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Improved Inorganic Ion Exchange Membranes

A new method has been developed for making solid ion exchange membrane electrolytes for use in hydrocarbon-oxygen and hydrogen-oxygen fuel cells. The membrane is a sintered composite of zirconia, phosphoric acid, and zeolite. A hydrogen-oxygen fuel cell using this membrane with platinum black as a catalyst operates at 0.70 volt and a current density of 30 ma/cm² at 100°C; in this cell, the anode and cathode were comprised of a tantalum screen impregnated with platinum black and polytetrafluoroethylene for water balancing purposes.

A requisite for fuel cell membranes is sufficient strength to be self-supporting and to resist vibrational and other destructive forces. In addition, low electrical resistance and high current density are desired. Inorganic membranes which satisfy these requirements have been made by the typical preparative methods described below.

In one method, the membrane is prepared by compacting equal amounts of zirconia, phosphoric acid, and zeolite, and sintering the compact to 400°C. The sintered membrane is then saturated with 80 percent phosphoric acid and resintered at 500°C. The resultant product is a membrane having a transverse strength of about 5500 psi and a resistance of 10 ohm/cm² at 25°C. Another method of preparation is to compact equal amounts of zirconia and phosphoric acid and sinter to 500°C. This material is then mixed with equal parts by weight of phosphoric acid and zeolite and sintered at 500°C. The resulting membrane has a transverse strength of 5000 psi and an electrical resistance of less than 10 ohm/cm² at 25°C.

A hydrogen-oxygen fuel cell using this solid membrane electrolyte material has been operated at

65°C for more than 500 hours at 0.5 volt and a current density of about 20 ma/cm². Using propane as the hydrocarbon fuel, cell performance of 0.25 volt and 14.9 ma/cm² at 123°C was achieved. To make these membrane materials effective at temperatures above 100°C, additives having controlled water vapor pressure characteristics can be admixed during the process of membrane preparation. Such materials as silicic acid, P₂O₅, Al₂(SO₄)₃, or other materials capable of retaining water at temperatures above 100°C can be used. A typical formulation in parts by weight is 1 part ZrPO₄ and 0.5 part silicic acid. An example of the effectiveness of the water-retaining additive in lowering the electrical resistance is noted in the following table:

Temperature, °C	Type	Resistance, Ohms
115	ZrPO ₄	3000
110	ZrPO ₄ + silicic acid	30

Note:

Additional work is in progress to improve the performance of the membranes in both hydrocarbon-oxygen and hydrogen-oxygen fuel cells.

Patent status:

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457(f)], to the McDonnell Douglas Corporation, 3000 Ocean Park Boulevard, Santa Monica, California 90406.

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