Abstract - Dissertation

Performance and Durability of Electrodes with Platinum Catalysts in Polymer Electrolyte Cells Prepared by Ultrasonic Spray Deposition

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Catalysts in the electrodes of polymer electrolyte cells serve a critical function in reactions which can be used to either generate electrical energy from chemical fuels or transfer electrical energy into chemicals. For low temperature electrochemical fuel cells, platinum is often utilized for its ability to catalyze the hydrogen oxidation and oxygen reduction of the anode and cathode, respectively. The valuable metal has excellent properties for both half reactions, but its limited supply and high demand are directly related to the prohibitive costs plaguing commercialization of this technology. Therefore, minimal amounts of the catalyst should be used to achieve the maximum output. Electrochemical behavior is governed by the available reactive surfaces of the metal. A conductive material with high surface areas can be used in a composite approach to maximize nanostructured electrocatalyst sites. The state-of-the-art makes use of carbonaceous materials as the support. However, parasitic corrosion reactions of these materials in the electrode cause irreversible loss of activity that limits the useful lifetime of the cell, ultimately leading to its failure. Furthermore, platinum promotes the oxidation of its carbon support. These problems pose a paradox for the same electrocatalysts which also make them work so well. Design of more resilient platinum catalysts could provide significant cost savings. An engineering challenge arises from their design and integration into the electrode.

Electron conductive paths, proton channels in the electrolyte, and porous space are required in joint formation of active catalyst sites in the electrode. Phase boundaries and interfaces with the catalyst are critical to design of this composite structure. Acidic ionomers,
known as Naftion®, were chosen in this study for their facile proton conductivity, thermo-
mechanical properties, and commercial availability. A process for depositing thin electrodes
directly on the polymer electrolyte membrane by ultrasonic spray deposition was developed to
produce uniform layers through an automated process. Construction methods were refined for a
variation of electrodes built with both supported and support-less platinum catalysts.
Characterizations of electrochemical performance were conducted to contrast catalyst behaviors
in working membrane electrode assemblies.

The catalyst should lower the activation energy of the reaction without being consumed.
Preservation of electrocatalyst activity is critical to the effective operation of the electrochemical
cell. Better platinum supports are needed for more reliable long-term performance. The
environment of the membrane electrode assembly is frequently under high potential and low pH,
limiting the selection of stable materials available to choose as an alternative to carbon.
Platinum is a noble metal which has good intrinsic stability, but carbon is not in a
thermodynamic equilibrium under these conditions. It is particularly problematic, as are many
platinum alloys. Less-noble metals tend to be sacrificed to protect platinum during passivation
under the application of potential. The performance of catalysts should come without sacrifices
to its stability. The nature and bonding of carbon atoms used in the framework are an important
determination of its corrosion resistance. Surfaces of carbon supports can also be functionalized
to enhance their interactions with the catalyst. When stable metal oxide phases are combined
with carbon, useful junctions within electrocatalyst composites can be formed.

An alternative catalyst support construction to the conventional carbon black with high
surface area and conductivity is viewed as an important goal in the development of performance
and durability of electrodes. Carbon nanotubes offer some advantages in their material structure
and properties. Multi-walled carbon nanotubes were selected for exceptional mechanical and transport behavior in the electrode, while also offering relatively inexpensive production methods. A long range graphitic order can reduce the carbon corrosion kinetics. However, even graphitized carbon is still susceptible to corrosion and it bonds relatively weakly with platinum catalysts. This can lead to loss of active surface area through diffusion and detachment of the catalysts. To prevent this, a second phase was included into composite supports. Titania, a common name for titanium oxides, was first chemically bonded to the surfaces of carbon nanotubes to help anchor the catalysts through strong metal-support interactions. Advantages from the carbon nanotube and titania supports toward performance and durability were contrasted against a set of controls and demonstrated in the cathode and anode.

A detailed literature review suggested further insight into the role of metal oxide interfaces with the catalyst can be developed by studying titania combinations in the anode. In this electrode, platinum catalyzed hydrogen oxidation suffers from contamination by trace amount of impurities that adsorb strongly on its surfaces. Carbon monoxide (CO) is one of the most persistent contaminants from reformation reactions and CO is also an intermediate in oxidation of other hydrocarbons, but despite its source, its adsorption onto reactive surfaces causes severe catalyst poisoning, limiting reactive sites. In order to restore activity, potential, temperature, and/or oxygen pressure are applied to remove adsorbed contaminants. Electrochemical stripping requires oxidizing conditions that can also corrode electrocatalysts. Strong interactions between platinum and titania can potentially limit this oxidative process while also opening active sites near their interface through a bifunctional mechanism. These interfaces can be characterized as Schottky junctions that result in a synergistic relationship between activity and stability. In order to enhance charge separation across the Schottky barrier
formed with n-type semiconductors, a doped form of titania was synthesized from niobium substitution in the transition metal oxide phase. Niobium was selected for its valence states, ionic radius, passivation behavior, and ability to form shallow donors. Advanced diagnostics were used to study titania supports in an electrochemical hydrogen pump to evaluate advantages for CO tolerance. Material characterization of electrocatalysts was used to correlate the effects of support construction on resilient performance. Enhancements to the bifunctional reaction for CO oxidation as well as stability are proposed from a perspective of defect principles formed at the metal-metal oxide junction. Performance and durability of electrochemical cells is improved by applying the science of materials and interfaces to the construction of catalyst supports for platinum in working electrodes, serving as an example for further progress and optimization.