Mechanistic Study of Electrooxidation of Ethanol on PtSn Nanoparticles in Alkaline and Acid Media

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In this study, we report on the structure-to-property relationship for PtSn ethanol electrooxidation catalysts in alkaline and acid environment. Relationship between surface chemistry, as determined by XPS and electrochemical performance in both acid and alkaline media, is facilitated by multivariate analysis. Upon transitioning from acidic to an alkaline environment, changes in the material structure and electrochemical reaction mechanisms are observed. Electrocatalysts containing larger particles with larger relative amounts of metallic Pt and Sn perform better in acid indicating inner-sphere electron transfer reaction on active PtSn alloy phase. PtSn electrocatalysts containing larger amounts of oxidized Pt and Sn perform better in alkaline indicating that hydroxyl species that are natively present on oxidized Pt and Sn are promoting an outer-sphere electron transfer.

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Direct hydrocarbon and direct alcohol fuel cells could find practical application due to the high energy densities of the fuels and the easier storage and delivery of liquid fuels. Direct ethanol fuel cells (DEFCs) are particularly attractive because ethanol can be generated from sustainable biomass derived feed stocks. There are several primary challenges that need to be overcome in order for DEFCs to see practical use. One of them is a relatively slow oxidation kinetics, which limits the power levels that can be achieved with the fuel cells. This is partly due to incomplete oxidation of ethanol to CO₂, which effectively negates the high energy density of the fuel. Recent developments in OH⁻ anion exchange membranes will allow for DEFCs to operate not only in acidic media, where reaction kinetics is less favorable, but also under alkaline conditions where the oxidation kinetics is much faster.

Platinum is found to be active for the ethanol electrooxidation in both acid and alkaline media, however Pt favors incomplete oxidation forming acetic acid and acetaldehyde in acid media and acetate and aldehyde in alkaline solutions.1 Complete oxidation of ethanol to CO₂ through the direct fission of the C-C bond at low overpotentials is the ultimate goal of direct ethanol fuel cells.2

Much of the current research into direct ethanol fuel cells is focused on the development of platinum group metal (PGM) electrocatalysts that contain metallic promoters to assist in the complete oxidation of ethanol to carbon dioxide and resist poisoning. Bimetallic Pt-based electrocatalysts such as PtSn, PtRu, PtPd, PtW,3-5 and ternary electrocatalysts such as PtRuW, PtRuMo, PtRuSn,6 PtSnNi7 and PtRhSnO₂8 have been tested for promotion of ethanol oxidation in acid media. Among several promoters, Sn or SnOₓ were identified as the best element to enhance the ethanol electrooxidation on Pt in acid,9,10 and Pt and Pd in alkaline media.11 DFT calculations of effect of alloyed metal on the catalytic activity of Pt for ethanol oxidation showed that among Ru, Sn, Re, Rd and Pd, only Sn enhances the rate constant of the dehydrogenation on the Pt site of PtSn as compared with that on Pt alone.12 Several factors are established to play a role in the performance of PtSn systems, such as surface and bulk composition, structure, morphology, particle size, degree of alloying and the presence of surface oxides. It was found that in acid media, the electrocatalyst performance depends substantially on the atomic ratios of elements present, and the optimal composition for PtSn varies depending on the synthesis procedure. Lamy et al. tested PtSn compositions ranging from 9:1 to 4:1 and found that the addition of Sn always promoted the ethanol electrooxidation if compared to Pt, whereas the presence of 10–20 at% Sn resulted in the best resistance to catalyst poisoning or deactivation. Zhou et al. observed the PtSn composition of 33–40 at% Sn to provide the best ethanol electrooxidation performance. The justification for the Pt:Sn ratio relates to the existing mechanism of the ethanol electrooxidation. The addition of Sn improves catalyst performance due to the bifunctional mechanism and/or the electronic effect. Well-ordered PtSn surface alloys supported on Pt (111) were shown to be particularly active toward ethanol electrooxidation in acidic media for structures where one Pt atom is in immediate contact to one or two surrounding Sn atoms.13 It is well-established that in the bifunctional mechanism, the dissociative adsorption of water produces oxygen containing species (OH⁻ads) on the promoter that can oxidize adsorbed carbon monoxide and other intermediates on Pt at lower potentials than on pure Pt. The bifunctional mechanism can also facilitate the oxidation of acetaldehyde to acetic acid.1 In the electronic effect, the added Sn decreases the bond strength between Pt and CO_ads and/or other intermediates thus favoring ethanol adsorption.14,15 The electronic effect may also cause water activation (OH⁻ads) on Pt at lower potentials.16

