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METAL INTERCALATION CHARACTERISTICS OF N-HFS2
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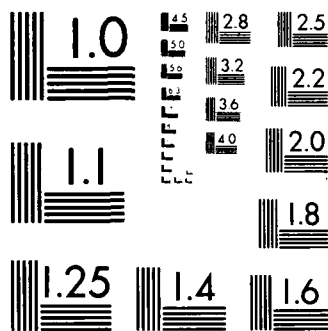
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the application of these intercalating photoelectrodes in both liquid non-aqueous and solid polymer electrolyte PEC storage devices.

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METAL INTERCALATION CHARACTERISTICS OF n-HfS₂ PHOTOELECTRODES IN NONAQUEOUS ELECTROLYTES

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Photoelectrodes of the Group IVb transition metal dichalcogenides HfS₂, HfSe₂, ZrS₂ and ZrSe₂ (which are all indirect gap materials possessing band gaps of respectively 1.96, 1.13, 1.68 and 1.2eV) have recently been shown compatible for the reversible intercalation of copper and iron species.^{1,2} Single crystals of these materials prepared by the halogen (I₂) 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 photoelectrochemical (PEC) deintercalation 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-HfS₂ 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 TBAPF₆ (tetrabutylammonium fluorophosphate) electrolytes with and without 0.1M CuCl present as the intercalating redox species. Ohmic contact to n-HfS₂ 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 surfaces were typically found to be between -220 and -240mV 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 500Hz 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 rationalizing this interfacial region was addressed using circuit analysis techniques previously discussed by others.^{4,5} The corresponding equivalent circuits obtained for both n-HfS₂ 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 impedance 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 $\mu\text{F}/\text{cm}^2$ 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-HfS₂ gave $V_{\text{FB}} = -0.51\text{V}$ vs SCE and $N_D = 7.1 \times 10^{17} \text{ cm}^{-3}$.

The initial photopotentials of n-HfS₂ 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 $\mu\text{F}/\text{cm}^2$.

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

1. B. G. Yacobi, F. W. Baswell and J. M. Corbett, J. Phys. C., 12, 2189 (1979).
2. H. Tributsch, Structure and Bonding, 49, 127 (1982).
3. H. Tributsch, Solar Energy Matls., 1, 705 (1979).
4. J. F. McCann, S. P. S. Badwal and J. Pezy, J. Electroanal. Chem., 118, 115 (1981).
5. J. F. McCann and S. P. S. Badwal, J. Electrochem. Soc., 129, 5551 (1982).

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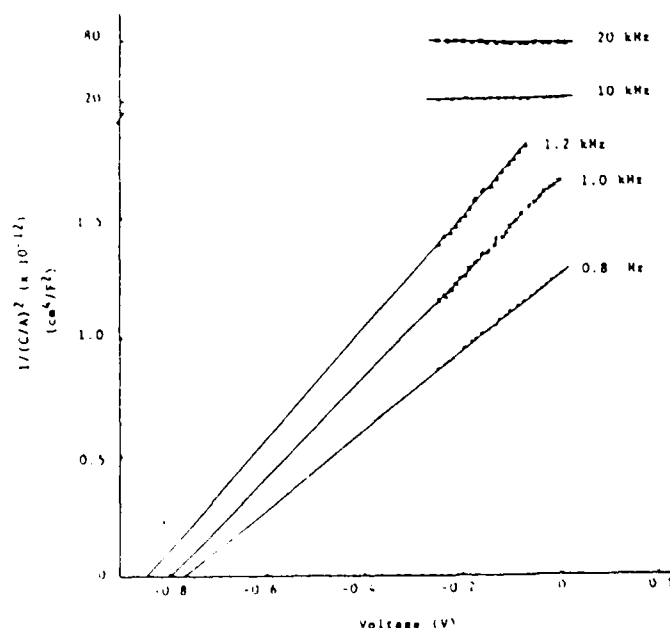


Figure 1. Frequency dependent Mott-Schottky plot for n-HfS₂ in 0.1M TBAPF₆ in CH₃CN oriented perpendicular to van der Waal layer in CH₃CN/0.1M TBAPF₆ electrolyte.

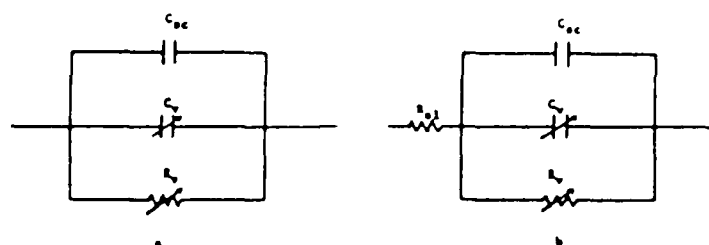


Figure 2. Equivalent circuits for n-HfS₂/CH₃CN interfacial region.
 a) n-HfS₂ perpendicular to van der Waals layers (i.e. intercalating edges exposed to electrolyte)
 b) n-HfS₂ parallel to van der Waals layer

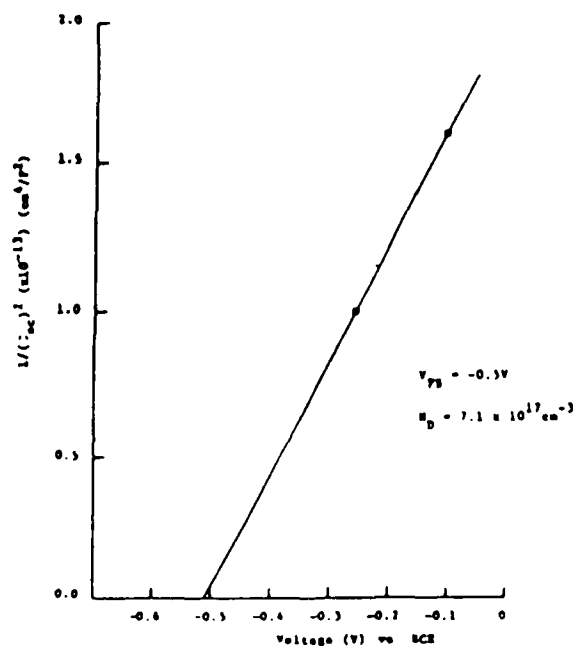


Figure 3. Frequency independent Mott-Schottky plot for n-HfS₂/CH₃CN interface oriented perpendicular to van der Waals layer.

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