

**Department of Chemistry**  
**Indian Institute of Technology Madras**

Ph.D. Research Colloquium

**Corrosion and sulfur tolerance study of Pt-electrocatalysts for Proton Exchange Membrane Fuel Cells**

Prithi Jayaraj (CY14D029) (Interdisciplinary – External)

Date: 01 Oct 2019

Guide: Prof. G. Ranga Rao, Dept. of Chemistry, IITM

Time: 3:00 PM

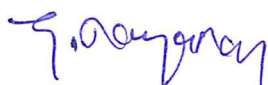
Co-guide: Dr. N. Rajalakshmi, Centre for Fuel Cell Technology, ARCI

Venue: CB 310

Polymer Electrolyte Membrane Fuel Cell (PEMFC) is gathering momentum in various commercial applications due to its high power density, high efficiency, and low/zero emissions and has made researchers evaluate its components rigorously to address the issues of durability and reliability. The durability of electrocatalyst plays a vital role in substantiating the longevity of fuel cell system. In this context, evaluation of the electrocatalysts and their supports are being studied extensively. Two of the major challenges affecting the durability of electrocatalyst are (i) the carbon support corrosion and (ii) contaminants in the fuel and oxidant stream. Therefore the objectives of the current research is to evaluate and identify electrocatalysts and supports for (i) carbon corrosion resistance and (ii) impurity tolerance by employing accelerated stress test protocols (AST).

Carbonaceous materials of good electrical conductivity and higher surface area are generally used as support materials for Pt metal nanoparticles. However, these carbon supports are susceptible to corrosion under PEMFC conditions and the corrosion gets accelerated when the fuel cell generates voltages  $> 1.2$  V during start-up/shut-down and gross fuel starvation. This condition leads to deterioration of electrocatalyst layer through various mechanisms such as Pt dissolution, Ostwald ripening, coalescence via particle migration affecting the electrochemical performance of PEMFC. Herein, we have identified five protocols to evaluate the stability of various electrocatalysts under different simulating conditions. The corrosion stability of carbonaceous supports is studied employing start-up and shut-down protocol formulated by U.S. Department of Energy (DoE) with target of  $< 40\%$  ECSA loss after 5000 cycles of accelerated stress test. Electrocatalyst supports namely, the conventional VXC, N-doped mesoporous carbon, acetylene black, ketjan black, hydrophobic coated carbon and ZrC has been studied for their corrosion stability. High surface area mesoporous carbons are synthesized using colloidal silica template LUDOX-AS-40 with varying percentage of nitrogen doping (11 wt% and 6 wt%) which showed good electrochemical activity with an ECSA of  $73 \text{ m}^2/\text{g}$  and  $59 \text{ m}^2/\text{g}$ , respectively. However, these supports show very poor stability due to their disordered structure resulting in  $> 40\%$  ECSA loss in 200 cycles and does not satisfy the DOE targets. Acetylene black (AB) carbon support which is in the graphitized form exhibited better corrosion resistance with only 6 % loss from its initial ECSA of  $52 \text{ m}^2/\text{g}$  (Pt/AB) after 5000 AST cycles. The acetylene black is functionalized to improve the Pt metal dispersion on the low surface area carbon (Pt/*f*-AB) which shows increased ECSA of  $79 \text{ m}^2/\text{g}$ . However, the higher loss of 16 % in ECSA is due to the presence of hydrophilic functional groups. In order to compensate the increased ECSA loss due to hydrophilic functional groups, the *f*-AB is coated with hydrophobic polymer (AB-PBI (poly [2,5-benzimidazole])) which minimized the ECSA loss from 16% to 7%. Zirconium carbide based supports are also studied for the first time as viable corrosion resistant support materials. The Pt/ZrC electrocatalyst shows low ECSA of  $1 \text{ m}^2/\text{g}$  but an increase in ECSA of about 22% after the AST. The activated carbide (*a*-ZrC) is used to increase the surface area for better dispersion of Pt metal nanoparticles (Pt/*a*-ZrC) which shows ECSA of  $30 \text{ m}^2/\text{g}$  and 19% ECSA loss after 5000 AST cycles meeting the DoE targets.

In addition, the fuel and oxidant contaminants also deteriorate performance of fuel cell. The prominent contaminant is  $\text{SO}_2$  in the air stream which has a detrimental irreversible effect. The  $\text{SO}_2$  molecules compete with oxygen for Pt active adsorption sites, and block the active Pt surface sites, thus hindering or modifying the oxygen reduction reaction (ORR). In the present work is focused on the synergistic effect of carbon support and Pt on the adsorption of sulfur in terms of sulfur coverage. It has been identified that the carbon support has a major role in  $\text{SO}_2$  adsorption. The sulphur coverage is higher around 94% for 20Pt/C compared to that of 71% for 40Pt/C and 53% for unsupported Pt black electrocatalysts. The graphitized support *f*-AB, however, shows higher tolerance towards  $\text{SO}_2$  with 25 % sulfur coverage.

  
Signature of Guide  
24/9/2019

  
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