An increase in the amount of surface Sn or Sn oxides may have a negative effect on PtSn performance since the adsorption and decomposition of ethanol occurs on Pt and contiguous Pt sites are needed to split the C-C bond.17 Promoters may cover Pt sites and reduce the number of available Pt sites. Although the electronic effect is beneficial in reducing the Pt-CO_ads bond strength, excess electronic effect decreases the Pt-C bond strength and favors acetaldehyde formation.18 Furthermore, the difference in surface energy between Sn (0.673 J/m²) and Pt (1.95 J/m²) may result in surface enrichment with Sn and hence a large difference between overall and surface composition.19 The performance of high at.% Sn electrocatalysts can also be reduced due to the low electronic conductivity of SnOₓ.

Furthermore, degree of PtSn alloying and presence of surface oxides appear to have an influence on PtSn catalytic performance in acid electrolytes. Zhu et al.18 showed that a large PtSn alloying degree promotes the ethanol oxidation reaction through the electronic effect while low alloying degree promotes ethanol oxidation through the bifunctional mechanism. Godoi et al.20 found that catalytic activity of PtSn/C for ethanol oxidation is strongly influenced by changes in the amounts of Sn in alloyed and oxidized forms and that the increase in the amount of alloy at the expense of the oxides improves the catalytic activity. Despite the large number of publication on the ethanol electrooxidation on PtSn catalysts, the evaluation of the role of various parameters, e.g., surface and bulk composition, role of alloyed phases and oxides, particle size effect on the catalytic enhancement, is not a straightforward task and remains to be elucidated. Therefore, in this study, we
average crystallite size according to the Debye’s formula as described in Ref. 21. The (220) peak was used for the analysis, because Vulcan XC-72 has reflections near 25 and 45°, corresponding respectively to graphite reflections 002 and 101, which overlap with the main fcc (111) and (200) diffraction peaks.

**Electrochemical Characterization.**—**Ethanol electrooxidation in alkaline solution.**—Electrochemical measurements were conducted in a glassy carbon rotating disk electrode configuration (RDE) using a Pine Rotating Disk electrode and Princeton Applied Research Versastat 3 potentiostat. A large area surface Pt-wire counter electrode and Hach Hg/HgO reference electrode were used to complete the cell. Electrocatalyst inks for electrochemical evaluation were prepared by dispersing 2.5 mg electrocatalysts in a mixture of 1.6 mL DI water (18 MΩ cm), 0.34 mL isopropanol (IPA) and 0.06 mL 0.5 wt% Nafion solution (Aldrich), using a 15 minute sonication. A thin film was formed on the glassy-carbon electrode with area of 0.196 cm² by applying 20 μL from 1 mg mL⁻¹ ink solution and allowing to the air dry 45 min. Cyclic voltammograms (CV) were obtained at room temperature in 1.0 M KOH (BDH, ACS grade) saturated with UHP grade bubbling nitrogen for blank as well as 1.0 M C₂H₅OH (Burdick and Johnson, HPLC grade) oxidation tests, and in the appropriate electrolyte saturated with UHP grade CO for CO oxidation tests. All equipment in contact with the electrolyte was confirmed to be stable in 1.0 M KOH. Chronoamperometric (CA) measurements were repeated for freshly deposited inks after the sample was cycled 20 times from −0.9 to 0.4 V at 50 mV s⁻¹ and then stepped to −0.4 V and held for 60 min at 1600 RPM. The electrode potentials in alkaline solution are reported versus RHE unless otherwise stated.

