1
2
3
4 **The Effect of the Surface Composition of Ru-Pt Bimetallic Catalysts for**
5
6
7 **Methanol Oxidation**
8
9

10
11
12 Taylor R. Garrick^a, Weijian Diao^a, John M. Tengco^a, Eric A. Stach^c, Sanjaya D. Senanayake^d,
13
14 Donna A. Chen^b, John Monnier^a, John W. Weidner^{a*}
15
16
17
18

19
20 ^aCenter for Electrochemical Engineering
21 Department of Chemical Engineering
22 University of South Carolina
23 Columbia, SC 29208
24

25
26 ^bDepartment of Chemistry and Biochemistry
27 University of South Carolina
28 Columbia, SC 29208
29

30
31 ^cCenter for Functional Nanomaterials
32 Brookhaven National Laboratory
33 Upton, NY 11963
34

35
36 ^dDepartment of Chemistry
37 Brookhaven National Laboratory
38 Upton, NY 11963
39
40
41
42
43
44

45
46 Original Submission: July 23, 2015
47

48 Resubmission of: SGS15-367 including comments on review
49
50
51
52
53
54
55
56
57
58
59

60 *author to whom correspondence should be addressed: weidner@cec.sc.edu
61
62
63
64

Abstract

A series of Ru-Pt bimetallic catalysts prepared by the electroless deposition of controlled and variable amounts of Ru on the Pt surface of a commercially-available 20 wt% Pt/C catalyst has been characterized and evaluated for the oxidation of methanol. The activity of each Ru-Pt catalyst was determined as a function of surface composition via cyclic voltammetry. For the Ru-Pt bimetallic catalysts, activity passed through a maximum at approximately 50% monodisperse Ru surface coverage. However, due to the monolayer coverage of Ru on Pt, the amount of metal in the catalyst is minimized compared to a bulk 1:1 atomic ratio of Ru:Pt seen in commercial bimetallic catalysts. Chemisorption and temperature programmed reduction experiments confirmed that the surface had characteristics of a true bimetallic catalyst. On a mass of Pt basis, the activity of this composition for methanol oxidation was 7 times higher than pure Pt and 3.5 times higher than a commercial catalyst with a 1:1 Pt:Ru bulk atomic ratio.

1. Introduction

Direct methanol fuel cells (DMFC) are a good candidate for a power source in portable electronic devices for several reasons, including high energy density and ease of handling liquid vs. high pressure H_2 . Platinum catalysts are effectively able to catalyze the oxidation of methanol to carbon dioxide in acidic media. However, surface Pt sites become rapidly poisoned by strongly adsorbed CO that is produced during the oxidation process, limiting the overall rate of methanol oxidation. Studies have shown that bimetallic catalysts composed of Pt and Ru are more active for the oxidation of methanol compared to catalysts composed solely of Pt.[1] The mechanism by which these bimetallic catalysts alleviate CO poisoning involves adsorption of H_2O on Ru sites to form a Ru-OH species, which oxidizes CO strongly adsorbed on Pt to form CO_2 and H^+ . [1] Thus, it is important for Ru and Pt to co-exist in close, proximal contact on the surface for Ru-assisted oxidation of CO to occur. It follows that a bimetallic catalyst where the Ru is evenly distributed in a controlled amount on the Pt surface should exhibit enhanced performance.

The main objective of the present study was to systematically vary the surface composition of Pt and Ru nanoparticles on XC-72 carbon support in a commercially viable process and then to measure electrochemical activity as a function of surface composition to confirm the roles of surface composition on activity. Several preparative methodologies exist, such as galvanic displacement,[2, 3] supercritical fluid deposition,[4] electroless deposition,[5] co-impregnation,[6] and reduction of metal salts.[7] Due to its commercial viability and ease at controlling surface composition, electroless deposition was selected as the preparative methodology to systematically vary the surface composition of Ru and Pt on a commercially-available 20 wt% Pt/XC-72 carbon support. Electroless deposition (ED) is a versatile method for

