Semiconductor Electrodes

XXXVI. Characteristics of n-MoSe₂, n- and p-WSe₂ Electrodes in Aqueous Solution

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ABSTRACT

Capacitance and voltammetric measurements were employed to investigate the electrochemical and photoelectrochemical (PEC) behavior of n-WSe₂, p-WSe₂, and n-MoSe₂ single crystal electrodes in aqueous solutions containing various redox couples (Br⁻/Br₂, I⁻/I₃⁻, Fe(CN)₆³⁻/Fe(CN)₆⁴⁻, Fe³⁺/Fe⁴⁺, HV⁺/HV₂⁺, and MV⁺/MV²⁺, where HV is heptyl viologen and MV is methyl viologen). In supporting electrolyte (0.5M Na₂SO₄), the conduction band edges of MoSe₂ and WSe₂, determined from the capacitance measurement, are at -0.14 and -0.44V vs. SCE, respectively, and the valence band edge of WSe₂ is at 0.93V vs. SCE. A bandgap of 1.4 eV for WSe₂ was determined either from the photocurrent action spectrum or from the capacitance measurement. The specific effects of iodide on the capacitance and voltammetric behavior of layer-type compounds are compared. The characteristics of several PEC cells are also described.

The application of semiconductor electrode photoelectrochemical (PEC) cells (1) for the utilization of solar energy for the production of electricity or chemical species depends on the discovery of inexpensive and abundant materials with an energy gap which matches the solar spectrum and which are capable of stable operation. Thus there has been an active search for new semiconductor materials for PEC cells which meet these requirements.

Kaufman and coworkers (2) introduced the concept of using layer-type electrodes (e.g., MoSe₂, MoS₂, WSe₂) for such applications and a number of recent papers (3-6) have described PEC cells based on these materials. These cells show quite good efficiencies and good stability in aqueous and acetonitrile solutions containing redox couples with reasonably positive redox potentials (e.g., I⁻/I₃⁻). Wrighton and co-workers demonstrated that MoSe₂ and MoS₂ can even photo-oxidize chloride in highly concentrated aqueous LiCl solutions (3).

The behavior and efficiencies of these cells depend strongly on the nature of the electrode surface (4-8). A wide range of scatter in the electrochemical parameters (e.g., flatband potential, Vₚₚ) and the PEC behavior is reported from different laboratories. These different results are apparently due to the significant sample-to-sample variations in the morphology of crystals. For example, the presence of exposed edges in the van der Waals surface (C-axis) has been shown to lead to significant dark anodic currents at n-type electrodes and lower photocurrent efficiencies (4c, 8b). In this report, we describe the voltammetric and impedance measurements of some carefully selected and well-behaved n-MoSe₂, n- and p-WSe₂ single crystals. Some physical properties, e.g., Vₚₚ and the bandgap, