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# Impedance and Admittance Measurements at Intercalated n-HfS<sub>2</sub>/Nonagueous Electrolyte Interface

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### ABSTRACT

Capacitance, impedance, and admittance studies were performed on single-crystal n-HfS<sub>2</sub> before and after copper intercalation from acetonitrile-based electrolyte. The n-HfS<sub>2</sub>/nonaqueous electrolyte interface was modeled by equivalent R-C circuits containing frequency dependent elements. Electrochemical intercalation by copper into n-HfS<sub>2</sub> introduced faradaic conductance effects. The composition of copper intercalated n-HfS<sub>2</sub> in close proximity to the interfacial region was obtained assuming a diffusion coefficient for copper in n-HfS<sub>2</sub> of  $10^{-8}$  cm<sup>2</sup>/s. The photoanode demonstrated apparent degeneracy for >0.1 moles of intercalated copper, suggesting that progressive electronic population of the n-HfS<sub>2</sub> conduction band was occurring. Capacitance values for intercalated n-HfS<sub>2</sub> were of the order  $10^{-6}$  F/cm<sup>2</sup>.

Group IVB transition metal dichalcogenides (TMD's) comprising HfS<sub>2</sub>, HfSe<sub>2</sub>, ZrS<sub>2</sub>, and ZrSe<sub>2</sub> are interesting materials for photoelectrochemical (PEC) study since they can, in principle, function as both a photoelectrode and simultaneously as the substrate electroactive material for the reversible intercalation of transition metal species (1-13). For example, it has already been reported that  $ZrS_2$ and HfS<sub>2</sub> are capable of maintaining their semiconducting properties after partial electrochemical intercalation by either Cu or Fe to form ZrM<sub>y</sub>S<sub>2</sub> and HfM<sub>y</sub>S<sub>2</sub> over the compositional range 0 < y < 0.22 (13). Such intercalation does, however, result in a decrease of the bandgap width. The group IVB TMD's have also been shown as being susceptible to cathodic intercalation by alkali and alkaline earth metals and organic species (7-12). As expected, intercalation into these materials results in a widening of the van der Waals layers (14). Group IVB TMD's possess an octahedral structure with electron photoexcitation within the semiconductor bandgap proceeding from energy bands derived from bonding sulfur p-orbitals into metal t<sub>2g</sub> dorbitals (6). These photoelectrodes possess indirect bandgaps with high absorption coefficients, since most incident photons become captured within 1000Å from the interfacial region (15).

Insight gained relating the dependency of photoelectrode properties for these materials on the presence or absence of intercalated metal species, will be of value for identifying conditions where they might be incorporated into PEC cells possessing in situ electrochemical energy storage. Work reported here applies impedance and admittance measurement techniques to single-crystal n-HfS<sub>2</sub> materials in nonaqueous electrolyte, oriented parallel to the c-lattice vector (||-c) where a high population of intercalation sites would be exposed. Measurements were performed on this photoanode before and after electrochemical intercalation by copper, which allowed us to preliminarily model the interfacial region. From such information liquid nonaqueous electrolyte and solid polymer electrolyte PEC storage cells using this photoanode might be more systematically prepared.

#### Experimental

Single crystals of  $n-HfS_2$  were prepared by the halogen (I<sub>2</sub>) vapor transport technique (Northwestern University). Initial solid-state chemical reaction between Hf (99.5%) and S (99.999%) was accomplished by heating an intimate mixture together with 5 mg I2/ml of the quartz transport tube volume. This was performed in a three temperature zone furnace. Typical thermal gradients used were between 875° and 800°C. Crystal growth occurred over 25 days. In all cases the relatively large crystals obtained were intrinsically n-type. Ohmic contact to n-HfS2 was accomplished by sparking indium onto one side of the crystal using a 15V dc power supply. This was performed using a fine indium wire as a cathode with the other pole of the power supply clamped to the n-HfS<sub>2</sub> single crystal. When the indium wire was within  $\cong 1$  mm of the crystal, a transient spark could be observed. This resulted in ion implantation of indium into the ohmic contact region. Current collection was performed with a Nichrome wire attached with silver epoxy and cured at 120°C for 1h. Photoelectrodes were then appropriately isolated from later contact with the electrolyte by epoxy (Norton Chemplast), so that only the single-crystal front face of interest was exposed. Typical photoelectrode areas for ||-c oriented crystals were 0.06 cm<sup>2</sup>

