

## V.A.5 Applied Science for Electrode Cost, Performance, and Durability

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Projected End Date: Project continuation and  
direction determined annually by DOE

### Objectives

- Verify methods for measuring Pt surface area (SA), to better define catalyst utilization.
- Explore effects of catalyst ink composition and processing on catalyst utilization and performance.
- Use microscopy and other tools to better understand losses in catalyst utilization, as well as the impact of electrode structure on performance.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

### Technical Targets

In this effort, LANL engages in studies that enable cost, performance and durability improvements for electrodes, by addressing processes and design criteria that are poorly defined. In Fiscal Year 2008, validating catalyst utilization measurements and understanding catalyst surface area losses throughout the membrane electrode assembly (MEA) fabrication process were specifically addressed. Insights gained from these studies will be applied toward the design and synthesis of fuel

cell materials that meet the following DOE 2010 targets (Table 3.4.4):

- Total precious metal content: 0.3 g/kW (peak)
- Cost: \$25/kW<sub>e</sub> stack; \$10/kW<sub>e</sub> MEA
- Durability with cycling: 5,000 hours

### Accomplishments

- Validated a CO adsorption method for heterogeneous SA measurements of Pt nanoparticles, for consistent reporting of catalyst utilization.
- Quantified the effect of different catalyst-ink processing conditions and component ratios on catalyst utilization for two types of Pt/C catalyst, in half-cell and fuel-cell tests.
- Correlated initial electrochemical surface area (ECSA) losses due to ink processing with detached Pt particles observed in high-resolution transmission electron microscope (HR-TEM) (both catalysts), and further losses with platinum agglomeration (for E-TEK 20 wt% Pt/C).



### Introduction

The goal of this project is to provide understanding of electrode processes and design, in order to assist the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program in meeting DOE milestones for cost, performance and durability. In FY 2008, this effort focuses on the impact of ink processing and composition on the catalyst utilization as well as the structure of the catalyst layer. The effects of using different commercially-available catalysts, Nafion<sup>®</sup>:C ratios, and ink-processing conditions were systematically explored. Improved electrode design and processing that result in higher catalyst utilization are necessary to achieve cost, performance, and durability targets.

### Approach

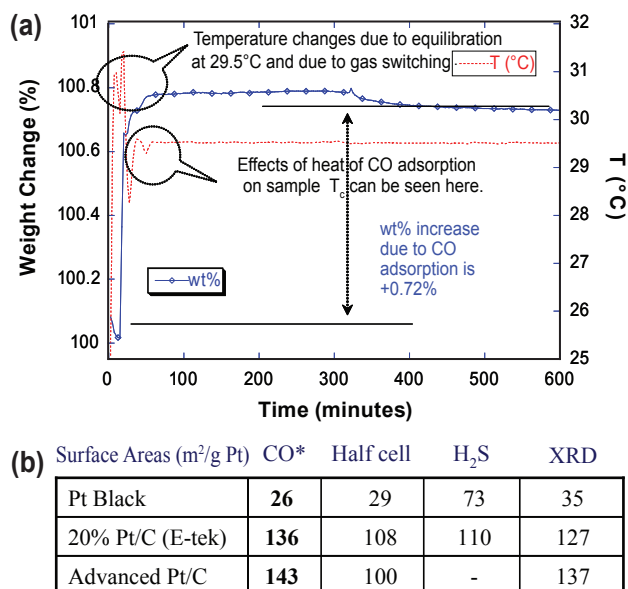
In this effort, LANL has explored the impact of changing catalyst ink components and processing conditions on catalyst utilization, electrode structure, and fuel cell performance, in order to achieve cost, performance, and durability targets. Projections suggest that Pt may contribute almost half of large-volume production costs [1]. To reduce the required amount of platinum, a better understanding of how to utilize all the available Pt SA for a high rate of reaction (with hydrogen or oxygen) is critical. We have studied catalyst

particle size, SA, and electrochemically-accessible surface area as a function of processing of catalyst inks and catalyst-ionomer mixtures. In particular, the relative impacts of electronic and ionic isolation have been evaluated using free acid in fuel cells, and then compared to HR-TEM images to correlate microscopic structure to performance.

