## The Effect of Bimetallic Surface Composition on the Activity Towards Ethanol Oxidation

T. R. Garrick<sup>a</sup>, W. Diao<sup>a</sup>, J. M. Tengco<sup>a</sup>, J. Monnier<sup>a</sup>, J. W. Weidner<sup>a</sup>

## <sup>a</sup>Center for Electrochemical Engineering, Department of Chemical Engineering University of South Carolina, Columbia, SC 29208

In the recent decade, electrochemical fuel cells, specifically proton exchange membrane fuel cells, have been a viable option as energy sources that are not dependent on fossil fuels.<sup>1-5</sup> Proton exchange membrane (PEM) fuel cells operating with hydrogen have received a lot of press recently, but research is also being done on PEM fuel cells that operate with methanol (MeOH) or ethanol (EtOH) as a fuel source. PEM fuel cells operating with MeOH or EtOH are not as efficient as their hydrogen counterparts, but they are more practical to use due to the difficulties presented with storing and transporting hydrogen.<sup>1, 4, 5</sup> Even though PEM fuel cells operating with MeOH are more efficient than direct ethanol fuel cells (DEFC), DEFC are preferred over direct methanol fuel cells (DMFC) because EtOH is less toxic than MeOH. Also, EtOH can be obtained from the fermentation of corn or other biomass.<sup>1-3, 5</sup>

One challenge for the DEFC is developing a catalyst for efficient oxidation of EtOH. Typically, Platinum (Pt) catalysts are used for DEFC and DMFC, because Pt is able to catalyze the oxidation of EtOH and MeOH to carbon dioxide (CO2). One problem that has been seen is that the Pt becomes poisoned by carbon monoxide (CO) that is produced when EtOH is initially adsorbed.<sup>3, 4, 6</sup> Studies have shown that bimetallic catalysts composed of platinum and tin or platinum and ruthenium on a carbon support are better able to catalyze the oxidation of ethanol compared to catalysts made of platinum supported on carbon resulting in less expensive catalysts.<sup>1, 4, 7-10</sup> The mechanism by which the bimetallic catalyst prevents the poisoning of the Pt is not known, however it has been proposed that tin or ruthenium helps oxidize the intermediates present in the oxidation reaction and thereby prevents the poisoning of the Pt in the catalyst. <sup>5,</sup>

The ideal ratio or surface composition of the current bimetallic catalysts for the use in EtOH oxidation is not known. There is also not a standard method of bimetallic catalyst preparation. However, we are able to make Pt-Ru and Pt-Sn catalysts with known ratios and surface compositions that can be characterized.

Determining the ideal ratio, surface composition, and best method of bimetallic catalyst preparation is important to the future of energy production. Developing efficient and durable catalysts for DEFC should increase the use of PEM fuel cells as an alternative energy source. The increased use of DEFC in our country would also help the economy by decreasing our dependence on oil and other fossil fuels while also adding jobs and increasing the agricultural output to meet the demand for corn and other biomass.

We prepared several catalysts composed of platinum and ruthenium in different ratios by depositing ruthenium on a platinum catalyst using an electroless bath. The theoretical ratio between Ru and Pt assuming a monolayer coverage ranged from 50% to 96%.

The activity and performance of each catalyst was then determined using cyclic voltammetry. A solution of isopropyl alcohol, water, and catalyst was prepared. The solution was then placed onto a working electrode, dried, and covered in a Nafion layer. The peak current of the catalyst was then determined using a typical three electrode cell setup and a potentiostat.

Once the peak current for each catalyst was determined, the surface area of the bimetallic catalyst was calculated using the hydrogen desorption peaks present in the CV curves. These calculations were checked using hydrogen chemisorption.

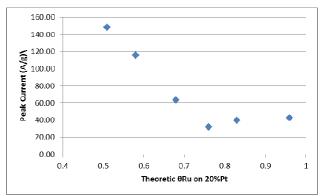


Figure 1: Change in activity with respect to Ru dispersion. In .5M MeOH and 1M sulfuric acid.

1.Antolini, E., Catalysts for direct ethanol fuel cells. J Power Sources 2007, 170, 1-12.

2.Wang, H.; Jusys, Z.; Behm, R. J., Ethanol electrooxidation on a carbon-supported Pt catalyst: Reaction kinetics and product yields. *J Phys Chem B* **2004**, *108*, 19413-19424.

3.Leger, J. M.; Rousseau, S.; Coutanceau, C.; Hahn, F.; Lamy, C., How bimetallic electrocatalysts does work for reactions involved in fuel cells?. *Electrochim Acta* **2005**, *50*, 5118-5125.

4.Simoes, F. C.; dos Anjos, D. M.; Vigier, F.; Leger, J. M.; Hahn, F.; Coutanceau, C.; Gonzalez, E. R.; Tremiliosi, G.; de Andrade, A. R.; Olivi, P.; Kokoh, K. B., Electroactivity of tin modified platinum electrodes for ethanol electrooxidation. *J Power Sources* **2007**, *167*,

5.Chen, D. A.; Myrick, M.; Monnier, J. R.; Weidner, J. W., New Catalysts for Direct Ethanol Fuel Cells. In ASPIRE: University of South Carolina, 2012;

6.Wang, Q.; Sun, G. Q.; Jiang, L. H.; Xin, Q.; Sun, S. G.; Jiang, Y. X.; Chen, S. P.; Jusys, Z.; Behm, R. J., Adsorption and oxidation of ethanol on colloid-based Pt/C, PtRu/C and Pt3Sn/C catalysts: In situ FTIR spectroscopy and on-line DEMS studies. *Phys Chem Chem Phys* **2007**, *9*, 2686-2696.

7.Lamy, C.; Rousseau, S.; Belgsir, E. M.; Coutanceau, C.; Leger, J. M., Recent progress in the direct ethanol fuel cell:. *Electrochim Acta* **2004**, *49*, 3901-3908.

8.Li, G. C.; Pickup, P. G., Decoration of carbon-supported Pt catalysts with Sn to promote electro-oxidation of ethanol. *J Power Sources* **2007**, *173*, 121

9.Datta, J.; Sen Gupta, S.; Singh, S.; Mukherjee, S.; Mukherjee, M., Significant Role of Ru-Oxide Present in the Pt-Ru Alloy Catalyst for Ethanol Electro-Oxidation in Acid Medium. *Mater Manuf Process* **2011**, *26*, 261

10.Fujiwara, N.; Friedrich, K. A.; Stimming, U., Ethanol oxidation on PtRu electrodes. *J Electroanal Chem* **1999**, 472, 120-125.