

## NON-NOBLE ELECTROCATALYSTS FOR ALKALINE FUEL CELLS

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Noble metals, when used as electrocatalysts for oxygen reduction in alkaline fuel cells, suffer from the disadvantages of high cost, susceptibility to poisoning and sintering. Carbons activated with macrocyclics have attracted increasing attention as alternative electrocatalysts for oxygen reduction. Initial activity of these catalysts is good, but performance declines rapidly. Pyrolyzing the macrocyclic on the carbon support leads to enhanced stability and the catalysts retain good activity.

Despite this promising method of treating macrocyclic-activated carbon catalysts, the performance decay is still too large to be acceptable. The approach described here is designed to develop bulk doped catalysts with similar structures to pyrolyzed macrocyclic catalysts. The transition metal and coordinated ligands are dispersed throughout the bulk of the conductive carbon skeleton.

Two approaches to realizing this concept are being pursued, both involving the doping of carbon precursors. In one approach, the precursor is a solid phase carbon-containing ion-exchange resin. The precursor is doped with a transition metal and/or nitrogen, and the resulting mixture is pyrolyzed. In the other approach, the precursor is a gas-phase hydrocarbon. This is introduced with a transition metal species and nitrogen species into a reactor and pyrolyzed. This paper will mainly discuss work conducted using the solid-phase pyrolysis approach.

For the solid-phase precursors, ion-exchange resins were selected. Weak acid cation-exchange resins and chelating resins have been used. Dopants have included  $\text{Fe}^{3+}$  (from  $\text{FeCl}_3$ ),  $\text{Fe}(\text{bipy})_3\text{SO}_4$  and  $\text{NH}_4\text{OH}$ . Typical pyrolysis temperatures have ranged from 700-900°C.

Gas-phase pyrolysis is carried out in a tube furnace. The gas-phase precursor, ammonia (the nitrogen source), and the iron-containing organometallic are introduced into the reactor. The heated zone of the furnace is maintained at a temperature of 1000°C.

Electrochemical tests are performed using the floating electrode technique. The electrodes are tested at 80°C in 7M KOH.

Several studies have been conducted to determine if there is a synergistic effect between the transition metal and nitrogen and the effect of different methods of introducing the M-N coordination on performance.

One approach was to introduce the metal and nitrogen separately, for example, by sequentially doping  $\text{FeCl}_3$  and  $\text{NH}_4\text{OH}$  into the resin. Catalysts were prepared from an undoped ion-exchange resin, a resin doped only with N, a resin doped only with Fe, and a resin doped with both Fe and N. Introduction of nitrogen alone has no beneficial effect on the performance of the catalysts. The introduction of the Fe alone significantly improves the performance in both the high and low current density regions. When both Fe

and N are introduced, the performance at lower current densities ("catalytic activity") is increased beyond that of the Fe-doped carbon, but the performance at higher current densities is similar to the carbon containing only Fe.

Catalysts prepared from resins- $\text{Fe}(\text{bipy})_3\text{SO}_4$  precursors have performance that is only slightly less than CoTMPP adsorbed and pyrolyzed on Vulcan XC-72. Their performance is much better than carbons which have had the N and Fe introduced separately.

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