

# **Fluorine-containing Polybenzimidazoles for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications**

by

Guoqing Qian

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Polymer chemistry

The original of the complete thesis is on file  
In the Rensselaer Polytechnic Institute Library

Examining Committee:

Brian Benicewicz, Thesis Adviser

Curt Breneman, Member

Chang Ryu, Member

Linda Schadler, Member

Lixiang Xiao, Member

Rensselaer Polytechnic Institute  
Troy, New York

November, 2008

(For Graduation December, 2008)

## ABSTRACTS

Polymer electrolyte membrane fuel cells (PEMFC), also called proton exchange membrane fuel cells, have increasingly become the most promising candidates as the zero-emission power sources for transportation, stationary cogeneration and portable applications. In particular, high temperature polymer electrolyte membranes operational above 120 °C without humidification offer many advantages including fast electrode kinetics, high tolerance to fuel impurities and simple thermal and water management systems. Phosphoric acid doped polybenzimidazole (PBI) is the most promising candidate for the high temperature polymer electrolyte membranes.

A hexafluoroisopropylidene-containing polybenzimidazole (6F-PBI) was synthesized using polyphosphoric acid (PPA) as both the polycondensation agent and the polymerization solvent. The use of newly developed polymerization conditions produced high molecular weight polymer. The resulting polymer showed excellent thermal and chemical stability, high solubility. The PPA process was used to prepare the phosphoric acid doped 6F-PBI membranes. These membranes showed high phosphoric acid doping levels, high mechanical properties, and higher proton conductivities than the membranes prepared by the conventional membrane fabrication processes. The fuel cells with phosphoric acid doped 6F-PBI membranes showed good performance and high CO tolerance.

Another fluorine-containing PBI (perfluorocyclobutyl containing polybenzimidazoles, PFCB-PBI) was synthesized in phosphorous pentoxide/methanesulfonic acid (PPMA). PPMA was used as reaction medium to replace PPA for its high monomer solubility. High molecular weight polymer was achieved with the optimized monomer/solvent ratio, polymerization temperature, and polymerization time. The resulting polymer showed good thermal and chemical stability, high solubility. Several different membrane preparation processes were investigated. A modified PPA process was developed to produce the phosphoric acid doped membranes. The mechanical properties of these membranes were sufficiently strong to fabricate into membrane electrode assemblies. The re-dissolution of PFCB-PBI in phosphoric acid at

temperatures above 140 °C limited the operation of fuel cells based on phosphoric acid doped PFCB-PBI membranes.

The incorporation of fluorine-containing PBIs into high temperature PEMFC electrode was conducted via four different methods: bilayer PBI membrane, casting PBI/PPA solution onto the electrodes, spraying PBI/DMAc solution onto the electrodes, mixing PBIs in the catalyst ink. The performances of fuel cells with bilayer membranes showed that 6F-PBI improved the electrode performance. The higher performances of fuel cells with 6F-PBI/PPA coated cathodes compared to the fuel cell with PPA coated cathodes and regular electrode showed the effects of eliminating the membrane-membrane interface and also clearly verified the enhancement of 6F-PBI on the fuel cell electrode performance. Cyclic voltammetry explained this enhancement of 6F-PBI on the fuel cell electrode performance. There was a significant increase of greater than 20 % in the electrochemical active area of the 6F-PBI/PPA coated electrode compared to the PPA coated electrode and regular electrode. It was postulated that the incorporation of 6F-PBI in the electrodes produced a better and more stable distribution of phosphoric acid surrounding the catalyst which was not present in the regular and PPA coated electrodes. Spray coating of PBI/DMAc solutions onto the regular electrodes was also investigated as a method to alter the electrode structure. Electrochemical impedance spectroscopy was conducted to explore the polymer chemical structure effects on fuel cell performance. The change of internal ohmic resistance of the fuel cell was attributed to the change of the interface resistance between the membrane and the cathode. The charge transfer resistances of fuel cells with PBI modified cathodes were less than the fuel cell with regular cathode. The incorporation of PBIs into the electrodes decreased the charge transfer resistance and improved the interfacial oxygen reduction reaction (ORR) kinetics due to the improved proton conduction in the catalyst layer with the PBI polymers in the electrodes. The research of mixing PBIs in the catalyst ink showed that PTFE still plays a critical role in the electrode, and the fluorine-containing PBIs can not replace its function at this time.

The durability of phosphoric acid doped PBI based PEM fuel cells was studied by measuring the phosphoric acid loss from the MEA, load cycling test, and

startup/shutdown cycling test. Through a comprehensive analysis of phosphoric acid loss from the MEA, the initial steps of cell assembly and initial heating were major factors in the loss of phosphoric acid from the MEA. A significant amount of phosphoric acid lost from the MEA was found in the micropores of the graphite flow plates, while the phosphoric acid loss in exhaust water accounted for less than 1 % of the total loss. A systematic investigation on fuel cell performance degradation during the load cycling test was conducted. The fuel cell performance degradation during load cycling tests exhibited two distinct stages. A statistical method was used to analyze the effects and interactions of variables on the first stage fuel cell performance degradation rates. These results define the conditions for fuel cell performance optimization and directions for further research. The reasons for the two stage performance degradation were also explored. The initial explanation based on the phosphoric acid loss was denied because the results from the experiments showed that phosphoric acid loss is not the main source of the fuel cell performance degradation. A convenient method to precisely control the OCV interval time during the startup/shutdown cycling test was demonstrated. A series of startup/shutdown cycling tests with different OCV interval times per cycle were designed to examine the effects of OCV time on the fuel cell performance degradation. The results also demonstrated that the thermal cycle also had strong effects on the fuel cell performance degradation during the startup/shutdown cycling test. A new procedure was proposed to reduce the OCV interval time and avoid the closed/heated system during the startup/shutdown cycle.