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Direct methanol fuel cells (DMFCs) have high potential for use in transportation applications because the fuel, unlike hydrogen, is relatively simple to generate, transport and store. To date, most DMFCs have been demonstrated using sulfonated polymer membranes, e.g., Nafion, as the electrolyte. While such polymers are generally adequate for H₂/O₂ fuel cells, they have serious drawbacks when applied to MeOH/O₂ cells. In particular, the polymeric membrane allows a large fraction of the methanol to diffuse directly from the anode to the cathode, where it is consumed in a parasitic combustion reaction. Moreover, the temperature range over which Nafion can be utilized is limited to less than ~ 90°C. At these rather low temperatures anode reaction kinetics are slow, resulting in high anode polarization losses and requiring the use of large quantities of precious metal catalysts. Thus, if the potential of DMFCs are to be realized, alternative membranes, ones which are impermeable to methanol and able to withstand slightly elevated temperatures, are required.

In the present work composite polymer/solid electrolyte materials have been evaluated for DMFC applications. Unlike other alternative membranes which have been recently proposed, the present materials contain no liquid phase. The polymer serves to provide mechanical stability and flexibility, whereas the solid electrolyte provides a pathway for proton transport. The conductivity of the composites at 130°C as a function of weight fraction polymer is shown in Figure 1. These samples were prepared by hot-pressing, and the conductivity measured under air by a.c. impedance spectroscopy. In addition we report the results of permeability measurements and the performance of prototype fuel cells. Optimization of the composite microstructure is expected to ultimately yield high conductivity membranes with the desired mechanical, chemical and thermal properties for DMFC applications.

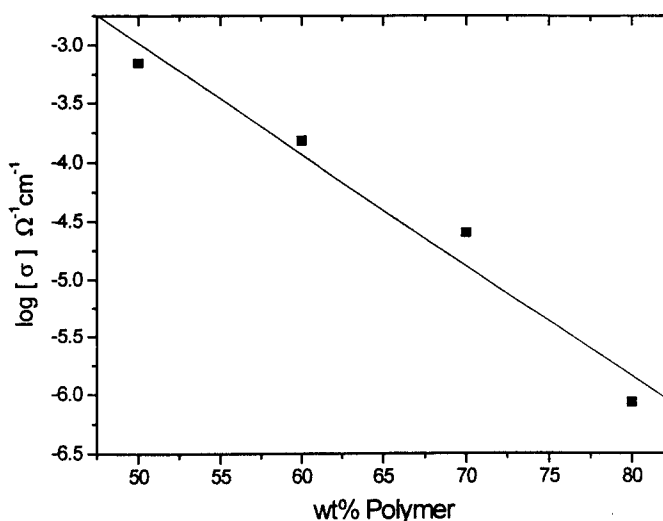


Fig. 1. Conductivity of the polymer/solid electrolyte composite at 130°C as a function of composition.

NOVEL POLYMER-SOLID ELECTROLYTE COMPOSITE (PSEC) MEMBRANES FOR FUEL CELLS

Novelty:

A membrane electrolyte for fuel cells based on a composite formed from a melt processable polymer such as PVDF and a solid proton conductor such as cesium hydrogen sulfate is an entirely new material and completely novel for fuel cells. This new membrane material opens up a whole range of possibilities hitherto not available with conventional membrane electrolytes. Specifically these possibilities include improved performance, reduction in material cost and increased amenability to manufacturing of fuel cells.

Technical Description:

Problem:

Proton conducting polymer electrolyte membranes form the basis of current hydrogen-air and methanol-air fuel cells. An example of a widely used membrane of this type is a perfluoro-sulfonated polymer known by the tradename Nafion (a DuPont Product). This membrane exhibits high conductivity and excellent stability in fuel cell environments. However, the key limitation to the extensive application of such membranes arise from the fact that they all require to be in a hydrated state to conduct protons. This requirement for water to be present in the matrix of the polymer for proton conduction translates to temperature limit of 90° C for membrane operation and also high methanol permeability. Being able to operate fuel cells at high temperatures such as 140°C would increase their tolerance carbon monoxide from reformat streams, a strong limitation faced by the state-of-art fuel cells operating on reformed fuels. Absence of water will reduce methanol permeability improve the efficiency and performance of methanol based fuel cells. Therefore, a new membrane electrolyte material, that is not based on water to provide protonic conduction, would be desirable.

Solution.

We have found that polyvinylidene fluoride- cesium hydrogen sulfate composite membranes could be a solution to the above problem. In this type of membrane, the polymer materials serves as a matrix to support the solid proton conductor, cesium hydrogen sulfate. Cesium hydrogen sulfate conducts protons by a mechanism that does not require water. At room temperature, the protons in cesium hydrogen sulfate are in a bound state and are not free to move. However at about 135-145°C the cesium hydrogen sulfate undergoes a phase transformation that renders significant rotational mobility to the proton. Therefore proton conductivity values as high as $10^{-1} \text{ Ohm}^{-1} \text{ cm}^{-1}$ are observed. These conductivity values are comparable to the values observed with the conventional polymer membranes. Thus immobilizing this proton conductor in a stable polymer matrix to form a membrane converts the inorganic proton conductor to become a membrane electrolyte suitable for implementation in fuel cells. The solid proton conductor cesium hydrogen sulfate belongs to a family of materials that exhibit conductivity transitions. It is believed, therefore, that a new class of proton conducting

composites can be derived using various solid proton conductors and melt processable polymers.

