METAL INTERCALATION CHARACTERISTICS OF N-HFS2 PHOTOELECTRODES IN NONAQUEOUS ELECTROLYTES (U) ELTRON RESEARCH INC AURORA IL K W SENKOW ET AL JUL 87
# Metal Intercalation Characteristics of n-HfS₂ Photoelectrodes in Non-Aqueous Electrolytes

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**Abstract:**
The photoelectrochemical (PEC) performance of single crystal n-HfS₂ was correlated with capacitance and impedance measurements obtained with the photoanode van der Waals layers oriented either parallel or perpendicular to acetonitrile-based non-aqueous electrolytes, with and without CuCl introduced as an intercalating redox species. For van der Waals layers perpendicular to the electrolyte (i.e., available for copper intercalation) space charge capacitance values of respectively 10⁻² and 1µF/cm² were obtained for the non-intercalated and copper intercalated photoelectrodes. The implications of these experimental observations were discussed in relation to...
the application of these intercalating photoelectrodes in both liquid non-aqueous and solid polymer electrolyte PEC storage devices.
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METAL INTERCALATION CHARACTERISTICS OF n-HfS\textsubscript{2} PHOTOELECTRODES IN NONAQUEOUS ELECTROLYTES

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Photoelectrodes of the Group IVb transition metal dichalcogenides HfS\textsubscript{2}, HfSe\textsubscript{2}, ZrS\textsubscript{2} and ZrSe\textsubscript{2} (which are all indirect gap materials possessing band gaps of respectively 1.96, 1.13, 1.68 and 1.26 eV) have recently been shown compatible for the reversible intercalation of copper and iron species. Single crystals of these materials prepared by the halogen (I\textsubscript{2}) vapor transport technique were found to be intrinsically n-doped. Intercalation occurs between the weakly bonded van der Waals planes of these materials. The electrochemical intercalation and photovoltaic effects (PEC) intercalation of redox species at the interfacial region of these layer type photoanodes with either liquid nonaqueous or solid polymer electrolytes (SPE), could be a viable strategy for PEC storage devices.

The PEC and electrochemical intercalation characteristics for single crystal materials is found highly dependent upon the crystal orientation exposed to the electrolyte of interest. In work to be discussed here, the PEC performance of n-HfS\textsubscript{2} is correlated with capacitance and impedance measurements obtained with the photoanode van der Waals layers exposed either parallel or perpendicular to the nonaqueous electrolyte. These measurements were performed in acetonitrile/0.1M TBAPF\textsubscript{6} (tetraethylammonium fluorophosphate) electrolytes with and without 0.1M CuCl present as the intercalating redox species. Ohmic contact to n-HfS\textsubscript{2} was achieved by sparking indium metal to the van der Waals layers, using a 15V dc power supply. Current collection was then accomplished via a nichrome wire attached via silver epoxy and the whole ohmic contact region suitably insulated. In the absence of CuCl, photopotentials for the (defect free) van der Waals surface were typically found to be between -220 and -260mV under simulated AM1 illumination. For photoelectrodes prepared where the intercalating edge steps were intentionally exposed to the nonaqueous electrolyte, somewhat smaller photopotentials between -80 and -160mV were found. Impedance and capacitance measurements taken over the frequency range 200Hz to 20kHz for the van der Waals surfaces indicated the presence of frequency dependent capacitance (Figure 1 from Mott-Schottky data) and resistive elements in parallel to the photoanode's space charge capacitance. An equivalent circuit rational to this interfacial region was addressed using circuit analysis techniques previously discussed by others. The corresponding equivalent circuits obtained for both n-HfS\textsubscript{2} crystal orientations are summarized in Figure 2.

Frequency independent capacitance data were obtained by initially measuring the total frequency dependent capacitance, conductance and impedance of the photoanode/electrolyte interfacial region. From this, the frequency dependence was obtained and used to eliminate the influence of the frequency dependent capacitance and resistance from the interfacial admittance. Space charge capacitance at the van der Waals surface, obtained using this approach, was found to be 10^{-2} \mu F/cm\textsuperscript{2} at open-circuit potential. Order of magnitude higher space charge capacitance values were found for materials whose van der Waals layers were exposed to the electrolyte. Here, frequency independent Mott-Schottky data obtained (Figure 3) for n-HfS\textsubscript{2} gave V\textsubscript{fb} = -0.51V vs SCE and N\textsubscript{D} = 7.1 x 10^{17} cm\textsuperscript{-3}.

The initial photopotentials of n-HfS\textsubscript{2} in acetonitrile containing CuCl were found to possess values of -50mV which decreased steadily during the potentiostatic intercalation of copper. Space charge capacitance at the same time was found to increase to 1 \mu F/cm\textsuperscript{2}.

The electrochemical deintercalation of copper could be achieved in the dark implying that the initially intercalated copper occupies energy levels close to the conduction band rather than in the forbidden gap close to the valence band. The implications of these experimental observations will be discussed in relation to the application of these intercalating photoelectrodes in both liquid nonaqueous and SPE, PEC storage devices.

REFERENCES

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Figure 2. Equivalent circuits for n-HfS$_2$/CH$_3$CN interfacial region.

a) n-HfS$_2$ perpendicular to van der Waals layers (i.e. intercalating edges exposed to electrolyte)

b) n-HfS$_2$ parallel to van der Waals layer

Figure 3. Frequency independent Mott-Schottky plot for n-HfS$_2$/CH$_3$CN interface oriented perpendicular to van der Waals layer.