the preparation of catalysts having true bimetallic properties, including carbon-supported Pt-Pd, Pt-Rh, and Pt-Co compositions for use in PEM fuel cells.[5] ED is a catalytic or autocatalytic process which is used for the selective deposition of metal salts onto catalytically active sites. It uses a controlled chemical reaction with a liquid-phase reducing agent that is activated by either the preexisting metal or the metal being deposited. In principle, this method results in the controlled deposition of specific amounts of the secondary metal on the surface of a monometallic catalyst and avoids the formation of isolated crystallites of the secondary metal on the catalyst support. All metals that can be deposited using electro-deposition can also be deposited using ED, without the difficulties of maintaining electrical conductivity.

In this article, we describe the ability of electroless deposition to systematically vary the amount of Ru deposited on the Pt surface to give known surface compositions of Pt and Ru. Characterization using selective chemisorption and temperature programmed reduction is used to confirm the formation of bimetallic surfaces before evaluation of the Ru-Pt compositions for methanol oxidation. Transmission Electron Microscopy was used to determine bimetallic particle sizes. Comparisons were also made to a commercial Ru:Pt catalyst with a 1:1 molar ratio.

2. Experimental

2.1 Catalyst Preparation

A series of ruthenium – platinum bimetallic catalysts were prepared by the electroless deposition (ED) method.[8] The base monometallic catalyst was 20 wt% Pt supported on Vulcan XC-72 (Premetek). Hexaammineruthenium(III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$) and formic acid (HCOOH) were used as the reducible ruthenium salt and reducing agent, respectively, in the electroless deposition bath. Targeted deposition of the ruthenium onto the Pt surface of the primary catalyst was achieved by controlling the pH and temperature of the ED bath. This

1
2
3
4 resulted in varying amounts of Ru deposited, calculated from the difference in bath Ru
5
6 concentration before and after deposition measured using a Perkin Elmer Optima 2000 DV
7
8 Inductively Coupled Plasma Optical Emission Spectrometer. After the ED experiments, the
9
10 bimetallic catalysts were filtered, washed copiously with DI water and dried at room temperature
11
12 before characterization and evaluation.
13
14

15 16 2.2 Temperature Programmed Reduction 17

18
19 Temperature programmed reduction (TPR) of oxygen-pretreated Pt, Ru, and Ru-Pt
20
21 surfaces was conducted to better define the temperature to be used for chemisorption analyses.
22
23 Before TPR, all samples were pre-reduced at 300°C for two hours in a stream of 10% H₂/balance
24
25 Ar followed by a purge for one hour in flowing Ar, also at 300°C. Samples were then cooled to
26
27 40°C in flowing Ar and then exposed to a gas stream of 10% O₂/balance He for 20 minutes to
28
29 cover both Pt and Ru surfaces with a layer of chemisorbed oxygen atoms in accordance with the
30
31 method of Liu.[9] Exposure to O₂ at 40°C ensures that only the surface layer is covered with
32
33 oxygen atoms, and that bulk oxidation of the metallic and bimetallic particles does not occur.
34
35
36
37

38
39 Following removal of residual gas-phase O₂, samples were purged for an additional 30
40
41 minutes in flowing Ar before the TPR experiment was started. Conditions used for TPR were
42
43 flowing 50 SCCM of 10% H₂/balance Ar over the temperature range 30 - 500°C at a ramp rate of
44
45 10°C per minute. Uptake of H₂ was measured using a Quantachrome analyzer that employed a
46
47 high sensitivity thermal conductivity detector to measure changes in H₂ concentration during
48
49 formation of H₂O from reaction with surface Pt-O and Ru-O species and subsequent formation of
50
51 Pt-H and Ru-H surfaces.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

2.3 Catalyst Chemisorption

Chemisorption using H₂ pulse titration of oxygen-precovered metal was performed using a Micromeritics Autochem II 2920 automated chemisorption analyzer to determine the concentration of accessible active surface sites, consistent with the method of Liu.[9] The temperatures used for the chemisorption experiments were 40°C and 250°C, which are approximately where the peaks occur in the TPR experiments.