**Ethanol electrooxidation in acid media.**—Electrochemical measurements were conducted using Parstat 2273 Advanced Electrochemical System (Princeton Applied Research). Experiments were carried out in a Pyrex three-compartment electrochemical cell. During the experiments, H₂ gas (99.997% Linde Canada) was bubbled through the Pt/Pr-black reference electrode compartment. High-purity N₂ gas (99.998% Linde Canada Limited) was passed through the working electrode compartment. The large surface area gauze Pt counter electrode was contained in a separate compartment. All potentials were measured with respect to a reversible hydrogen electrode (RHE) immersed in the supporting electrolyte solution (0.5 M H₂SO₄) in a separate compartment provided with a Luggin capillary. Sulfuric acid (Fisher-Scientific, 98% ACS grade), ethanol (Commercial Alcohols Inc., 100% ACS grade) and DI water (18 MΩ cm) were used to prepare solutions. A glassy carbon disc electrode (GC DE) (0.196 cm²) was used as a working electrode. Electrocatalyst inks for electrochemical evaluation were prepared by dispersing 13 mg of the carbon-supported catalyst powders in 1 mL of H₂O and 0.3 mL of Nafion solution for 15 min. Subsequently 2.5 μL of the catalyst ink was applied to a glassy carbon disc and allowed to the air dry for 45 min. The ethanol electrooxidation was carried out at 10 mV s⁻¹ in 1.0 M C₂H₅OH + 0.5 M H₂SO₄ saturated with UHP grade bubbling N₂. CVs were recorded between 0.1 and 1.0 V starting from open circuit potential for 25 cycles. The last cycle is shown, unless otherwise stated. For CA measurements, the potential was first held at 0.1 V for 300 s, then stepped to 0.5 V for 1 h.

**CO stripping measurements in 1 M KOH and 0.5 M H₂SO₄.**—Electrolyte saturation time was 30 minutes under electrode rotation, and for CO stripping experiments the sample was cycled in bubbling N₂ until stable. CO was bubbled while a sample was held at −0.85 V vs Hg/HgO for 5 min in 1 M KOH then CO was shut off and N₂ bubbled to purge CO while samples still held at −0.85 V. In 0.5 M H₂SO₄, CO was bubbled while a sample was held at 0.215 V vs RHE for 5 min then CO was shut off and N₂ bubbled to purge CO while samples still held at 0 V Finally CVs were collected at 50 mV s⁻¹. All electrode potentials in acid solution are reported versus RHE, whereas in alkaline media versus Hg/HgO reference electrode.
Catalysts characterization.— Average crystallite size and structure of the carbon-supported PtSn catalysts were obtained from X-ray diffraction patterns as described in details in Ref. 21. Carbon-supported Pt5Sn3 catalysts were analyzed by Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. The XPS analysis was conducted at 140 W using monochromatic Al Kα source and pass energy of 20 eV. The peak positions were corrected for sample charging by setting the maximum of C 1s peak to the binding energy of 284.7 eV. Data analysis and quantification were performed using CasaXPS software. A linear background subtraction was used for quantification of C 1s and O 1s and Shirley for quantification of Pt 4f and Sn 3d spectra. Sensitivity factors provided by the manufacturer were utilized. 70% Gaussian/30% Lorentzian line shape was used in the curve-fit. For species identification, Pt 4f spectra have been deconvoluted based on the constraints of equal spin-orbit splitting of 3.4 eV. FWHM was used based on that for Pt 4f spectrum from Pt foil.

Data analysis.— The curve-fit results from Pt 4f and Sn 3d spectra were combined with electrochemical surface area (ECSA) and normalized current density at 0.6 V vs. RHE (i) for both acid and alkaline media and average particle size found from XRD (d) into one table for PCA analyses. PCA (in PLS_Toolbox 5.0) in MATLAB) using autoscaling as data preprocessing method were applied. Autoscaling mean centers and scales data to unit variance making sure that all of the variables are equally weighted so that species present in very small amounts have the same importance as species present in large quantities. PCA extracts the key mathematical principal components (PC) from a large data matrix, by converting it into two smaller matrices that are easier to examine and interpret. The first PC accounts for the largest part of the variance in the data; the second PC accounts for the second-largest part of the variance, and so forth. The results of PCA are usually displayed as score plots (reflecting the significance of each variable in a principal component), loading plots (reflecting the significance of each variable in a principal component) and biplots (showing both samples and variables for two principal components). Biplots of PCA components will be used herein for analysis of correlation between variables as they provide a more instructive visualization of the clustering of samples for identification of variables that are the most or least important for a specific sample group. Correlated variables and samples will be located in the same regions on a biplot.

