluorinated ethanol derivatives. Our conclusion is that these fluorinated alcohols

SCHEME 1: The Stepwise Oxidation of Ethylene Glycol to Oxalic Acid<sup>a</sup>

<sup>a</sup> The current–voltage curves corresponding to the oxidation of the intermediates are shown for comparison. The concentration of the fuel was 20 vol % or weight in 0.5 M  $\text{H}_2\text{SO}_4$ . The scan rate was 5 mV/s. The voltage range was  $-0.1$  to  $0.4$  V vs SCE in all cases.

are relatively unreactive at the Pt–Sn catalyst surface, but may block the surface to some extent, with no irreversible adsorption.

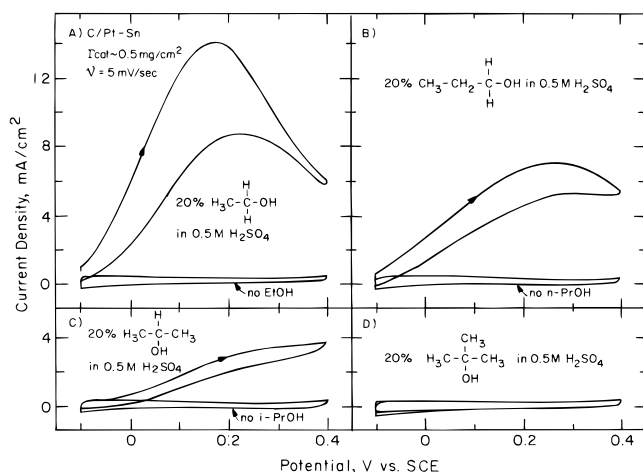
Substitution by nonhalogen groups at the carbon  $\beta$  to the hydroxyl group also affects the reactivity of larger alcohol molecules at Pt–Sn. Benzyl alcohol, neopentyl alcohol, and 2-Me-1-PrOH all show some reactivity on Pt–Sn electrodes. At 0 V vs SCE, the oxidation current for each of them is about twice the oxidation current of 2-fluoroethanol. However, they are 20 times less reactive than EtOH on the same electrode.

## Discussion

Studies of MeOH oxidation on bare Pt have shown that the oxidation of this alcohol is inhibited by poison formation and the poison has been identified as a  $-\text{CO}$  or a  $-\text{COH}$

species.<sup>17,73–75</sup> The  $-\text{COH}$  species has been suggested to be a detectable intermediate in the formation of  $-\text{CO}$  on Pt.<sup>76</sup> The mechanism presented in Scheme 2 has been proposed to explain the poison formation from the electrochemical oxidation of MeOH on Pt.<sup>73</sup> The initial adsorption steps comprise the formation of Pt–O and Pt–C bonds by  $\alpha$ -H and  $\beta$ -H elimination. Successive H abstractions by the Pt surface lead to the formation of  $-\text{COH}$ , then to  $-\text{CO}$ , in the linear or bridge conformations.

On Pt–Sn surfaces, there is a lower onset for oxidation currents in the oxidation of MeOH when compared to bare Pt surfaces, but the overpotential for MeOH oxidation is still large on Pt–Sn. It is likely that, also on Pt–Sn surfaces, the initial oxidation of some MeOH molecules in the same fashion as for



**Figure 6.** Comparison of the reactivities of primary vs secondary and tertiary alcohols. The cyclic voltammograms were recorded in 0.5 M  $\text{H}_2\text{SO}_4$  containing 20 vol % of the fuel. The scan rate was 5 mV/s.