2.4 Cyclic Voltammetry

The cyclic voltammetry experiments utilized a 5 mm diameter Pt disk coated with the catalyst as the working electrode, a luggin capillary Hg/HgSO₄ reference electrode, and Pt a wire as the counter electrode. The ink used for the electrode solution consisted of 10 mg of electrode material (20% Pt by weight) sonicated with 5 mL of DI water and 5 mL of isopropyl alcohol to obtain a 1:1 gram:liter ratio between the catalyst and the DI:IPA solution. A volume of 18.5 microliters was placed on the Pt working electrode, corresponding to a Pt mass of 3.7 micrograms on the electrode surface. This volume was chosen due to the uniform film present on the electrode surface after drying. The sample was bound to the working electrode using 5 microliters of a solution of 5 wt% nafion:IPA (1:20 ratio).[10] The CV experiments were run in 0.5 M H₂SO₄ and 1 M methanol used as the electrolyte at 25°C. A scan window of -0.1 to 1.3 V vs. a SHE reference (approximately -0.7 to 0.7 vs Hg/HgSO₄) was used to obtain the peak current. Smaller scan windows were used initially and compared to the peak current scans to ensure no changes were present indicative of the oxidation and dissolution of Ru. The catalyst was conditioned at 50 mV/s for 35 cycles, and then three cycles were recorded at 5 mV/s. These three scans overlaid each other for the results reported here. For each different Ru coverage, 3-10 sets of scans were run to confirm reproducibility of the resulting peak currents. The average

peak currents were used as a measure of relative catalyst activity. Since peak potentials were essentially constant at 0.85 V vs SHE and the scans were slow, this is consistent with previous studies that report catalyst activity towards methanol oxidation via constant current at a fixed potential [11-15].

3. Average Diameter Calculations

The average particle diameter for the PtRu bimetallic particles can be calculated using the number of available surface sites on a per mass basis as measured using chemisorption. This can be done by calculating the theoretical dispersion of one catalyst particle based off of atomic data and applying this to the total sample. The equation for the average particle radius is:

$$r_p = 3 \frac{N_A W_T m V_A}{A_{CSA} N_S M} \quad [1]$$

Where, N_A is the Avogadro constant, W_T is the weight loading of the metal, m is the mass of catalyst used in measurement, V_A is the volume of one atom in the unit cell, A_{CSA} is the cross sectional area of one atom, M is the molar mass, and N_S is the number of surface sites on a per mass basis as determined from chemisorption. Using the above equation, and noting that the Ru deposited on the Pt surface sites does not increase the particle size, the average particle size for the PtRu bimetallic particles is approximately 5.16 nm.

4. Results and Discussion

Figure 1 shows a representative TEM image of a 0.51 theoretical coverage bimetallic catalyst prepared using ED. A variety of different sized particles are seen in this image, showing good dispersion and particle distribution. Several different images were taken of each catalyst sample to visually confirm the absence of large particles which decrease the available surface area on a metal weight basis. The grey background in the image corresponds to the carbon support, while the darker spots represent areas with a higher atomic number. As seen in the TEM

1
2
3
4 image, the ruthenium particles are distributed on different platinum surface sites and not
5
6 agglomerated in large particles. Measuring the average particle diameter for multiple particles
7
8 yielded an average particle diameter of 2.5 nm. However, when using Equation 1, the average
9
10 particle diameter determined through chemisorption measurements is 5.67 nanometers. The
11
12 difference in the particle sizes is primarily due to the assumptions in the calculations. When
13
14 measuring particle sizes using TEM, the maximum diameter and minimum diameter of each
15
16 particle was measured and averaged to determine the overall particle size. This method has a
17
18 noticeable amount of error when compared to chemisorption, which measures the total number
19
20 of available surface sites in the sample and calculates the average particle size assuming that the
21
22 particles are uniformly distributed and semi-spherical in nature. Previous studies^[15] have shown
23
24 that chemisorption should be used to determine the total number of surface sites on a per mass
25
26 basis, from which the average particle size can be calculated. Particle diameters calculated from
27
28 chemisorption are listed in Table I.
29
30
31
32
33
34