## Results

Platinum utilization in electrodes has not been reported extensively, and no consistent definition of the term exists in the literature. Notably, Gasteiger et al. (GM) reported utilization numbers for several E-TEK and TKK catalysts [2]. In that work, platinum utilization was defined as the ratio of the ECSA measured in fuel cell tests to that measured in half cells. This resulted in very high values, up to 97%. We noted previously that the ECSA from half cells is much lower than the Pt surface area predicted from X-ray diffraction (XRD) crystallite size [3]. Following these observations, we have proposed a more general definition of utilization: the ratio of the ECSA in fuel cells to the total Pt SA measured heterogeneously. In this way, Pt particles in poor electronic contact are not excluded from the surface area measurement. After evaluating several methods for measuring the heterogeneous SA [3], CO uptake from the gas-phase as detected by mass change was selected [4]. As shown in Figure 1, the CO uptake corresponds to a surface area of  $136 \text{ m}^2/\text{g}$  for E-TEK 20 wt% Pt/C, in good agreement with the value predicted from XRD,  $127 \text{ m}^2/\text{g}$ . Using the fuel cell ECSA value for E-TEK 20% Pt/C from the GM report [2],  $65 \text{ m}^2/\text{g}$ , the utilization number by our definition would be 48% rather than 87-97%.

Applying the above definitions for SA, ECSA, and utilization, the effects of catalyst ink-processing conditions were addressed in half-cell and fuel-cell tests. In half-cells, the free acid provided additional ionic conductivity, allowing the impact of ink processing on electronic conductivity to be examined. As shown in Figure 2, the half-cell ECSA of E-TEK 20% Pt/C was reduced to  $\approx 60\%$  of the SA value ( $\approx 135 \text{ m}^2/\text{g}$ ) after only five minutes of stirring or, alternately, 30 min of sonication ( $75\text{-}80 \text{ m}^2/\text{g}$ ). Correspondingly, HR-TEM images of inks after 30 min sonication (Figure 2b) clearly show Pt particles inside ionomer “webs” that have lost contact with the carbon-support network, apparently electronically isolated. Extended sonication times (6 h) were found to cause further decreases in half-cell ECSA to  $\approx 40 \text{ m}^2/\text{g}$ , i.e., only 30% of the original SA. As shown by the HR-TEM images in Figure 2c, increased sonication time leads to lower porosity (see inset), particle agglomeration, and particle size growth (confirmed by XRD). These structural changes correlate to the decreased ECSA noted above, as well as decreased fuel cell performance (not shown). Ball