Measurements were performed in a standard glass H-cell arrangement using a platinum counterelectrode. SCE was used as a reference to the working electrode compartment via a salt bridge. Photoelectrode potentials were controlled by a Stonehart Associates BC 1200 potentiostat. Impedance, conductance, and capacitance measurements were performed using a Hewlett-Packard 4276A digital LCZ meter over the frequency range 20 kHz-100 Hz.

## **Results and Discussion**

Work performed was directed towards investigating the interfacial characteristics of single-crystal n-HfS2 in liquid nonaqueous electrolyte (acetonitrile containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte) in the presence of 0.001M CuCl,

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Fig. 1. Impedance response for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub>) at OCP (-0.295V).

both with and without copper intercalation. From capacitance, impedance, and admittance measurements the n-HfS<sub>2</sub>/liquid junction could be modeled by an equivalent circuit which incorporated frequency dependent resistances,  $R_v$ , capacitances,  $C_v$ , together with the n-HfS<sub>2</sub> space charge capacitance,  $C_{\rm sc}$  and the cell resistance  $R_{\rm el}$ . The presence of frequency dependent elements may originate from a variety of charge accumulation modes such as surface states caused by adsorption, inhomogeneous doping, and crystal defects. Expressions for the total admittance Y, impedance Z, conductance G, and susceptance B, for an equivalent circuit consisting of a large number of R-C elements, could be represented by the following relationships (16, 17)

$$Y = a\omega^n + kb\omega^n$$
 [1]

$$Z = A\omega^{-n} - jB\omega^{-n}$$
 [2]

$$G = a\omega^n$$
 [3]

$$B = b\omega^n$$
 [4]

Low

Frequency



Fig. 2. Admittance response for I-c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub>) at OCP (-0.295V).

where A, B, a, b, and n are characteristic circuit constants and  $\omega$  is the angular frequency.

Impedance and admittance responses for -c oriented n-HfS<sub>2</sub>/acetonitrile interface were performed over the frequency range 20 kHz to 100 Hz in the dark. The impedance and admittance results for this interfacial region in the absence of any copper intercalation within the n-HfS2 or copper present in the electrolyte are shown respectively in Fig. 1 and 2. The dark photoelectrode possessed an initial open-circuit potential of -0.295V vs. SCE. The impedance data (Fig. 1) could be approximated by two linear regions corresponding to high and low frequencies. From our previously reported work (18) on ||-c oriented n-HfS<sub>2</sub>, linear dependencies were found between real and imaginary impedance over this whole frequency range for dark photoelectrodes possessing an OCP of -0.103V. However, at -0.253V, two linear regions were observed, analogous to the result obtained here. A change in dependence between real and imaginary parts of the cell impedance with frequency, as in Fig. 1, suggested a complex equivalent circuit for the interfacial region in which the impedance response of one part predominates at low and another part at



Fig. 3. (a, left) Equivalent circuits for -c oriented n-HfS2 in CH3CN (0.1M TBAPF6) at high (A) and low (B) frequencies, and (b, right) equivalent circuit for copper intercalated |-c oriented n-HfS2 in CH3CN (0.1M TBAPF6 + 0.001M CuCl) at high (A) and low (B) frequencies.

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Fig. 4. Impedance response for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1*M* TBAPF<sub>6</sub> + 0.001*M* CuCl) after 42 min copper intercalation ( $\cong$ 10  $\mu$ A) at -0.26V vs. SCE.

higher frequencies. From this data the cell resistance ( $R_{el}$ ) was obtained by extrapolating the high frequency impedance data to infinite frequency giving  $R_{el} = 165\Omega$ .

The admittance data shown in Fig. 2 gave a semicircular plot. The intercept of the semicircle to the *G*-axis gave  $1/R_{\rm el}$ . No additional semicircular regions were observed indicating a different frequency dependence of admittance at high and low frequencies. Therefore, if the n-HfS<sub>2</sub> interfacial region could be represented by one general equivalent circuit acting as two separate circuits responsive to re-

spectively high and low frequency regions, their time constants must be similar (19, 20). Impedance and admittance responses for the *l*-c oriented n-HfS<sub>2</sub> interface can be explained by the equivalent circuits shown in Fig. 3a. In this figure C<sub>sc</sub> represents a frequency independent capacitance attributed to the photoanode space charge capacitance, while  $C_{v}$  and  $R_{v}$  represent the frequency dependent capacitance and resistance, respectively, operating in high and low frequency regions. The magnitude of  $C_{
m sc}$  is usually relatively small compared to  $C_{y}$  and in the low frequency region its contribution can be neglected (19, 20). The network operating at higher frequencies (A) accounts for the linear impedance response observed above 1 kHz, crossing the real impedance axis at  $R_{\rm el}$  (Fig. 1), as well as for a semicircular admittance response of radius  $1/R_{el}$  (Fig. 2). Another network (B) accounts for a change in impedance slope at frequencies below 1 kHz and appears to possess a semicircular response analogous to that found at high frequencies. Upon introducing 0.001M CuCl into the above cell, the dark n-HfS<sub>2</sub> OCP changed from -0.295 to -0.11V vs. SCE. Copper intercalation proceeded into the n-HfS<sub>2</sub> by potentiostating the electrode at -0.26 V vs. SCE when a steady-state cathodic current of the order of  $\approx 10 \ \mu A$  occurred. The cathodic electrochemical intercalation of n-HfS<sub>2</sub> by copper could proceed in the dark since the necessary electrons are present as majority carriers. Impedance and admittance data were obtained after respectively 42 and 129 min after initiating intercalation (Fig. 4 to 7). Assuming a diffusion coefficient for copper intercalation of  $D = 10^{-8}$  cm<sup>2</sup>/s, then a mean intercalation depth X given by Eq. [5] can be calculated

$$X = \sqrt{2Dt}$$
 [5]

and the respective degree of intercalation to this depth X after 42 and 129 min would correspond to the stoichiometries  $HfCu_{0.18}S_2$  and  $HfCu_{0.3}S_2$ . The impedance data obtained (Fig. 4 and 6) approximated a linear relationship between real and imaginary parts in the low frequency region with a circular dependence being observed at higher frequencies. This latter observation suggested an additional resistive element in parallel to the variable resistance in the network operating in the high frequency region shown in Fig. 3a. A value for this new resistance  $R_o$ 



TBAPF<sub>6</sub> + 0.001M CuCl) after 42 min copper intercalation ( $\approx$ 10 µA) at -0.26V vs. SCE.

Fig. 6. Impedance response for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1*M* TBAPF<sub>6</sub> + 0.001*M* CuCl) after 129 min copper intercalation ( $\cong$ 10  $\mu$ A) at -0.26V vs. SCE.

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Fig. 7. Admittance response for  $\|$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub> + 0.001M CuCl) after 129 min copper intercalation ( $\cong$ 10  $\mu$ A) at -0.26V vs. SCE.

was estimated on the basis of the semicircular radius drawn through experimental data in this high frequency region. For n-HfS<sub>2</sub> copper intercalated for 42 min  $R_{\circ}$  was found to be of the order  $\approx 200\Omega$ . Such resistance was not found in the absence of copper intercalation suggesting that  $R_{\circ}$  may represent resistance for reversible intercalation by copper in n-HfS<sub>2</sub>.

