

Development of High Temperature Proton Exchange Membrane Fuel Cells

Goal

The ultimate goal of the program is to develop a high temperature polymer electrolyte fuel cell (PEFC) using new polymeric and composite materials. The impetus for developing the higher temperature fuel cells is that at higher temperatures (1) faster reaction rates decrease or even eliminate the need for noble metal catalysts and should yield greater tolerance to CO poisoning at the anode, (2) the higher proton mobility will decrease the membrane resistivity, and (3) water evaporation should mitigate the "flooding" problem at the cathode.

Team

This research program is an interdisciplinary effort that brings together a team that has a long experience in the fields of high temperature electrochemistry and electrochemical energy conversion systems (in The Energy Institute's Electrochemical Laboratory) and a research group with a unique expertise in the design and synthesis of polyphosphazene polymer membranes (Penn State's Department of Chemistry). Also, the U.S. Department of Energy and Los Alamos National Laboratory play a significant role and support the development and implementation of the high temperature PEFC concept at Penn State.

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Background

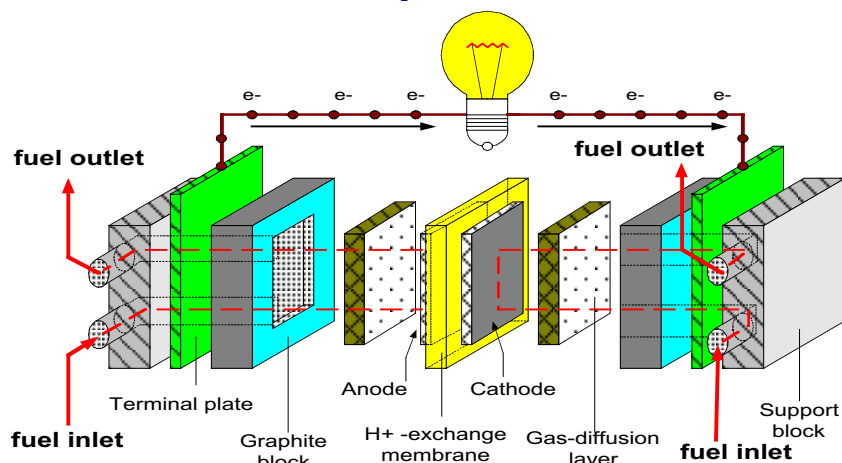
Creation of new energy conversion devices is a major challenge for sustainable development in our society. The use of fuel cells is a fundamentally different way of generating electrical power from a variety of fuels. The key feature of a fuel cell is its high-energy conversion efficiency. Fuel cells are being developed to potentially replace the internal combustion engines because they are clean, quiet, energy efficient, and fuel-flexible. It was recently announced that the Bush administration's new Freedom Cooperative Automotive Research (CAR) initiative is a \$1.5-billion effort intended to further develop fuel cell technologies for automotive applications. According to Secretary of Energy, Spencer Abraham, "Enhancing energy efficiency is an important goal of the President's National Energy Policy." In addition, formation of the DOE High Temperature Membrane (HTM) Working Group was announced at the June 2001 Annual National Laboratory R&D Meeting of the DOE Fuel Cells for Transportation Program. The Working Group was established to draw upon the expertise of academic, government, and industry scientists to address the very challenging need for polymer electrolyte membranes that can operate at high temperatures.

Project Discussion

Polymer electrolyte fuel cells (PEFCs), which employ proton exchange membranes (PEMs), are considered to be one of the most promising sources of electrical energy. Possible applications for PEFCs are stationary power stations, engines of automobiles, and power sources for portable electronics. The main advantage of a PEFC is its high-energy conversion efficiency and simplicity in design, resulting in reliability and convenience.

A PEFC consists of a proton-conducting polymer membrane, such as Nafion, sandwiched between two electrodes. The electrodes are in contact with current collectors, which deliver electrons to the

Basic Components of PEFC



Project Discussion cont.

external load. Electricity is generated by oxidation of fuel at the anode, which produces electrons, and the reduction of oxygen at the cathode, which consumes electrons.

