

## Evaluation of Durability and Catalytic Activity of Different Pt Oxygen Electrocatalysts

Héctor Colón, Hansung Kim and Branko Popov  
Department of Chemical Engineering  
University of South Carolina, Columbia, SC 29208

### Introduction

The search for oxygen reduction reaction (ORR) catalysts that are more active and less expensive than Pt has resulted in the development of Pt alloys. It has been reported that alloying platinum with transition metals such as Co, Cr, V, Ni, Fe, etc. enhances the electrocatalytic activity for ORR [1]. The improvement in the ORR of Pt alloys has been attributed to various structural changes caused by alloying. Jalan and Taylor claim that the enhancement of activity results from the shortening of the Pt-Pt interatomic distance after alloying [2]. Mukerjee *et al.* [3] explain the enhanced ORR activity on the basis of the interplay between the electronic Pt d-vacancy and Pt coordination number. Toda *et al.* [4] suggest an enhancing mechanism of the ORR based on an increased d-electron vacancy of the thin Pt surface layer caused by underlying alloy. Regardless of the reasons ascribed to the improvement of the catalytic activity toward ORR, there is evidence of dissolution of the transition metal from the Pt alloy. The observed decay in the performance of Pt alloy catalysts has been explained by the loss in active surface area caused by particle agglomeration [5-6] or by the leaching of the alloying non-precious metal to the electrolyte [7-8]. The operating environment of the PEM fuel cell is not sufficiently benign to prevent the corrosion of the Pt alloy. However, this process is not nearly as severe as in phosphoric acid fuel cells. As a consequence, evaluating durability in PEM fuel cells requires much time. In this study, an accelerated durability test (ADT) is developed in which the long-term performance of the Pt alloys will be compared with the fuel cell data. Besides the durability of Pt transition alloys will be studied as a function of transition metal content in the alloy. The objective is to determine a clear relationship between the content of the alloy, the alloy durability and its catalytic activity. Through these studies we expect to determine the optimum Pt/transition metal ratio in terms of the catalyst stability and its electrocatalytic activity.

### Experimental

Cathode catalysts containing 20 wt.% supported on Vulcan XC-72 were purchased from E-TEK. The electrodes were prepared by blending ultrasonically a mixture (3:1) of carbon catalyst : Nafion (ALDRICH) and i-propanol. The catalyst solution was sprayed on the gas diffusion (ELAT from E-TEK) layer until a loading of  $0.4\text{mg}/\text{cm}^2$  was achieved. In the accelerated durability test the electrodes were immersed in 0.3 M  $\text{H}_2\text{SO}_4$  solution saturated with oxygen. Once the electrodes are immersed we proceed to apply a fixed potential while the current was recorded in a three electrode set up. As time proceeds samples from solution were extracted in order to quantify the dissolution rate of the non-noble catalyst in the solution. The solution samples were then analyzed using atomic absorption spectroscopy (AAS). The same procedure is used to determine the stability and activity of the Pt-alloy catalysts prepared in-house with different Pt/M atomic ratios.

After the electrodes were tested we proceed to analyze the changes in particle size and composition of the catalyst. The cathode electrodes were analyzed by using transmission electron microscopy (TEM), X-ray diffraction and electron probe microanalysis.

### Results and Discussion

Figure 1 shows the oxygen reduction current for different catalysts. As the results indicate, the oxygen reduction current decreases as the ADT proceeds. The oxygen reduction current profile matches the dissolution profile of Co in the Pt alloy (not shown). At the beginning of the ADT, the current initially increases until reaches a maximum value. This initial increase is believed to occur as part of the initial wetting and saturation of the thin Nafion layer covering the catalyst particles. Once the current reaches the maximum, it starts to decrease and stabilizes within 250 hrs. The highest decrease in performance was observed for Pt catalyst. Figure 2 shows the TEM data for two different catalysts. As the results indicate, the particle size of platinum estimated at 0.8 V vs. SHE increases from 2.86 nm to 4nm after 250 hrs of ADT analysis. The observed increase in Pt particle size is probably due to crystallite migration and aggregate to form larger particle sizes. The TEM images of  $\text{Pt}_3\text{Co}_1$  catalyst when fresh and after the ADT analysis. No agglomerates of metal particles are observed in this figure. The average particle size diameter for the fresh sample is calculated to be 3.61 nm, which is larger than that of Pt/C. For the samples polarized at 0.8 V vs. SHE, the particle size is measured to be approximately 4.00 nm. Overall, the increase in the particle size is almost negligible despite the fact that a greater decrease in oxygen reduction current is observed. The correlation of the fuel cell and ADT data of the catalysts will be discussed in the presentation.

### References

1. T. R. Ralph, and M. P. Hogarth, *Platinum Metal Rev.* 46 (2002) 3.
2. V. Jalan, E. J. Taylor, *J. Electrochem. Soc.* 130 (1983) 2299.
3. S. Mukerjee, S. Srinivasan, and M. P. Soriaga, *J. Electrochem. Soc.* 142 (1995) 1409.

4. T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, *J. Electrochem. Soc.* 146 (1999) 3750.
5. A. Honji, T. Mori, K. Tamura, and Y. Hishinuma, *J. Electrochem. Soc.* 135 (1998) 355.
6. P. Bindra, S. Clouser, and E. Yeager, *J. Electrochem. Soc.* 126 (1979) 1631.
7. K. T. Kim, Y. G. Kim, and J. S. Chung, *J. Electrochem. Soc.* 142 (1995) 1531.
8. M. Watanabe, K. Tsurumi, T. Mizukami, T.

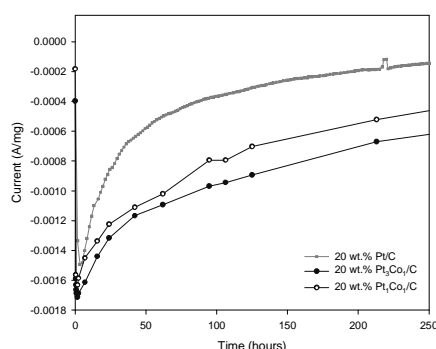


Fig. 1 ORR current as a function of time for different electrodes polarized at 0.8 V vs. SHE

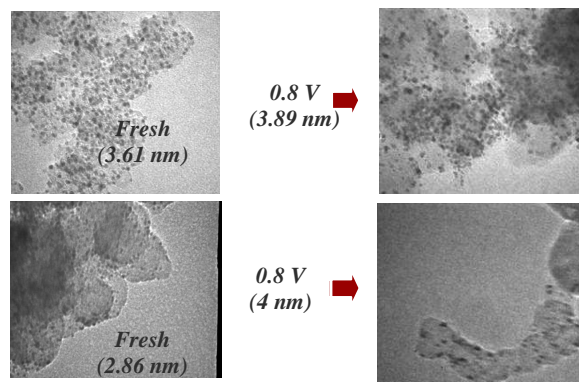


Fig. 2 TEM picture for (Top)  $\text{Pt}_3\text{Co}_1/\text{C}$  and (Bottom)  $\text{Pt}/\text{C}$  catalyst fresh and after testing for 250 hrs.