Detailed Description:

Membrane Preparation and Characterization:

Polymer-solid electrolyte composite (PSEC) membranes can be fabricated by following procedure. The solid proton conductor such as cesium hydrogen sulfate and the polymer material such as polyvinylidene fluoride (PVDF) are combined in the required proportions. The compositions varied from about 10% to 60% by weight of proton conductor. The cesium hydrogen sulfate is ground into fine particles along with required amounts of Kynar 741(a commercial powder form of PVDF). Appropriate amounts of these are placed in a die and hot pressed at temperatures in the range of 160- 190 °C. This procedure resulted in membrane or films could be used for further testing. The properties of these membranes could be improved by changing the temperatures and pressures during the hot pressing process. Membrane samples of about 2"x 2" could be easily prepared by this method. Alternate methods of preparation that were also successful started with a slurry of the proton conductor and the PVDF powder in an organic solvent such as acetone or isopropanol . These slurries were then cast on a press plate and allowed to dry before hot pressing. The latter method was expected to yield films of lower gas permeability.

The conductivity of such films as a function of temperature have been measured using AC impedance methods for various compositions of the film. Preliminary results are shown in Fig. 1 indicate high conductivity in the range of 10^{-2} to 10^{-3} $\text{Ohm}^{-1}\text{cm}^{-1}$ for these films.

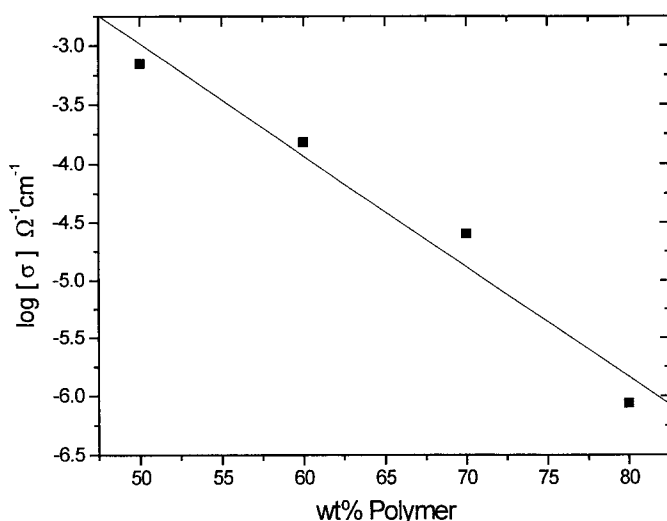


Fig. 1. Conductivity of the polymer/solid electrolyte composite at 130°C as a function of composition

Fuel Cell Evaluation:

These electrolyte films will be tested in fuel cells after preparation of a membrane electrode assembly. The preparation of a membrane electrode assembly for this type of membrane is different from that used with Nafion type membranes and therefore needs to be developed and optimized. Some of the possible procedures involved in this preparation are described in the following.

The membrane-electrode assembly consists of two electrodes bonded to either side of the proton conducting membrane. The two electrodes that constitute the anode and cathode of the fuel cell are made up of electrocatalyst layers and backing layers. The catalyst layer is the site of electrochemical reaction. The backing layers serve to supply the reactants and remove the products and also conduct the electrons. For hydrogen-air cells the preferred material would be platinum black for the anode and cathode. However, for methanol fuel cells, the preferred material is an in-house prepared platinum-ruthenium alloy for the anode and platinum for the cathode. The catalyst layer is formulated from the polymer binder, proton conducting material and an appropriate electrocatalyst. This could be applied as a powder and hot pressed on to the membrane. Alternately, the electrocatalyst layer can be pre-coated on a backing layer such as a Toray Carbon paper and then hot pressed on the membrane. The catalyst layer may also be sputtered on to the membrane electrolyte. Carbon fiber paper, carbon cloth, sintered metal are among the alternatives available for the backing layers. Processes for catalyst and backing layer application are currently under development specifically for these membranes.

The membrane-electrode assemblies so prepared will be characterized in fuel cell test holders to establish the current voltage performance. These tests will include polarization of the cell at various temperatures, reactant pressures and flow rates. The effect of carbon monoxide on the cell performance will be studied to evaluate the tolerance of the fuel cell for reformat fuel operation. The cell will be tested on hydrogen and vapor-feed of methanol and water. Existing fuel cell holders and test arrangements will be modified to accommodate the new membrane material. It is anticipated that we will be able to report the test results along with new procedures for fabrication of membrane-electrode assemblies in a future NTR.