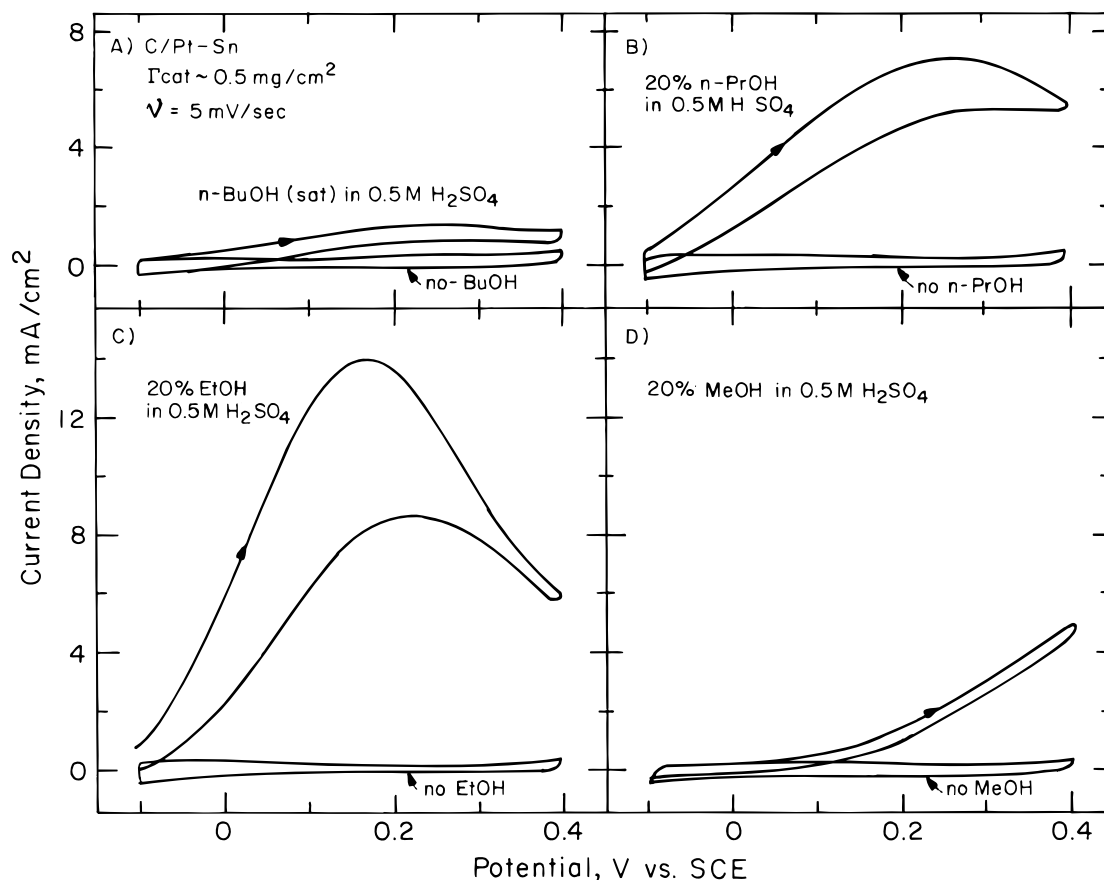
bare Pt probably leads to the formation of a monolayer of poison that inhibits further oxidation of MeOH at low ( $E < 0.1$  V vs SCE) potentials. The lower onset for MeOH oxidation on Pt-Sn with respect to bare Pt would correspond to earlier poison oxidation due to the presence of excess O at the surface, supplied by Sn species.<sup>77</sup>

In alcohols that have a C-C bond, such as EtOH or *n*-PrOH, formation of poison at Pt-Sn does not occur at low temperatures and low potentials to the same extent as for MeOH, because C-C bond breaking does not occur on Pt-Sn under such conditions. Yet, another factor may also be significant in the accomplishment of the oxidation of these alcohols on Pt-Sn at

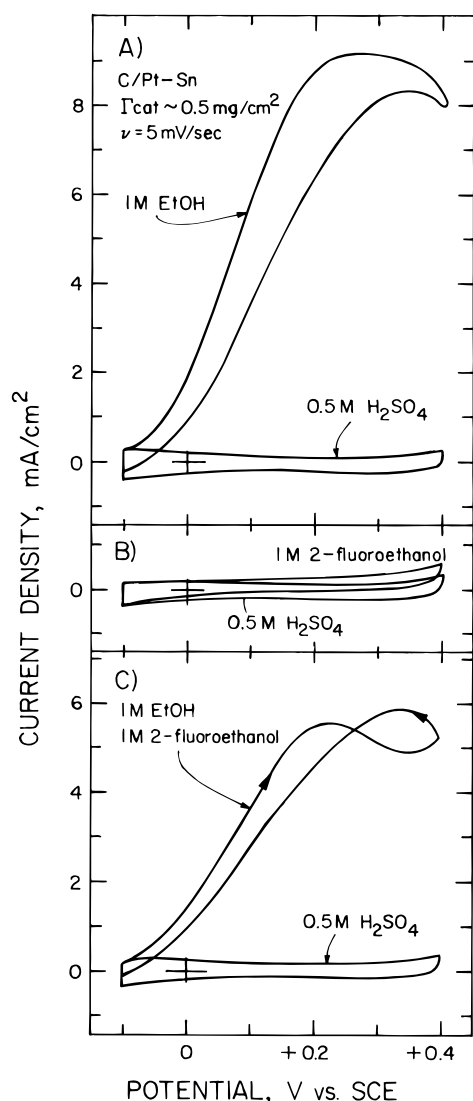
low potentials. H abstractions from both the C  $\alpha$  and  $\beta$  to the hydroxyl group could lead to the formation of a stabilizing enol structure which could convert to the aldehyde. This conversion would be facilitated by an O-rich surface like Pt-Sn because attack on the enol form by adsorbed water could easily form the hydrated aldehyde.