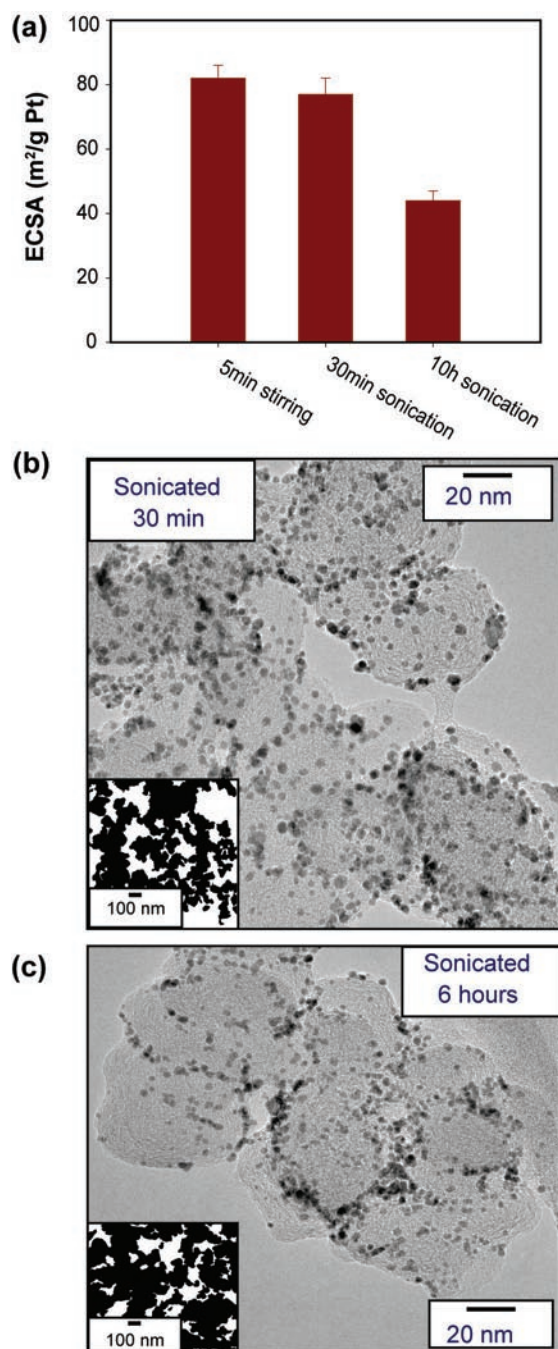


**FIGURE 1.** (a) Mass change with CO uptake on HiSPEC 1000 Pt black as determined by a Netzsch STA-449 high precision thermogravimetric analysis/differential scanning calorimetry;  $16.3 \text{ \AA}^2$  was used for the surface coverage of a single CO molecule [4]; (b) tabulated values for platinum surface area as measured by different methods.

milling was also used to prepare inks, giving similar results to 30 min of sonication (not shown). To summarize, the Pt-carbon interaction is sufficiently weak in E-TEK 20% Pt/C that only five minutes of mixing reduces the ECSA to 60% of the SA; further processing reduces the ECSA to even lower levels.

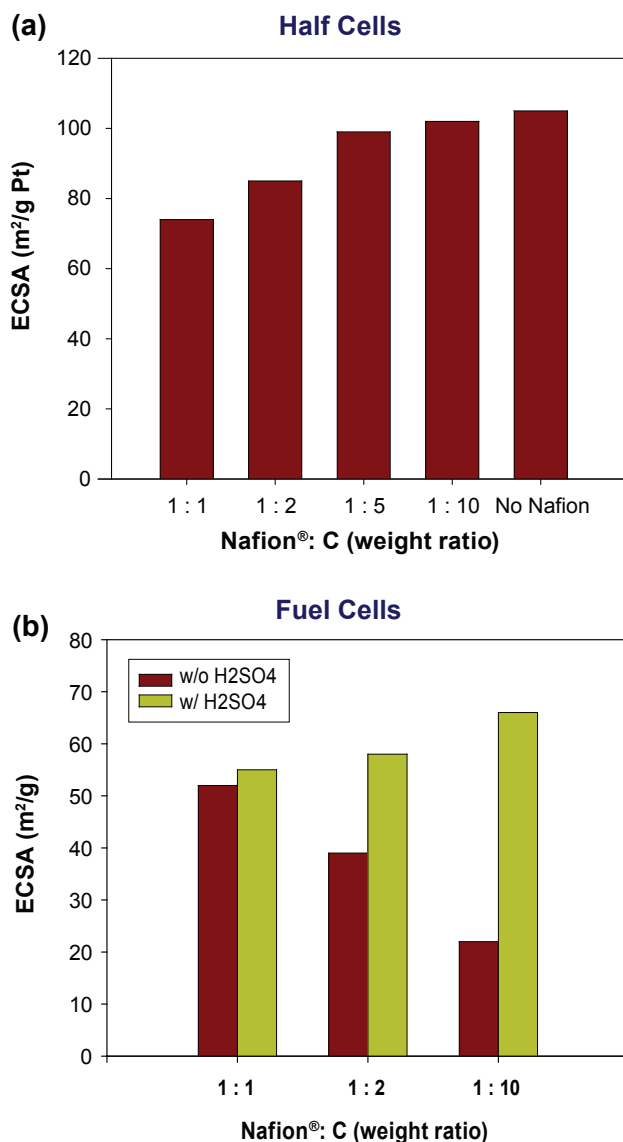
The effect of the ionomer:carbon ratio on the ECSA of E-TEK 20 wt% Pt/C was then systematically examined. Using half cells, the ECSA was found to decrease as the Nafion<sup>®</sup>:C ratio increased, from  $\approx 105 \text{ m}^2/\text{g}$  with no Nafion<sup>®</sup> to  $\approx 75 \text{ m}^2/\text{g}$  with Nafion<sup>®</sup>:C = 1:1, as shown in Figure 3(a). In fuel cell electrodes, however, in which Nafion<sup>®</sup> must provide the ionic conduction, the ECSA was highest at  $\approx 55 \text{ m}^2/\text{g}$  with Nafion<sup>®</sup>:C = 1:1. Upon the addition of free acid to the fuel cell electrodes, the ECSA followed the same trend as the half cell experiments, with Nafion<sup>®</sup>:C = 1:10 giving the highest ECSA value. Although a 1:1 ratio of ionic conductor to electronic conductor gave the highest ECSA, addition of free acid did not recover much of the surface area, indicating severe loss of electronic connection. Detachment of Pt particles from carbon induced by the interaction with Nafion<sup>®</sup> or the mixing process itself can be inferred, based on the HR-TEM images in Figure 2.

Next, an alternative Pt/C catalyst was examined in a similar manner. The ECSA in half cell tests after five minutes stirring was only slightly higher than E-TEK 20% Pt/C at  $\approx 90 \text{ m}^2/\text{g}$  = 63% utilization. Longer processing times, however, resulted in much lower



**FIGURE 2.** (a) ECSA measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> for dried catalyst inks containing E-TEK 20 wt% Pt/C and Nafion<sup>®</sup> with a ratio of 1:2 Nafion<sup>®</sup>:C after different stirring or sonication times; (b) HR-TEM image of a dried catalyst ink after 30 min of sonication; (c) after 6 h of sonication.

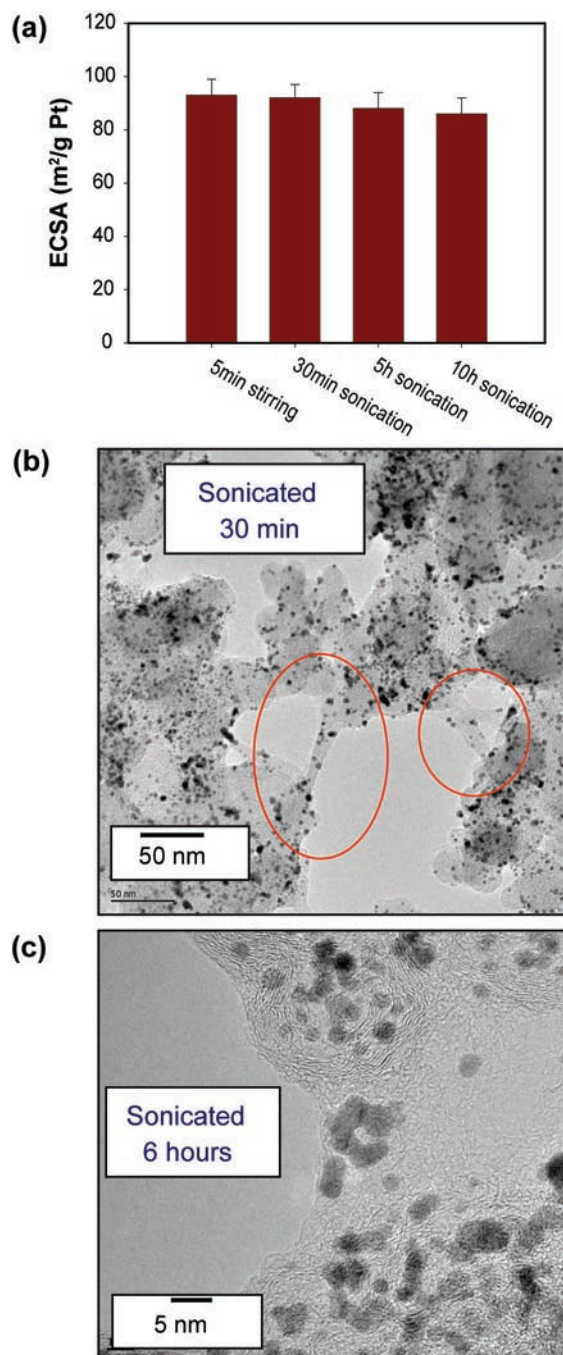
ECSA loss than for E-TEK 20% Pt/C. After 10 h of sonication, the ECSA remained  $\approx 85$  m<sup>2</sup>/g, as shown in Figure 4(a). HR-TEM images of inks after 30 min of sonication (Figure 4(b)) showed some Pt particles detached from the carbon similarly to E-TEK 20% Pt/C, but longer sonication times did not induce significant



**FIGURE 3.** (a) ECSA measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> for dried catalyst inks containing E-TEK 20 wt% Pt/C and Nafion<sup>®</sup> with different Nafion<sup>®</sup>:C ratios; (b) ECSA measured in fuel cell electrodes with different Nafion<sup>®</sup>:C ratios, with and without 0.5 M H<sub>2</sub>SO<sub>4</sub>.

changes (Figure 4(c)). Thus, the Pt-carbon interaction seems to be stronger on the alternative catalyst than for the E-TEK catalyst, at least for the Pt remaining after the initial loss of Pt particles. Future studies will address the possible reasons for this difference (carbon pretreatment, surface groups, porosity, etc.). Additionally, the presence of Nafion<sup>®</sup> was shown to cause a greater initial loss of ECSA than water alone for short processing times, but for longer processing times the Nafion<sup>®</sup> inhibited Pt loss, implying a protective effect.

Some preliminary dynamic light scattering and neutron scattering studies at LANL have been performed



**FIGURE 4.** (a) ECSA measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> for dried catalyst inks containing an alternative Pt/C catalyst and Nafion<sup>®</sup> with a ratio of 1:2 Nafion<sup>®</sup>:C after different stirring or sonication times; (b) HR-TEM image of a dried catalyst ink after 30 min of sonication; (c) after 6 h of sonication.

to characterize the ink solutions as well as the electrode structures. Such measurements are intended to correlate materials properties and interactions with the final arrangement of the Pt, carbon, and ionomer phases.

## Conclusions

- CO adsorption measurements were validated as a probe of heterogeneous surface area.
- Platinum ECSA decreases significantly even with minimal processing ( $\approx 40\%$  loss) for both types of Pt/C catalyst investigated; the ECSA loss correlates with isolated Pt particles observed in HR-TEM.
- Further loss of SA occurs with longer processing, but the degree depends on the support.
- Nafion<sup>®</sup> likely leads to Pt “displacement” from typical supports. For longer processing times, Nafion<sup>®</sup> can have a protecting effect holding Pt in contact with support.

## Future Directions

- Pt Activity Studies
  - Examine conductivity pathways to individual Pt particles (not all are equal) of MEAs with AFM, to identify “active” Pt.
- Materials Interaction Measurements
  - Evaluate materials properties of different carbon supports (nuclear magnetic resonance, infrared, porosimetry, XRD, etc.), and correlate to the strength of Pt interaction.
  - Investigate interaction of carbons with ionomer, depending on pre-treatment and solvents.
- Electrode Structure Studies
  - Determine electrode structures with neutron and X-ray scattering, and HR-TEM.
  - Explore layered and gradient structures of MEAs to improve catalyst utilization, supported by modeling efforts.
- Additional Industrial Samples (catalysts, carbons, MEAs, as available)

## FY 2008 Publications/Presentations

1. J.Chlistunoff, F.Uribe, and B.Pivovar, Oxygen Reduction at the Pt/Recast-Nafion<sup>®</sup> Film Interface. Effect of the polymer equivalent weight, ECS Trans. 2, (8) 37 (2007).
2. J.Chlistunoff and B.Pivovar, Hydrogen Peroxide Generation at the Pt/Recast-Nafion Film Interface at Different Temperatures and Relative Humidities, ECS Trans. 11, (1) 1115 (2007).
3. H. Xu, E. Brosha, F. Garzon, C. Johnston, F. Uribe, M. Wilson and B. Pivovar, Electrochemical Characterization of Catalyst Utilization in Half and Fuel Cells, Meet. Abstr. - Electrochem. Soc. 702, 428 (2007).
4. B. Pivovar, H. Xu, E. Brosha, J. Chlistunoff, F. Uribe, M. Wilson, M. Hawley and F. Garzon, The Effect of Electrode Ink Processing and Composition on Catalyst Utilization, ECS Trans. 11, (1) 383 (2007).

## References

1. Lasher, S.; “Cost Analyses of Fuel Cell Stack/Systems.” DOE Hydrogen Program Annual Report, 2007. [http://www.hydrogen.energy.gov/pdfs/progress07/v\\_a\\_5\\_lasher.pdf](http://www.hydrogen.energy.gov/pdfs/progress07/v_a_5_lasher.pdf).
2. Gasteiger, HA; Kocha, SS; Sompalli, B; Wagner, FT, *App. Cat. B*, **56**, 9 (2005).
3. Pivovar, B.; Brosha, E.; Chlistunoff, J.; Garzon, F.; Springer, T.; Uribe, F.; Wilson, M.; Xu, H. “Applied Science for Electrode Cost, Performance, and Durability.” DOE Hydrogen Program Annual Report, 2006. [http://www.hydrogen.energy.gov/pdfs/progress07/v\\_a\\_4\\_pivovar.pdf](http://www.hydrogen.energy.gov/pdfs/progress07/v_a_4_pivovar.pdf).
4. Shinozaki, K.; Hatanaka, T.; Morimoto, Y. *ECS Trans.*, **11**, 497 (2007).