Making Single-Source Precursors of Ternary Semiconductors

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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 ≤ x ≤ 1 and 0 ≤ y ≤ 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 CuIn\(_{x}\)Ga\(_{1-x}\)S\(_{y}\)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 flexibility needed for synthesis of a variety of precursors.

A single-source precursor of the type of interest here is denoted by the general formula \( L_{2}M(\mu-ER)_{2} \), 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 \( \text{MX}_{3} + 4\text{NaER} + \text{M} \rightarrow L_{2}M(\mu-\text{ER})_{2} \), where \( X \) signifies a halogen.

In a demonstration, the following synthesis was performed: Under anaerobic conditions, InCl\(_{3} \) was reacted with sodium ethanethiolate in methanol in a 1:4 molar ratio to afford the ionic stable intermediate compound \( \text{Na}^{+}[\text{In}(\text{SEt})_{3}]^{-} \) (where Et signifies ethyl group). After approximately 15 minutes, a heterogeneous solution of CuCl and the Lewis base \( \text{PH}_{3} \) (where Ph signifies phenyl) in a 1:2 ratio in a mixture of \( 	ext{CH}_{3}\text{CN} \) and \( 	ext{CH}_{2}\text{Cl}_{2} \) was added directly to the freshly prepared \( [\text{In}(\text{SEt})_{3}]^{-} \). After 24 hours, the reaction was essentially complete. The methanolic solution was concentrated, then the product was extracted with \( 	ext{CH}_{2}\text{Cl}_{2} \), 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 \( (\text{PPh}_{3})_{2}\text{Cu}(\text{P}\text{SEt})_{3}\text{In}(\text{PSEt})_{3} \) which is known to be a precursor of the ternary semiconductor 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 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 °C. In addition, the stability of perfluorinated ionomers at temperatures >100 °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 °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 reacted 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 \( (\text{P4VPBS})_{2} \text{SiO}_{2} \text{SiO}(\text{HOSiO})_{2} \).

The granular P4VPBS produced in the first-mentioned synthesis was dissolved in water to make a gluelike, turbid solution; the granular P4VPBS/silica composite produced in the second-mentioned synthesis was mixed with water to make a turbid, gluelike 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.