On bare Pt, the -CO molecule also forms as poison when formaldehyde or HCOOH are used as fuels instead of MeOH.<sup>17,73</sup> Thus, at least for HCOOH, Pt is not only breaking C-H bonds, but it is also breaking a C-O bond. Interestingly, we have found that the Pt-Sn catalysts work extremely well for the oxidation of formaldehyde or HCOOH. In fact, from the spectrum of molecules that we have studied, formaldehyde is the most easily oxidized fuel on Pt-Sn surfaces. This probably means that poison formation at the potentials, temperature, and time scales of our experiments does not occur when oxidizing formaldehyde. This result is difficult to explain based on the mechanism discussed previously for poison formation from MeOH oxidation, Scheme 2; adsorption of formaldehyde (HCOH) onto the surface by just one C-H bond breaking would lead to immediate formation of the -COH species, a precursor to the -CO poison.

Still, there is a significant structural difference between MeOH and formaldehyde and HCOOH. Oxidation of MeOH to  $\text{CO}_2$  requires the addition of one O atom, besides the loss of six H atoms. However, formaldehyde exists 99.99% hydrated in aqueous solutions in the form of a diol, methylene glycol ( $\text{H}_2\text{C}(\text{OH})_2$ ).<sup>78</sup> Thus, the two necessary C-O bonds that will constitute the final product  $\text{CO}_2$  are already present in both formaldehyde (as two seminal C-OH bonds) and HCOOH (as one C=O bond and one C-OH bond). We can anticipate

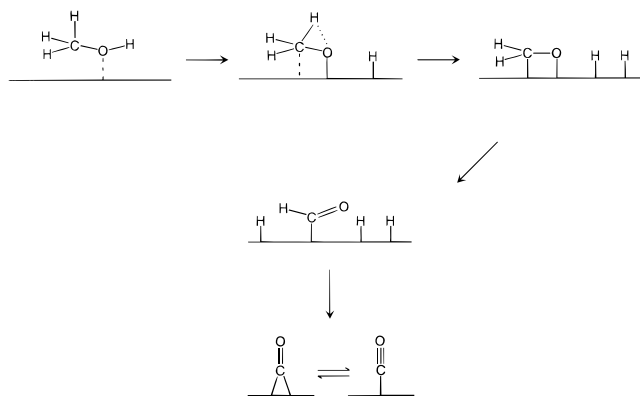


**Figure 7.** Comparison of the reactivities of primary alcohols with different C-chain lengths. The concentration of the fuel is 20 vol % in 0.5 M  $\text{H}_2\text{SO}_4$  in each case. The scan rate is 5 mV/s.



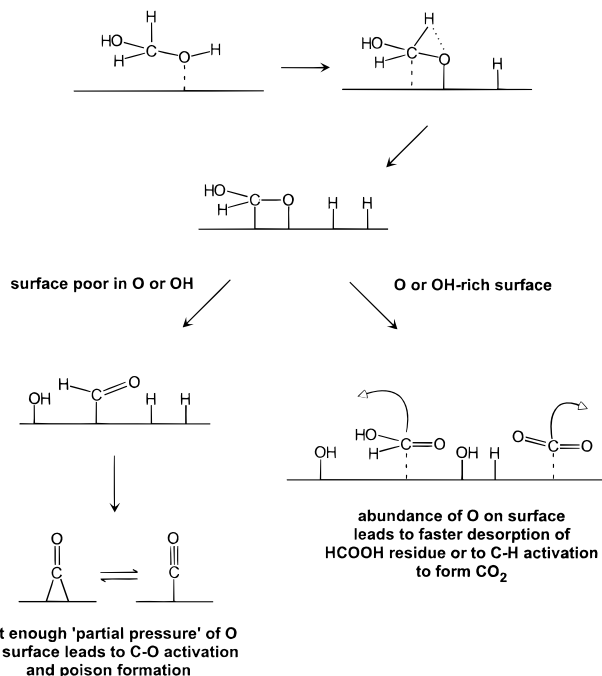
**Figure 8.** Comparison of EtOH and 2-fluoroethanol oxidation at a Pt-Sn modified electrode. (A) Oxidation of 1 M EtOH at a Pt-Sn modified electrode. (B) Oxidation of 1 M 2-fluoroethanol at the same Pt-Sn modified electrode. (C) Oxidation of 1 M EtOH in the presence of 1 M 2-fluoroethanol.