At measurement frequencies below 1 kHz the imaginary part of the cell impedance was found to decrease by an order of magnitude after initial copper intercalation and progressively decreased upon further intercalation as shown by reference to Fig. 1, 4, and 6. This observation suggested an increased capacitive cell response in the low frequency region attributable to the presence of intercalated copper. Similar conclusions could also be drawn from the admittance data shown in Fig. 2, 5, and 7. For measurement frequencies below  $\cong$ 1 kHz copper intercalated n-HfS<sub>2</sub> showed higher susceptance values (Fig. 5 and 7) compared to when copper was absent (Fig. 2). This suggests the presence of a capacitive element associated with faradaic copper intercalation  $C_0$ , in series with  $R_0$  in this lower frequency range.

Admittance data obtained after respectively 42 and 129 min of copper intercalation demonstrated a semicircular response in both the low and high frequency region, as shown respectively in Fig. 5 and 7. This observation may be attributable to differences in time constants for predominant circuit elements operating in high and low frequency ranges for copper intercalated n-HfS<sub>2</sub>. The overall impedance and admittance response experimentally observed for copper intercalated n-HfS<sub>2</sub> in acetonitrile could be modeled by the equivalent circuits shown in Fig. 3b. This circuit combines all the network elements explaining experimental observations in the high and low frequency regions. In these equivalent circuits the capacitance element  $C_o$  associated with reversible copper intercalation may be omitted in the high frequency region, whereas n-HfS2 space charge capacitance Csc may be eliminated at lower frequencies.

To investigate the influence of intercalated copper on  $n-HfS_2 C_{sc}$  in acetonitrile, impedance, and admittance responses were analyzed as previously described by others (16, 17).  $C_{sc}$  for  $\parallel$ -c oriented  $n-HfS_2$  in acetonitrile was obtained by subtracting susceptance values associated with



Fig. 8. Frequency dependent capacitance for  $\parallel$ -c oriented HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1*M* TBAPF<sub>6</sub>) at OCP (-0.295V vs. SCE). Geometric electrode area 0.06 cm<sup>2</sup>.

cell resistance,  $R_{\rm el}$ , from measured susceptance and by extrapolating capacitance data to infinite frequency (Fig. 8). A value for  $C_{sc}$  of  $\approx 3.2 \times 10^{-7}$  F/cm<sup>2</sup> at -0.295 V vs. SCE was obtained, higher than  $2.5 \times 10^{-7}$  F/cm<sup>2</sup> at -0.103V vs. SCE determined in a previous study (18) by us using similar single-crystal material, as expected at the more negative electrode potential used here. The dark  $C_{sc}$  for n-HfS<sub>2</sub> increased to  $1.4\times10^{-6}$  F/cm² after intercalating copper at -0.26V vs. SCE and remained essentially constant during the intervening (129 min) intercalation (Fig. 9). The potential of the dark n-HfS<sub>2</sub> electrode after 10-129 min intercalation was relatively constant and remained at  $\approx -0.1 V vs$ . SCE during 129 min of intercalation. This suggested an equilibrium concentration of intercalated copper present after about 10 min with further intercalation resulting in deeper copper incorporation into the crystal structure. For longer copper deposition times than 129 min unit activity copper was evident on the n-HfS<sub>2</sub> surface after which the



Fig. 9. Frequency dependent capacitance for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub> + 0.001M CuCl) after copper intercalation at -0.26V vs. SCE ( $\cong$ 10  $\mu$ A) for 10 min (curve A), 42 min (curve B), and 129 min (curve C). Geometric electrode area 0.06 cm<sup>2</sup>.

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Fig. 10. Cyclic voltammograms for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub> + 0.001M CuCl) after copper intercalation of -0.26V ( $\cong$ 10  $\mu$ A) for (A) 2 min, (B) 5 min, and (C) 10 min. Scan rate: 20 mV/s.