Results and Discussion

HRTEM and XRD.— Figure 1 shows HRTEM images representative of two types of PtSn catalysts — alloy and bi-phase. The lattice spacing between 0.1988 and 0.228 is assigned to PtSn nanoparticles #1-3, the 2θ(220) reflection is shifted to lower 2θ values (∼66.5°) compared to the 220 position for bulk fcc Pt, (67.5°) into one table for PCA analyses. PCA (in PLS_Toolbox 5.0) in MATLAB) using autoscaling as data preprocessing method were applied. Autoscaling mean centers and scales data to unit variance making sure that all of the variables are equally weighted so that species present in very small amounts have the same importance as species present in large quantities. PCA extracts the key mathematical principal components (PC) from a large data matrix, by converting it into two smaller matrices that are easier to examine and interpret. The first PC accounts for the largest part of the variance in the data; the second PC accounts for the second-largest part of the variance, and so forth. The results of PCA are usually displayed as score plots (reflecting the significance of each sample in a principal component), loading plots (reflecting the significance of each variable in a principal component) and biplots (showing both samples and variables for two principal components). Biplots of PCA components will be used herein for analysis of correlation between variables as they provide a more instructive visualization of the clustering of samples for identification of variables that are the most or least important for a specific sample group. Correlated variables and samples will be located in the same regions on a biplot.

Figure 2. XRD patterns representative of alloy (PtSn #3) and bi-phase (PtSn #5) carbon-supported PtSn/C electrocatalysts. Numbers are idem.

Electrochemistry.— Ethanol electrooxidation on the six carbon supported PtSn/C catalysts were reported earlier in acid and alkaline solutions. Representative cyclic voltammograms and chronamperograms in ethanol containing electrolyte is shown in Figure 3, while CO stripping in alkaline and acid solutions is shown in the Supporting Information (Figs 1S–2S). Several characteristics, such as electrochemical surface area (ECSA) found from CO stripping CVs and electrooxidation current densities (i) obtained from CV experiments in 1.0 M ethanol containing solutions are summarized in Table I. The table also shows average diameter of all six samples and the bulk structure found from XRD measurements as well as XPS data.

XPS.— Table II shows atomic % and relative distribution of Pt and Sn types as determined by XPS. The stoichiometry of the sample depends on the concentration of the NaOH solution during synthesis. At higher % NaOH, the composition of bi-phases samples, as determined by XPS is much closer to stoichiometric Pt70Sn30 composition. Alloy samples, on the other hand, have Sn enrichment in comparison with the theoretical composition. As we will discuss below, the absolute composition, is not as important as chemical environment of Pt and Sn.
Table I. PtSn characteristics used for statistical structure-property relationship: ECSA from CO striping (Supporting Information Figs 1S, 2S), \(i\) at 0.6 V from CVs in acidic solution containing ethanol and \(i\) at 0.37 V from CVs in alkaline solution containing ethanol. Potentials are vs. RHE.

| Sample # | \(C_{NaOH}/M\) | Structure | ECSA/\(cm^2\) | \(ECSA/m\text{A}cm^{-2}\) gPt | Average size, \(d/\text{nm}\) XRD |
|----------|----------------|-----------|---------------|------------------------------|-------------------------------|
| 1        | 0.08           | alloy     | 1.45          | 29.3                         | 1.46                          | 10.5                          | 4.2                           |
| 2        | 0.10           | alloy     | 2.50          | 75.5                         | 1.75                          | 4.6                           | 5.0                           |
| 3        | 0.12           | alloy     | 5.32          | 51.2                         | 2.16                          | 7.3                           | 4.5                           |
| 4        | 0.15           | Bi-phase  | 3.03          | 20.9                         | 3.06                          | 17.8                          | 2.8                           |
| 5        | 0.20           | Bi-phase  | 1.49          | 32.6                         | 1.35                          | 15.8                          | 4.6                           |
| 6        | 0.30           | Bi-phase  | 2.34          | 134.0                        | 1.40                          | 12.2                          | 6.5                           |