### SCHEME 2: Surface Mechanism of Poison Formation from MeOH Electro-oxidation on Bare Pt<sup>73</sup>



formaldehyde (methylene glycol) oxidation to occur at a surface following a mechanism like the one depicted in Scheme 3. According to the type of catalytic surface, two possible events may occur once the initial H abstractions are accomplished. If the surface is poor in  $-O$  or  $-OH$  species (e.g., bare Pt), the

### SCHEME 3: Mechanism of Formaldehyde Oxidation on Oxygen-Poor and Oxygen-Rich Surfaces



catalyst will split one of the C-O bonds and formation of  $-COH$  will result, leading to surface poisoning. If, on the other hand, the surface is rich in  $-O$  or  $-OH$  species (e.g., Pt-Sn catalysts), the abundance of oxygenated species will lead to the fast desorption of the  $HCOOH$  residue formed in the initial adsorption steps or to further C-H activation to form the final product  $CO_2$ .  $HCOOH$  or  $CO_2$  formation by C-H activation in this case is faster than C-O activation and poison formation.

For MeOH, the presence of excess  $-O$  or  $-OH$  species on the surface is not enough for the activation of this molecule at low potentials because extra driving force (higher potential) is needed to form an extra C-O bond in order to get to  $CO_2$  as the final oxidation product. Interestingly, acetaldehyde, which is also reactive to electrochemical oxidation onto Pt-Sn, is  $\sim 50\%$  hydrated in aqueous solutions at room temperature, whereas acetone, an inert molecule on Pt-Sn, is nearly nonhydrated.<sup>79</sup> Also, it is interesting to relate the comparative reactivities of two different molecules, MeOH and formaldehyde, to the relative reactivities of the alcohol and the aldehyde group in the multifunctional molecule glycolaldehyde. As for the case of formaldehyde, hydration of the aldehyde group in glycolaldehyde may be contributing to enhance the oxidation of the aldehyde with respect to the oxidation of the alcohol group, which leads to production of glycolic acid instead of glyoxal, vide supra.

It is surprising that the F-substituted ethanol show no reactivity even at 0.4 V vs SCE. The inactivity of these molecules may not be related to thermodynamic constraints alone. Moreover, according to our estimates of the equilibrium potentials for the  $2e^-$  oxidation of these fluorinated alcohols, the (thermodynamic) onset values for oxidation should be close to 0 V vs SCE. The inertness of these alcohols could also be attributed to electronic effects, given the strong electronegativity of fluorine. The electron withdrawing effect, extended to the carbon  $\alpha$  to the hydroxyl group, hinders the ability of the surface to accomplish  $\beta$ -hydrogen abstractions. This translates in the inability to achieve enol stabilization and further oxidation. This effect should be attenuated by separating the hydroxyl-carbon



from the halogen-carbon. Indeed,  $\beta$ -substituted PrOH's (2-chloro-1-PrOH and 1-chloro-2-PrOH) are very inert toward oxidation on the Pt-Sn electrodes, but there is some reactivity at  $E > 0.1$  V vs SCE for the  $\gamma$ -substituted PrOH, 3-chloro-1-PrOH, which may correspond to a decreased electronic effect exerted by the Cl atom on the C-H bonds  $\alpha$  to the hydroxyl group.