OCP became -0.4V vs. SCE. Cyclic voltammograms for copper intercalated n-HfS<sub>2</sub> in acetonitrile are shown in Fig. 10. The current peak corresponding to the reversible intercalation of copper was found to increase somewhat with time as the degree of copper intercalation was increased. Again this suggested that the semiconductor surface came relatively quickly to equilibrium (within  $\approx 10$  min) in the concentration of intercalated copper. For single-crystal n-HfS<sub>2</sub> used in this work the initial photopotential obtained prior to intercalation was 217 mV under 100 mW/cm,<sup>2</sup> ELH illumination, but was found to decrease to 55 mV upon initial copper intercalation, 36 mV after 5 min at  $\approx 10 \ \mu$ A and 18 mV after 10 min. No photopotential was observed after 42 min.

To gain further insight into the influence of intercalated copper on the behavior of n-HfS<sub>2</sub> admittance spectroscopy analysis of the admittance data was performed (21, 22). Results of this analysis are summarized in Fig. 11. In the simplest case the n-HfS<sub>2</sub>/electrolyte interface was assumed to consist of the space charge capacitance,  $C_{\rm sc}$ , connected in series with a bulk conductance  $G_{\rm el}$ . By comparing real and imaginary parts of the admittance equation for such an equivalent circuit, with the appropriate in-phase admittance components being obtained experimentally, the following relationship can be obtained

$$G/\omega = \frac{\omega C_{\rm sc}^2 G_{\rm el}}{G_{\rm B}^2 + (\omega C_{\rm sc})^2}$$
[6]

where *G* represents the measured in-phase cell conductance. By plotting  $G/\omega vs. \omega$  a maximum was given at

$$G/\omega_{\rm max} = C_{\rm sc}/2$$
 [7]

from which the space charge capacitance was determined. The peak  $G/\omega$  (where G corresponds to the total cell conductance) was identified with the n-HfS<sub>2</sub> space charge capacitance (curve A). Upon introducing CuCl into the electrolyte (curves B-D) evidence for an additional parameter in the equivalent circuit became evident. This was interpreted as corresponding to a faradaic conductance in parallel to  $C_{sc}$ , as shown by a linear log  $G/\omega$  vs. log  $\omega$  relationship (21, 22). At sufficiently low frequencies, the measured conductance became equal to the faradaic conductance. Thus, increased conductance in the low/middle frequency region for copper intercalated HfS<sub>2</sub> gave evidence for the faradaic intercalation-deintercalation reaction of copper.



Fig. 11. Relationship between G/ $\omega$  and  $\omega$  for  $\parallel$ -c oriented n-HfS<sub>2</sub> in CH<sub>3</sub>CN (0.1M TBAPF<sub>6</sub>) without (curve A) and with (curves B-E) 0.001M CuCl. Curve A at OCP -0.295V vs. SCE. Curves B, C, and D after 10, 42, and 129 min, respectively; copper intercalation at -0.26V ( $\cong$ 10  $\mu$ A) (OCP -0.1V); E after 130 min when copper deposition on the n-HfS<sub>2</sub> surface became evident (OCP -0.4V vs. SCE).

Unfortunately, increased conductance by the cell due to electron transfer at the interface overshadows effects from the space charge capacitance. Deposition of copper onto the n-HfS<sub>2</sub> surface (curve E) shifted the conductance associated with the faradaic reaction to even higher values. This suggested a higher exchange current density for this copper compared to that intercalated within the n-HfS<sub>2</sub>.

