

## ◆ Making Single-Source Precursors of Ternary Semiconductors

Commercially available reagents are used in a simplified synthesis.

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A synthesis route has been developed for the commercial manufacture of single-source precursors of chalcopyrite semiconductor absorber layers of thin-film solar photovoltaic cells. The semiconductors in question are denoted by the general formula  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$ , where  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ .

A closely related class of single-source precursors of these semiconductors, and their synthesis routes, were reported in "Improved Single-Source Precursors for Solar-Cell Absorbers" (LEW-17445-1), *NASA Tech Briefs*, Vol. 31, No. 6 (June 2007), page 56. Heretofore, the synthesis of single-source precursors of  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$  has involved expensive and/or non-commodity starting reagents and cumbersome, lengthy processes — suitable for laboratory settings but not for commercialization. The present synthesis route is better suited to commercialization because it is simpler and involves the use of commercially available agents, yet offers the flexibil-

ity needed for synthesis of a variety of precursors.

A single-source precursor of the type of interest here is denoted by the general formula  $\text{L}_2\text{M}'(\mu\text{-ER})_2\text{M}(\text{ER})_2$ , where L signifies a Lewis base; M signifies Al, In, or Ga; M' signifies Ag or Cu; R signifies an alkyl, aryl, silyl, or perfluorocarbon group; E signifies O, S, Se, or Te; and  $\mu$  signifies a bridging ligand. This compound can be synthesized in a "one-pot" procedure from ingredients that are readily available from almost any chemical supplier. The synthesis of this compound can be summarized in simplified form as  $\text{MX}_3 + 4\text{NaER} + \text{M}'\text{X} + 2\text{L} \rightarrow \text{L}_2\text{M}'(\mu\text{-ER})_2\text{M}(\text{ER})_2$ , where X signifies a halogen.

In a demonstration, the following synthesis was performed: Under anaerobic conditions,  $\text{InCl}_3$  was reacted with sodium ethanethiolate in methanol in a 1:4 molar ratio to afford the ionic stable intermediate compound  $\text{Na}^+[\text{In}(\text{SEt})_4]^-$  (where Et signifies ethyl group). After approximately 15 minutes, a heterogeneous solution of  $\text{CuCl}$  and the Lewis

base  $\text{PPh}_3$  (where Ph signifies phenyl) in a 1:2 ratio in a mixture of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  was added directly to the freshly prepared  $\text{Na}^+[\text{In}(\text{SEt})_4]^-$ . After 24 hours, the reaction was essentially complete. The methanolic solution was concentrated, then the product was extracted with  $\text{CH}_2\text{Cl}_2$ , then the product was washed with dry ether and pentane. The product in its final form was a creamy white solid. Spectroscopic and elemental analysis confirmed that the product was  $(\text{PPh}_3)_2\text{Cu}(\mu\text{-SEt})_2\text{In}(\mu\text{-SEt})_2$ , which is known to be a precursor of the ternary semiconductor  $\text{CuInS}_2$ .

*This work was done by Aloysius Hepp of Glenn Research Center and Kulbinder K. Banger of the Ohio Aerospace Institute. Further information is contained in a TSP (see page 1).*

*Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17625.*

## ◆ Water-Free Proton-Conducting Membranes for Fuel Cells

Fuel cells could be operated at higher temperatures for greater efficiency.

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Poly-4-vinylpyridinebisulfate (P4VPBS) is a polymeric salt that has shown promise as a water-free proton-conducting material (solid electrolyte) suitable for use in membrane/electrode assemblies in fuel cells. Heretofore, proton-conducting membranes in fuel cells have been made from perfluorinated ionomers that cannot conduct protons in the absence of water and, consequently, cannot function at temperatures  $>100^\circ\text{C}$ . In addition, the stability of perfluorinated ionomers at temperatures  $>100^\circ\text{C}$  is questionable. However, the performances of fuel cells of the power systems of which they are parts could be improved if operating temperatures could be raised above  $140^\circ\text{C}$ . What is needed to make this possible is a solid-electrolyte material, such as P4VPBS, that can be cast into membranes and that both retains proton conductivity and remains stable in the desired higher operating temperature range.

A family of solid-electrolyte materials

different from P4VPBS was described in "Anhydrous Proton-Conducting Membranes for Fuel Cells" (NPO-30493), *NASA Tech Briefs*, Vol. 29, No. 8 (August 2005), page 48. Those materials notably include polymeric quaternized amine salts. If molecules of such a polymeric salt could be endowed with flexible chain structures, it would be possible to overcome the deficiencies of simple organic amine salts that must melt before being able to conduct protons. However, no polymeric quaternized amine salts have yet shown to be useful in this respect.