These results are interesting in view of a report which states that the principal structural feature affecting the electrochemical reactivity of alcohols on Pt is the presence of hydrogen atoms bonded to the carbon atom with the hydroxyl group.<sup>72</sup> For the Pt-Sn modified electrodes other features also affect the electrochemical reactivity of alcohols at the catalyst surface. Indeed, the presence of hydrogen atoms on the hydroxyl carbon is necessary to achieve reactivity at the Pt-Sn catalyst; *t*-BuOH is inert to oxidation on Pt-Sn over the potential range of  $-0.1$  to  $+0.4$  V vs SCE. However, our results show that the substituents on the carbon atom  $\beta$  to the hydroxyl group can have profound effects on electrochemical reactivity of a particular alcohol, when comparing the oxidation of EtOH with the oxidations of fluorinated EtOH's or the oxidation of *n*-PrOH with the oxidations of 2-Me-1-PrOH and neopentyl alcohol at Pt-Sn. Our conclusion is that the presence of hydrogen atoms on both the  $\alpha$ - and  $\beta$ -carbons of an alcohol is necessary for catalytic oxidation to be observed at low overpotentials on Pt-Sn.

## Conclusions

We have compared the oxidation of small organic molecules in 0.5 M H<sub>2</sub>SO<sub>4</sub> at electrodes modified with Pt-Sn at low ( $-0.1$  V to  $0.5$  V vs SCE) potentials. Alcohols and diols containing only the elements C, H, and O, and having hydrogen atoms at the positions  $\alpha$  and  $\beta$  to the hydroxyl group show an extremely low overpotential (compared to the potential for oxidation of H<sub>2</sub>) for the onset of electrocatalytic current. The activity for these materials on Pt-Sn is significantly improved compared to their oxidation on Pt alone. However, the substitution of fluorine for one of the hydrogen atoms on the  $\beta$  carbon causes the alcohol to become almost completely inert to electrocatalytic oxidation at the Pt-Sn catalyst.

EtOH and *n*-PrOH are oxidized to acetic acid and propionic acid, respectively, on Pt-Sn electrodes, the oxidation yields being  $4 e^-$  per molecule, and *i*-PrOH is oxidized to acetone, which is unreactive at Pt-Sn surfaces. The onset for oxidation current of ethylene glycol occurs at low potentials ( $E < 0.0$  V vs SCE) on Pt-Sn electrodes. However, glycolic acid, an intermediate for the oxidation of ethylene glycol, is not oxidizable at these low potentials. Thus, glycolic acid behaves as a stopper in the oxidation chain of ethylene glycol to oxalic acid. As a result, the electron yield of the oxidation of ethylene glycol at Pt-Sn surfaces is  $4 e^-$  per molecule instead of the value of  $8 e^-$  per molecule which corresponds to the oxidation of ethylene glycol to oxalic acid.

MeOH, which has the highest electron yield on Pt-Sn ( $6 e^-$  per molecule), is the least reactive primary alcohol from the series studied in this work. On the other hand, formaldehyde, which exists in aqueous solutions as methylene glycol, shows the highest electrocatalytic currents on Pt-Sn. Formic acid is also readily oxidized on these surfaces. Thus, in the stepwise oxidation of MeOH to CO<sub>2</sub>, the first  $2 e^-$  oxidation step, the conversion of MeOH to formaldehyde (as methylene glycol), is the rate-determining step. The elementary step which determines the rate might be either C-H bond breaking or C-O bond formation. Additional experimentation is needed to

definitely establish which is the rate-determining elementary step. Previously, the reactivities of MeOH and formaldehyde have been compared on Pt, where both molecules are inert at low potentials ( $E < 0.2$  V vs SCE). On bare Pt, no oxidation of MeOH, formaldehyde, or formic acid occurs without poison formation. In contrast, on Pt-Sn, poison formation seems to depend strongly on the structure of the fuel molecule.

Oxidation of formaldehyde on Pt-Sn is very efficient, due to hydration; formation of poison is slow compared to the rate of conversion of formaldehyde to formic acid and/or CO<sub>2</sub>. The fact that the alcohol group is much less reactive than the aldehyde group can be seen not only by comparing formaldehyde with MeOH, but also by studying the oxidation of glycolaldehyde, a multifunctional molecule that contains both an alcohol group and an aldehyde group. Hydration of the aldehyde group likely plays a key role in the electrocatalytic oxidation of aldehydes; hydration leads to conversion of the aldehyde group to a diol which results in more efficient oxidation on Pt-Sn. The two C-O bonds in the gem diol (two C-O's on the same C) likely behave as seminal bonds for the formation of the double C=O bonds in the ultimate oxidation product CO<sub>2</sub>.

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