It has been suggested that metals intercalated into group IVB TMD's result in the formation of energy levels within the bandgap (7). Copper deintercalation from voltammetric experiments occur even in the absence of any measurable photopotential suggesting the formation of energy levels close to the conduction band during intercalation. A similar explanation has been postulated (23) for cyclopropylamine intercalated HfSe<sub>2</sub>. Intercalation by copper or iron into  $ZrS_2$  and  $HfS_2$  by others (13) has indicated that the electrode remains semiconducting at intercalation levels below HfCu<sub>0.22</sub>S<sub>2</sub>. It is probable, that in work discussed here, the degree of copper intercalation may have been higher than calculated using the diffusion coefficient  $10^{-8}$  cm<sup>2</sup>/s. To preserve n-HfS<sub>2</sub> semiconducting properties the total charge passed during copper intercalation should be lower than 0.3C per 1 cm<sup>2</sup> for ||-c oriented material. Such intercalating photoelectrodes may eventually be of interest in liquid nonaqueous or solid polymer electrolyte cells. In the latter cells the deintercalated transition metal ions would be stored in close proximity to the electrode/solid electrolyte interfacial region.

### Conclusion

The  $\parallel$ -c oriented n-HfS<sub>2</sub>/nonaqueous electrolyte interface can be modeled by equivalent circuits consisting of space charge capacitance, cell resistance, and frequency dependent R-C elements. In the presence of intercalated copper in n-HfS<sub>2</sub> increased faradaic conduction became evident related to intercalation-deintercalation at the interfacial region. The space charge capacitance of n-HfS<sub>2</sub> in acetonitrile was obtained by eliminating the capacitive response of frequency dependent elements and was found to be of the order 10<sup>-7</sup> F/cm<sup>2</sup>. This increased to 10<sup>-6</sup> F/cm<sup>2</sup> after intercalating >18 m/o copper into this semiconductor. Electrochemical copper deintercalation proceeded in the dark suggesting that the semiconductor became degenerate at this degree of intercalation with a high population of electrons being localized close to the n-HfS<sub>2</sub> conduction band.

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# Electrochemical Impedance Spectroscopy on 3-D Inhomogeneous Surfaces

# **Corrosion in Neutral Aerated Solutions**

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# ABSTRACT

A physical model describing corrosion processes on a 3-D inhomogeneous surface is developed. The derived theoretical transfer function is discussed in terms of transport and charge-transfer controlled corrosion steps. Simulations show "depressed capacitive semicircles" depending on the hydrodynamic conditions and the metal corrosion rate. In principle, the differential corrosion rate can be determined by an exact analysis of the complete transfer function of the system un-der test. The use of the polarization resistance and the application of the well-known Stern-Geary relation lead to exact information on the corrosion rate under certain limiting conditions only. The model is tested by experimental impedance results obtained for the system Fe (RDE)/0.5M Na<sub>2</sub>SO<sub>4</sub>, aerated,  $6 \le pH \le 8$ , T = 298 K in the absence and in the presence of hexan (1,6)-biphosphonic acid as inhibitor. The system-specific parameters obtained by a nonlinear fit procedure are discussed in terms of the model used. The differential corrosion rate is checked by nonelectrochemical solution analysis. The porous oxidic 3-D surface layer acts as an interphase inhibitor.

Real surfaces of solid electrodes (metals, semiconductors, oxides, etc.) are always inhomogeneous because of the distribution of active and inactive domains on an atomic or macroscopic scale.

Atomic domain structure arises by the crystallographic and physical nature of solid surfaces, i.e., the density of crystal imperfections as grain and subgrain boundaries, monoatomic steps with kinks, flat terraces, adatoms, points of emergence of edge and screw dislocations, atomic disorder, lattice distortions, etc. It is a well-known fact that these surface singularities may act as active growth or dissolution centers in metal deposition or dissolution processes, as active centers for electron charge-

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transfer in redox processes, as active surface states of semiconductor electrodes, and as preferential sites in sorption processes.

Macroscopic inhomogeneity may arise either by the morphology of the solid surface or by sorption phenomena leading to partial blocking effects.

The distribution of a solid surface inhomogeneity can be considered approximately as a 2-D structure if the extension of the domains perpendicular to the phase boundary solid/liquid does not exceed atomic or molecular dimensions. The electrochemical kinetics of solid electrodes must be strongly influenced by 2-D surface inhomogeneities changing transport, charge transfer, adsorption, and electrocrystallization steps. However, these influences

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