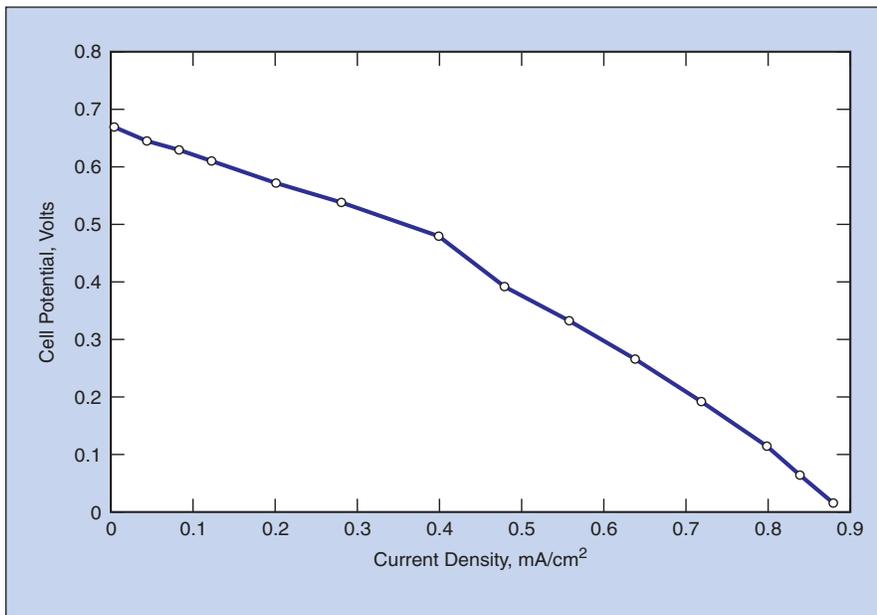
The present solid electrolyte is made by quaternizing the linear polymer poly-4-vinylpyridine (P4VP) to obtain P4VPBS. It is important to start with P4VP having a molecular weight of 160,000 daltons because P4VPBS made from lower-molecular-weight P4VP yields brittle membranes.

In an experimental synthesis, P4VP was dissolved in methanol and then re-

acted with an excess of sulfuric acid to precipitate P4VPBS. The precipitate was recovered, washed several times with methanol to remove traces of acid, and dried to a white granular solid.

In another synthesis, nanoparticles of silica rich with surface hydroxyl groups were added to P4VP in methanol solution, which was then reacted with excess sulfuric acid to precipitate granules of a composite that most probably had the composition  $(\text{P4VPBS})\text{-SiO}_2\text{-SiO}(\text{HSO}_4)_2$ .

The granular P4VPBS produced in the first-mentioned synthesis was dissolved in water to make a glue-like, turbid solution; the granular P4VPBS/silica composite produced in the second-mentioned synthesis was mixed with water to make a turbid, glue-like suspension. The proportions of polymer salt to water in such preparations can be varied; it was found that approximately equal parts of water and polymer salt yield a solution or suspension amenable to further processing.



Cell Potential vs. Current Density was measured in a test of an experimental membrane/electrode assembly in a hydrogen/oxygen fuel cell at a temperature of 183.5 °C.

Each of these preparations was brushed onto an open mat of glass fibers. The coated mats were dried in flowing air at a temperature of 60 °C for about an hour. The coated mats were further dried in a vacuum oven at 60 °C to remove traces of water.

The thermal stability of P4VPBS was evaluated by differential scanning calorimetry. The results showed that P4VPBS undergoes a glass transition at a temperature of about 182 °C and that it melts at about 298.7 °C, with no evidence of decomposition. These thermal properties are consistent with the requirements for stability under operating conditions in fuel cells.

The coated mats were tested to determine their ionic conductivities and to quantify their performances as membranes in hydrogen/oxygen fuel cells.

The ionic conductivity of the mat coated with the P4VPBS/silica composite was slightly greater than that of the mat coated with P4VPBS: this was expected because the composite contains additional molecular groups that are presumably available for forming hydrogen bonds. On the basis of the observed temperature dependence of the conductivity, the activation energy for conduction was estimated to be about 0.1 eV, suggesting hopping-type conduction through hydrogen bonds. While the measured conductivity values were two orders of magnitude lower than desirable for fuel-cell applications, the degree of solid-state proton conduction was the highest observed thus far in polymeric salts. It is anticipated that the polymer backbone could be modified to facilitate formation of hydrogen bonds to obtain more sites

for proton hopping and, hence, greater proton conductivity.

In preparation for the tests of fuel-cell performance, the coated mats were further coated with catalytic anode and cathode layers to form membrane/electrode assemblies. No attempt was made to optimize the catalytic layers. In the fuel-cell tests, stable maximum cell potentials of 0.85 V were attained. The anticipated maximum cell voltage was 1.0 V. The decrease from the expected maximum value was attributed to some crossover of hydrogen and oxygen through the membranes. The figure shows some of the data from the fuel-cell test of the mat coated with the P4VPBS/silica composite. The power density indicated by these data is low for a fuel cell operating at the indicated temperature — presumably because of the lack of optimization of the catalyst layers. Nevertheless, the data suggest that optimization of catalysts and enhancement of conductivity should make it possible to realize high-temperature fuel cells.

*This work was done by Sekharipuram Narayanan and Shiao-Pin Yen of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).*

*In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:*

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