

## INVESTIGATION OF INTERCALATION COMPOUNDS FOR PHOTOELECTROCHEMICAL ENERGY STORAGE

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Fabrication and evaluation of intercalation electrodes for the storage of electrical energy generated in photoelectrochemical storage cells are the project objectives.

Layered chalcogenides of general formula  $MX_2$  were investigated for the storage of electrical energy generated by photoelectrochemical solar cells. These storage materials can be highly economical and have excellent volumetric energy densities, allowing direct incorporation into flat plate photovoltaic modules. Two approaches were evaluated: (1) intercalation electrodes, such as  $Cu_xTiS_2$ , which can be charged by a separated regenerative photoelectrochemical cell, and (2) 'active' photointercalation/photodeintercalation cells in which the storage step is effected directly by irradiating a layered semiconducting photoelectrode.

A cell of the first kind was demonstrated in a cell consisting of an n-GaAs photoelectrode and  $TiS_2$  intercalation electrode. The intercalant was Cu in an acetonitrile-tetrabutylammonium chloride electrolyte. During the charging reaction,  $CuCl_2^{-1}$  was oxidized to  $CuCl_4^{-2}$  at the n-GaAs photoanode and reduced to  $Cu_xTiS_2$  at the cathode. The best results were obtained with  $TiS_2$ , which had been pressed onto Ta exmet screen. The cell was charged under tungsten lamp irradiation of  $40 \text{ mW/cm}^2$  until the  $TiS_2$  was 36 percent utilized. The spontaneous discharge cycle was continued until 64 percent of the stored charge was recovered. The major problem encountered in the cycling experiments was deterioration of the physical structure of the  $TiS_2$  electrode, although the system itself appears to be chemically reversible between  $0 < x < 0.6$ .

A new electrode bonding procedure based on presintered  $MX_2$ /Teflon/graphite mixtures was developed and produced much more robust electrodes. Use of  $VSe_2$  as the intercalation material resulted in a spontaneous intercalation rate of Cu in aqueous solutions, which was almost six times that obtained for  $TiS_2$ .

Studies of 'active' photointercalation devices were made on four single-crystal semiconducting layered dichalcogenides:  $HfS_2$ ,  $HfSe_2$ ,  $ZrSe_2$ , and  $ZrS_2$ . These were prepared as single crystals by iodine vapor transport. The photoelectrochemical properties of the four compounds were measured in electrolytes with different redox potentials.  $HfS_2$  and  $ZrSe_2$  showed both p- and n-type photoresponse indicative of nearly intrinsic, highly compensated-type material. No photoresponse was observed with the  $ZrS_2$  crystals. Cu was spontaneously intercalated into  $HfS_2$  in aqueous solution. As the intercalation progressed toward 0.5 equivalent/mole passed, the photovoltage and photocurrent increased, and the crystal showed pronounced n-type charac-

ter. After passage of more current, the crystal became more metallic with resulting decreases in photoresponse. Similar results were obtained for spontaneous intercalation of Li in  $\text{HfS}_2$  crystals in propylene carbonate electrolytes.

## STUDY OF AMORPHOUS HYDROGENERATED BORON THIN FILMS

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The objective is to characterize hydrogenated amorphous boron as a novel material to be employed in photoelectrochemical cells for the conversion and storage of solar energy.

The optimum optical band gap of a semiconductor electrode for the maximum theoretical photovoltaic conversion efficiency of the solar spectrum in a photoelectrochemical cell is approximately 1.45 eV. Therefore, amorphous hydrogenated boron, whose optical band gap can be consistently controlled at approximately 1.5 eV, becomes an attractive active electrode material. Amorphous boron, without hydrogenation, has been known to have poor semiconducting properties. However, in analogy with the situation existing for amorphous hydrogenated silicon, the presence of boron-hydrogen bonding is believed to have significantly improved its semiconducting characteristics. In view of these advantages, Giner Inc., carried out an evaluation of the performance of this material as a photoelectrode in a photoelectrochemical cell. As far as is known, no previous attempt of this type has ever been made.

In this study, the electrochemical and photoelectrochemical characteristics of amorphous hydrogenated boron in both aqueous and nonaqueous redox electrolytes were investigated. A systematic screening of redox couples, mostly in acetonitrile, covered a redox potential range from 1.08 to  $-1.00$  on the standard calomel electrode (SCE) scale. Furthermore, the long-term stability of this material was determined.

The results indicate that amorphous hydrogenated boron currently produced by the radio frequency (RF) glow discharge of diborane appears to be chemically stable in several redox electrolytes. As to its suitability as a photoelectrochemical cell electrode material, the current n-type a-B:H was found to produce a photovoltage of several millivolts, and p-type material did not exhibit any photovoltage response at all, despite the wide redox potential range covered in the work. The semiconducting properties of a-B:H will have to be significantly improved in order to produce a more useful photoelectrical effect. Specifically, boron films with higher carrier mobility, as well as better photoconductivity, must be obtained to be used as an