Figure 3. (a) Cyclic voltammograms of ethanol electrooxidation at a sweep rate of 10 mV s\(^{-1}\); (b) chronoamperograms at 0.5 V vs. RHE of carbon supported PtSn catalysts in 0.5 M \(\text{H}_2\text{SO}_4\) + 1 M \(\text{C}_2\text{H}_5\text{OH}\); (c) cyclic voltammograms of ethanol electrooxidation at \(v = 50\) mV s\(^{-1}\), 1600 rpm and (d) chronoamperograms of ethanol electrooxidation on the carbon-supported PtSn catalysts in 1 M \(\text{KOH}\) + 1 M \(\text{C}_2\text{H}_5\text{OH}\), \(E = 0.57\) V vs. RHE, 1600 rpm. Current densities are per ECSA. Numbers are idem.

from PtSn alloy. The Sn 3d\(^{5/2}\) core level peaks were deconvoluted using two components. The much smaller peak at 485.9 eV was assigned to Sn metal and major peak at 487.4 eV to tin oxide SnO\(_x\), in good correspondence with reference reported values.\(^{28–30}\) The position of Sn(0) that is alloyed to a metal with different electronegativity may shifts toward higher values. The highest shift reported in the literature is 1.8 eV which is close to the position of 487.4 eV that we have identified as SnO\(_x\).\(^{30}\) There may be small contribution of the Sn alloy into this peak for alloyed samples, but large contribution of this peak for bi-phase samples and prominent peak at the position of metallic

Table II. Atomic % and Pt/Sn speciation as derived from XPS.

| Sample # | \(C_{NaOH}/M\) | Structure | Pt% | Sn% | Pt\(_x\)O\(_y\) | Sn | SnO |
|----------|----------------|-----------|-----|-----|----------------|----|-----|
| 1        | 0.08           | alloy     | 0.17| 0.14| 45.1           | 54.9| 12.7| 87.3|
| 2        | 0.10           | alloy     | 0.10| 0.17| 48.4           | 51.6| 11.4| 88.6|
| 3        | 0.12           | alloy     | 0.22| 0.40| 43.9           | 56.1| 7.7 | 92.3|
| 4        | 0.15           | bi-phase  | 0.86| 0.39| 40.9           | 59.1| 7.9 | 92.1|
| 5        | 0.20           | bi-phase  | 0.41| 0.24| 38.6           | 61.4| 9.0 | 91.0|
| 6        | 0.30           | bi-phase  | 0.19| 0.09| 55.5           | 44.5| 16.9| 83.1|
Sn (0) present in both alloyed and bi-phase samples make us believe that the major contribution is due to oxidized tin. Binding energies for SnO₂ and SnO are quite similar, so it is difficult to distinguish between these two species. We have combined all but metallic types of Pt as oxidized Pt (PtO + Pt(OH)₂ + PtO₂), PtxOy, for correlations as shown in Table I, which shows the relative % of metallic Pt and Sn and relative % of oxidized Pt and Sn.

Bi-phase samples show a larger range of relative % of metallic Pt. Sample #6 with the largest average size shows largest relative amounts of both Pt and Sn metallic. We have reported before that relative distribution of types of Pt and Sn is more important than the absolute amounts. Largest ECSA in both acid and alkaline media is present for samples #3 and 4 that have largest absolute amounts of Sn and hence largest amounts of both metallic Sn and SnO. Largest density current in alkaline is observed for bi-phase samples that also have the largest amount of total Pt and hence largest amounts of both metallic and oxidized Pt. Therefore, correlating performance to the absolute amount of metallic and oxidized part of metal present will point to the same conclusions as total amounts of metal detected. Relative % of metallic and oxidized Pt and Sn were, therefore, combined for statistical structure-to-property correlation analysis.

Statistical correlations.— Principal component analysis transforms original variables into mathematical uncorrelated variables called principal components. Each principal component is a linear combination of original variables in Table I and Table II. Loading shows the relationship between variables and are coefficients of linear combinations of the original variable that generate the principal component. Scores describe the relationship between samples and contain coordinates of the original data in the new coordinate system of principal components. Biplots displaying both loadings for each variable and scores for each sample for the PC1 and PC2 produce the way to study clustering of the samples with respect to variables, such as amounts of certain chemical species and electrochemical parameters. Correlated variables and samples are located within the same half or quadrant of the biplot.