Existing PEFCs are attractive for a variety of power applications but must operate near ambient temperature. At temperatures above 80°C, dehydration of Nafion occurs, resulting in deactivation of the material. Moreover, the low operating temperature makes the platinum-based anode catalyst susceptible to poisoning by contaminants in the fuel stream. If there were a PEFC that could operate at higher temperatures, this would eliminate or greatly reduce the need for noble metal catalysts, the effect of CO poisoning, and the degree of water flooding at the cathode. Thus, raising the operating temperature of PEFCs above 100°C should result in a substantial reduction in cost and an increase in power yield.

Current PEMs (e.g., Nafion) can only be used at temperatures below 100°C. Recently, a number of new proton conductive polymers have been examined for use in PEFCs. However, the list of candidates for such applications is limited by the stringent demands placed upon the polymeric properties. The polymer should demonstrate good chemical and mechanical stability, low permeability of fuel, and high ionic conductivity in order to be considered for such applications. It has been demonstrated that polyphosphazene membranes possess high proton conductivity, low small-molecule permeability, and good mechanical strength. If the production of the membranes is scaled up, the price could be much less than that of Nafion membranes. Consequently, polyphosphazenes are a prime candidate for membrane electrode assembly (MEA) construction. The resulting MEAs should demonstrate the efficiency, poisoning-resistance, and long-term stability in a fuel cell operating at temperatures exceeding 100°C.



Jim Heffel's Hydrogen Cobra at the University of California. Zero-emitting Car with a Current Speed Record 120 mph.

Results

We have developed a new class of ion-exchange polyphosphazene-based membranes for PEFCs. These membranes are used because of the thermo-oxidative and reductive stability of the phosphorus-nitrogen backbone and because of the ability of this system to permit large or subtle changes to be made in side group structure to optimize membrane properties. We have designed and synthesized a number of new proton conducting membranes that demonstrated the high proton conductivity, low methanol crossover, high ion exchange capacity, low water swelling and high mechanical, chemical and thermo-oxidative stability. One of the most important results is the development of the polyphosphazene-based proton conducting membranes that have much smaller methanol crossover (more than one order of magnitude smaller) than Nafion 117 and proton conductivity comparable to Nafion 117 for a wide temperature range from 20 to 120°C. Finally, the recently developed sulfonimide polyphosphazene-based membrane electrode assembly tested in a H₂/O₂ fuel cell showed an electrical performance similar a Nafion 117-based fuel cell. Ongoing research is underway to further improve the composition and performance of the polyphosphazene-base membranes and membrane electrode assemblies.

Key Publications

Allcock H.R., Hofmann M.A., Lvov S.N., Zhou X. Y., Chalkova E., and Weston J.A. Phenyl Phosphonic Acid Functionalized Poly[aryloxyphosphazenes] as Proton-Conducting Membranes for Direct Methanol Fuel Cells, *J. Membr. Sci.*, 2001, v. 201, p. 47-54.

Fedkin M.V., Zhou X.Y., Hofmann M.A., Chalkova E., Weston J.A., Allcock H.R., Lvov S.N. Evaluation of Methanol Crossover in Proton-Conducting Polyphosphazene Membranes, *Materials Letter*, 2002, v. 52, p.192-196.

Hofmann M.A., Ambler C.M., Maher A.E., Chalkova E., Zhou X.Y., Lvov S.N., Allcock H.R. Synthesis of Polyphosphazenes with Sulfonimide Side Groups, *Mactomolucules*, 2002 (in press).

Chalkova E., Zhou X.Y., Ambler C.M., Hofmann M.A., Weston J.A., Allcock H.R., and Lvov S.N. Sulfonimide Polyphosphazene-Based H₂/O₂ Fuels Cells, *Electrochemical and Solid State Letters*, 2002 (in press).

This publication is available in alternative media on request.

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