### Materials

#### Glass Frit Filters for Collecting Metal Oxide Nanoparticles

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Filter disks made of glass frit have been found to be effective as means of high-throughput collection of metal oxide particles, ranging in size from a few to a few hundred nanometers, produced in gas-phase condensation reactors. In a typical application, a filter is placed downstream of the reactor and a valve is used to regulate the flow of reactor exhaust through the filter. The exhaust stream includes a carrier gas, particles, byproducts, and unreacted particle-precursor gas. The filter selectively traps the particles while allowing the carrier gas, the byproducts, and, in some cases, the unreacted precursor, to flow through unaffected. Although the pores in the filters are much larger than the particles, the particles are nevertheless trapped to a high degree: Anecdotal information from an experiment indicates that 6-nm-diameter particles of MnO₂ were trapped with >99-percent effectiveness by a filtering device comprising a glass-frit disk having pores 70 to 100 μm wide immobilized in an 8-cm-diameter glass tube equipped with a simple twist valve at its downstream end.

This work was done by John Ackerman, Dan Buttry, Geoffrey Irvine, and John Pope of Blue Sky Batteries, Inc., for Johnson Space Center. For further information, contact the Johnson Innovative Partnerships Office at (281) 483-3809. MSC-23425

#### Anhydrous Proton-Conducting Membranes for Fuel Cells

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Polymeric electrolyte membranes that do not depend on water for conduction of protons are undergoing development for use in fuel cells. Prior polymeric electrolyte fuel-cell membranes (e.g., those that contain perfluorosulfonic acid) depend on water and must be limited to operation below a temperature of 125 °C because they retain water poorly at higher temperatures. In contrast, the present development of anhydrous membranes is expected to function well at temperatures up to 200 °C.

The developmental membranes exploit a hopping-and-reorganization proton-conduction process that can occur in the solid state in organic amine salts and is similar to a proton-conduction process in a liquid. This process was studied during the 1970s, but until now, there has been no report of exploiting organic amine salts for proton conduction in fuel cells.

The present development work exploits and extends the previous research on water-free proton conduction in organic amine salts. This work has included an investigation of acid salts of triethylenediamine in which each molecule contains two tertiary nitrogen atoms that can be quaternized. It has been demonstrated that by combining such a proton conductor with nanoparticles of suitable oxide (for example, silica) and a stable binder (for example, poly(tetrafluoroethylene)), one can fabricate a polymeric electrolyte membrane inexpensively. The figure depicts the results of measurements of the ionic conductivity of such a membrane made from triethylenediamine sulfate. The activation energy for proton transport, obtained from the slope of the plot, lies in the range of 0.15 to 0.20 eV — a low range indicative of facile transport of protons.

Proton-conducting membranes to be investigated in the continuing development effort are divided into the following three classes according to the amine salts and related compounds on which they are based:

- **Type I**: Organic tertiary amine bisulfates, triflates ( trifluoromethanesulfonates), and hydrogen phosphates.
- **Type II**: Polymeric quaternized amine bisulfates, triflates, and hydrogen phosphates.
- **Type III**: Polymeric quaternized bisulfates, hydrogen phosphates, and triflates combined with perfluorosulfonic acid-based polymers.

As in the case of the membrane described in the preceding paragraph, a proton-conducting membrane of type I would...
be fabricated from one or more salts of type I by processing a mixture of fine salt particles, oxide nanoparticles, and poly(tetrafluoroethylene).

Fabrication of membranes of type II would involve synthesis of polymers, followed by casting of the polymers into membranes. Depending on the starting ingredients and process used to make a given membrane, either the quaternized nitrogen atoms would automatically be incorporated into the membrane during polymerization, or else it would be necessary to quaternize the membrane in a bisulfate or a hydrogen phosphate.

A membrane of type III would be a two-component polymeric system cast from a solution containing a perfluorosulfonic acid-based polymer and a quaternary-nitrogen-containing polymer salt of type II. This polymer would make it possible to exploit the strong acidity of the dry perfluorosulfonic acid and the flexibility of its polymer back bone. The general objective in formulating such a two-component system is to increase the number of sites available for proton hopping and provide for additional relaxation and reorganization mechanisms in order to reduce the heights of barrier to the transport of protons.

This work was done by Sekharipuram Narayanan and Shiao-Pin S. Yen of Caltech for NASA’s Jet Propulsion Laboratory. For further information, access the Technical Support Package (TSP) free online at www.techbriefs.com/tsp under the Materials category.

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