35
36 Table I shows the chemisorption titration results for the commercial monometallic
37
38 platinum catalyst, the commercial monometallic ruthenium catalyst, and three of the eight Ru-
39
40 Pt/XC-72 catalysts that were prepared using ED, as well as particle sizes for select catalysts. The
41
42 first and second columns show the percentage of ruthenium and platinum of the total metal
43
44 composition. It should be noted that all catalysts are 20% metal:support by weight. The third
45
46 column lists the total amount of ruthenium deposited using electroless deposition. This was
47
48 calculated by taking the difference in the ruthenium salt concentration in the initial bath vs the
49
50 concentration at the deposition completion. The fourth column is a ratio between the ruthenium
51
52 deposited by ED and the number of available Pt sites present in the Pt/C catalyst used for Ru
53
54 deposition, seen in the second line of the fifth column. The fifth column is the concentration of
55
56
57
58
59
60
61
62
63
64
65

titrated sites at 40°C, which is a measure of the number of platinum surface sites, as well as the ruthenium surface sites that were reduced due to platinum-assisted reduction. The concentration of titrated sites at 250°C, seen in the sixth column, is a measure of the number of ruthenium sites that retained oxygen at the lower temperature. These surface concentrations can be compared to the ideal concentration of surface sites calculated from the difference in the initial and final ruthenium salt concentrations in the ED bath seen in the third column. The seventh column in Table I is a quantitative representation of platinum-assisted reduction of ruthenium at 40°C, according to the following equation:

$$f = \frac{C_{40}}{(1-\theta_{\text{Ru}})C_{40}^0} \quad [2]$$

Where C_{40} is the concentration of titrated sites at 40°C, θ_{Ru} is the theoretical monodisperse coverage of ruthenium on platinum, and C_{40}^0 is the concentration of titrated sites at 40°C for the monometallic platinum base catalyst seen line 2 of Table I. Values of $f > 1$ indicate Pt-assisted reduction, which was seen for all ED catalysts. For example at $\theta_{\text{Ru}} = 0.83$, $f = 5.40$ means that 5.4 times as much hydrogen was titrated per Pt-O site exposed. For all three catalysts made via ED, these values indicate that the H_2 uptake for the Pt sites at 40°C was always higher than expected, while the H_2 uptake for the Ru sites at 250°C was approximately a factor of one hundred lower than the number of surface Ru sites.^[16-18] This is consistent with spillover of hydrogen adsorbed at Pt sites at 40°C to adjacent Ru-O. This can only happen when surface Pt and Ru atoms are highly interactive and mixed at the atomic level, which indicates the formation of a true Ru-Pt bimetallic surface.

Figure 2 shows the temperature programmed reduction for six different catalysts. TPR was used to determine that titration of the platinum sites occurs at 40°C and titration of the ruthenium sites occurs at 180°C, which can be seen in the second and first spectra from the

bottom respectively. As expected, the physical mixture of both monometallic catalysts (third spectra from the bottom) shows TPR peaks at both 40°C and 180°C because no bimetallic surfaces exist. For the two Ru-Pt catalysts prepared using ED, there is no H₂ uptake at 180°C because a true bimetallic surface exists. If the Ru existed as isolated particles on the surface of XC-72[5, 9] or as non-interactive species on the Pt surface[5, 9], there should be a TPR peak at 180°C. Neither is the case. However, the intensities for the H₂ consumption peaks at 40°C for the two bimetallic catalysts are very similar to that for the 20 %Pt/XC-72 sample, suggesting similar metal surface site concentrations. That is, the Pt is close enough to the Ru-O sites to reduce those oxygen atoms (i.e., Pt-assisted reduction). The TPR spectra for the commercial Ru:Pt bimetallic catalyst show H₂ uptake over a broader temperature range, indicating that the surface coverage of Ru:Pt is not as uniform as the surface coverage achieved using ED.