Figure 5 shows PCA biplot calculated from data in Table I and Table II combined which shows both samples (diamonds) represented as scores and variables (circles and stars) represented as loadings. The major difference between samples properties such as surface chemistry and electrochemical behavior is captured by the principal component #1, which represents ~57% of the variance in the data. Positively contributing variables into PC1 are total amounts of Pt and Sn detected, ECSA in both media, density current in alkaline and relative % of Pt oxide and Sn oxide detected. Negatively contributing variables are density current in acid, the relative amount of metallic Pt and Sn and size of particles as determined by XRD. There is no sharp separation between alloy and biphase samples in terms of better performance in acid vs. alkaline media. The overall trend, however, is
that biphase composition shows better performance in alkaline than alloy samples,26 while alloy samples show better performance in acid than in alkaline.

Direct correlations between the overall amount of both metals present and relative distribution of types of metals are shown in Figures 6 and 7. Considering heterogeneous nature of these materials, these relationships between chemistry, as determined by XPS, and performance in acid and alkaline, as manifested by ECSA measures, are evaluated for presence of any positive or negative trend pointing toward higher/lower amounts of certain species present contributing toward particular type of electrochemical behavior.

ECSA values obtained by CO stripping, show that in both acid and alkaline solutions the same types of chemical species contribute...
to the removal of CO. The higher the total amounts of Sn in the sample, as detected by XPS, the larger ECSA (Figure 6a and 6b) in both media. This dependence is a little stronger in alkaline media than in acidic. In alkaline media, there is also slightly more pronounced dependence of ECSA on the total amount of Pt present. There is no significant dependence between the relative amount of Pt in oxidized environment and ECSA (Figure 6c). However, stronger dependence of ECSA is observed as a function of the relative amount of SnO (Figure 6). It indicates that the presence of Sn that is oxyphilic and, therefore, present as mainly Sn oxide at the surface of the particle enhances the number of active sites. It is known that CO adsorbs on Pt and does not adsorb on Sn atoms, therefore the increase of ECSA with the higher amount of SnO may be explained by the formation of additional active sites, PtSnOx neighboring sites that are active toward the reaction.

Striking differences are observed when one looks into dependence of the intrinsic performance of these catalysts in both environments as a function of surface structure as determined by XPS. Figure 7 plots the most notable dependencies observed. Relative amounts of both Pt and Sn metallic have high positive contribution into current densities in acid while these dependencies are reversed in alkaline, i.e. the larger relative amount of metallic Pt and Sn, which is also correlated with larger particle size, the poorer the performances observed. The opposite is observed when one looks into the performance dependence on relative amounts of oxidized part, i.e. PtO and SnO. Higher current densities are detected in alkaline media for larger amounts of oxides of both metals that are present for smaller particles. The dependence of performance on relative speciation of Pt is quite stronger than on that of Sn.

To summarize, in acid media the major contributions into ECSA are from oxidized part of the material while intrinsic performance mainly depends on a metallic part of the material. In alkaline media, the major dependencies for ECSA and current densities are the same, i.e. the larger total amount of metals, the better performance, and larger ECSA. The contributions into electrochemical parameters are the same, in contrast with acid media, i.e., larger current densities and surface areas come from relative amounts of oxidized part of PtSn catalysts, not the metallic one. Such difference in contribution of metallic versus oxidized part of both metals in intrinsic activity may be explained by different mechanism of electron transfer in acid and alkaline. It is suggested that the mechanism of the ethanol electrooxidation in acid is via inner-sphere electron transfer while the mechanism of the ethanol electrooxidation in alkaline media within outer-sphere plane. We suggest that in acid, metallic Pt and Sn are the active phases for molecular adsorption of reactant species necessary for electron transfer to occur. The trend observed for the acidic environment, shows that higher activity is indeed observed for materials with higher relative amount of both Pt and Sn. The rate determining step on PtSn in acid is believed to be the first electron transfer step to the adsorbed reagents with or without rapid proton transfer. The trend observed in an alkaline environment, shows the opposite behavior – higher activities are observed for samples with smaller amounts of metallic and higher degree of oxidized metals. We suggest that a surface-independent outer-sphere electron transfer is facilitated by larger amounts of hydroxyl groups that are native to oxidized Pt and Sn.

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