75c Novel Nitrogen-Containing Carbon Catalysts for the Oxygen Reduction Reaction in Acidic Electrolytes

Paul H. Matter, Umit S. Ozkan, Maria Arias, and Eugenia Wang

The development of less expensive and more active alternative catalysts to Pt for use in PEM fuel cell cathodes will help to initiate their wide-scale commercialization. Alternative catalysts based on organo-metallic macro cycles, such as Fe porphyrins, have been studied with some success, although their poor stability limits their practical use. It has been discovered that these catalysts can be stabilized in the electrode environment by subjecting them to pyrolysis above 600oC. More recently researchers have discovered that a wide variety of metal, nitrogen and carbon precursors will form active oxygen reduction reaction (ORR) catalysts upon pyrolysis. Work in our lab has revealed that Fe particles, when subjected to treatments in nitrogen and carbon containing atmospheres at elevated temperatures, act as catalysts for the formation of nitrogen-containing carbon nano-fibers with significant edge plane exposure. Although Fe is not necessary for elevated ORR activity, edge plane exposure and nitrogen content in the carbon was observed to increase activity. In the current study catalysts for the ORR in acidic electrolytes were prepared by pyrolysis of acetonitrile over carbon and metal oxide supports impregnated with Fe or Ni acetate. In the case of metal oxide supports, the support and exposed metal particles were removed by washing the pyrolysis product with a strong acid. Catalysts were also prepared by treating various preformed carbon structures with ammonia at temperatures in excess of 600oC. Activity measurements were made using a Rotating Disk Electrode (RDE) half –cell set-up using 0.5 M sulfuric acid as the electrolyte, and a 5 cm2 PEM fuel cell test stand. Materials were characterized with BET surface area analysis, pore volume distributions, Temperature Programmed Oxidation (TPO), and X-Ray Photo-electron Spectroscopy (XPS). High-resolution Transmission Electron Microscopy (TEM) images of the nano-structures were obtained with a Tecnai TF-20 microscope to determine the nanostructure of the materials formed. Catalytic activity of the new materials are comparable to the activity of commercial Pt cathode catalysts. Activity is strongly dependant on the edge plane exposure and nitrogen functionalities present. Necessary improvements in other properties of these materials will be discussed. Research suggests it may be possible to prepare very active and practical catalysts for the ORR that contain no noble metals by optimizing the nano-structure of nitrogen-containing carbon.