Figure 3 shows three representative voltammograms for methanol oxidation corresponding to the third cycle obtained at 5 mV/s after the catalyst had been conditioned. During the forward scan, a peak around 0 volts is observed, corresponding to the desorption of hydrogen which was adsorbed during the previous reverse scan. A shoulder is observed around 0.75 volts, corresponding to the oxidation of methanol to form a Pt-CO complex, which is further oxidized to gaseous CO₂ at approximately 0.85 V vs SHE. This peak potential was essentially constant across all catalysts. At higher potentials (>1.2 V), oxidation of the clean Pt surface sites is observed. During the reverse scan, this adsorbed oxygen then further reacts with adsorbed CO to form CO₂. This peak at 0.6 V observed during the reverse scan has a higher peak current than the forward oxidation peak due to the heightened presence of adsorbed oxygen during the reverse scan. Since the forward peak occurred at 0.85V for all catalysts tested here, the peak currents at this potential were used to indicate the relative activity of the catalysts. Baseline scans of the

1
2
3
4 bare Pt electrode were taken and indicated that the Pt electrode is essentially inert because the
5
6 background around the peak potential was small and within the standard deviation of the peak
7
8 current for the Pt-Ru catalysts.
9

10
11 Figure 4 shows the peak current versus the theoretical, monodisperse coverage of Ru on
12
13 Pt. For most trials, the error bars corresponding to one standard deviation were smaller than the
14
15 symbol in the figure. A coverage of 0.51 Ru on Pt exhibits higher activity than catalysts with
16
17 higher or lower theoretical coverages of Ru on Pt. From Table 1, this catalyst is composed of
18
19 20.0 wt% Pt and 1.1 wt% Ru. The optimum bimetallic Ru-Pt/C catalyst prepared by ED is ~3.5
20
21 times more active than the commercial counterpart, while also using much lower loadings of Ru.
22
23 This catalyst is also ~7 times more active than a commercial monometallic Pt/C catalyst
24
25 containing 20 wt% Pt, as shown in Figure 4. The decrease in performance is appreciable when
26
27 moving away from the 1:1 Pt:Ru surface coverage. This shows the need to accurately control the
28
29 surface coverage of Ru on Pt, and ED is an easy and inexpensive method to do this.
30
31
32
33
34
35
36
37

38 **Conclusion**

39
40 We have shown that electroless deposition can be used to accurately control the surface
41
42 composition of a bimetallic Ru:Pt catalysts. The activity of this composition for methanol
43
44 oxidation was 7 times higher than pure Pt and 3.5 times higher than a commercial catalyst with a
45
46 1:1 Pt:Ru bulk atomic ratio. Since activity was shown to be very sensitive to surface coverage,
47
48 ED is an easy and inexpensive method to accomplish this. In addition, the ideal surface coverage
49
50 can be achieved with a minimal amount of the second metal. Although in the example shown
51
52 here the base metal (i.e. Pt) is the most expensive surface metal, in principle ED could be used to
53
54 decorate the surface of an inexpensive metal with a more expensive one.
55
56
57
58
59
60
61
62
63
64
65

Acknowledgements

The work presented here was partially funded by the University of South Carolina ASPIRE grant, the University of South Carolina Magellan Program, the University of South Carolina Honors College SURF Grant, and the Department of Energy.

1. H. A. Gasteiger, N. Markovic, P. N. Ross and E. J. Cairns, *J Phys Chem-US*, **97**, 12020 (1993).
2. C. L. Lee and C. M. Tseng, *Journal of Physical Chemistry C*, **112**, 13342 (2008).
3. C. L. Lee, C. M. Tseng, R. B. Wu, C. C. Wu and S. C. Syu, *Electrochim Acta*, **54**, 5544 (2009).
4. M. Watanabe, T. Akimoto and E. Kondoh, *Ecs Journal of Solid State Science and Technology*, **2**, M9 (2013).
5. J. Rebelli, A. A. Rodriguez, S. G. Ma, C. T. Williams and J. R. Monnier, *Catalysis Today*, **160**, 170 (2011).
6. S. Alerasool and R. D. Gonzalez, *Journal of Catalysis*, **124**, 204 (1990).
7. M. H. Liu, W. Y. Yu, H. F. Liu and J. M. Zheng, *Journal of Colloid and Interface Science*, **214**, 231 (1999).
8. W. J. Diao, J. M. M. Tengco, J. R. Regalbuto and J. R. Monnier, *Acs Catal*, **5**, 5123 (2015).
9. D. X. Liu, Y. M. Lopez-De Jesus, J. R. Monnier and C. T. Williams, *Journal of Catalysis*, **269**, 376 (2010).
10. R. E. Fuentes, B. L. Garcia and J. W. Weidner, *J Electrochem Soc*, **158**, B461 (2011).
11. A. S. Arico, P. L. Antonucci, E. Modica, V. Baglio, H. Kim and V. Antonucci, *Electrochim Acta*, **47**, 3723 (2002).
12. G. A. Camara, R. B. de Lima and T. Iwasita, *J Electroanal Chem*, **585**, 128 (2005).
13. G. A. Camara, R. B. de Lima and T. Iwasita, *Electrochem Commun*, **6**, 812 (2004).
14. H. A. Gasteiger, N. Markovic, P. N. Ross and E. J. Cairns, *J Electrochem Soc*, **141**, 1795 (1994).
15. D. Chu and S. Gilman, *J Electrochem Soc*, **143**, 1685 (1996).

Table I. Characterization results for both monometallic 20 wt% Ru/XC-72 and 20 wt% Pt/XC-72 and selected Ru-Pt/XC-72 catalysts. Experimental conditions used for titration experiments are shown at the top of each column.

Ru wt loading (%)	Pt wt loading (%)	Ru deposited by ED (atoms/g cat)	Monodisperse θ_{Ru} on Pt	C_{40} (sites/g cat)	C_{250} (sites/g cat)	f
100	0	n/a	n/a	0	6.91×10^{19}	n/a
0	100	n/a	0	1.33×10^{20}	0	1
5.39	94.61	6.80×10^{19}	0.51	1.19×10^{20}	1.91×10^{18}	1.86
8.38	91.62	1.09×10^{20}	0.83	1.21×10^{20}	1.22×10^{18}	5.40
9.54	90.46	1.26×10^{20}	0.96	1.17×10^{20}	1.25×10^{18}	22.18

Figure 1. Representative TEM image of 0.51 PtRu catalyst prepared using ED.

Figure 2: Plot of H₂ consumption during temperature programmed reduction (TPR) by different catalysts. Monometallic catalysts show clear consumption peaks at the expected temperature for Ru (180°C) and Pt (40°C). A physical mixture of Pt and Ru catalysts shows consumption peaks at both temperatures. Bimetallic catalysts give only one consumption peak at 42°C due to Pt-assisted reduction of Ru-O bonds. The commercial Ru:Pt catalyst has a distorted peak, suggesting that the particles are not uniform bimetallics.

Figure 3: Three representative voltammograms for methanol oxidation vs a standard hydrogen electrode (SHE). The dashed line shows the peak during the forward scan.

Figure 4. Direct methanol fuel cell performance of Ru-Pt/C catalysts prepared by electroless deposition (ED) and comparison to a commercial 1:1 molar ratio of Ru-Pt/C. For the ED catalyst, maximum activity was at 0.5 theoretical monolayer coverage of Ru on Pt surface.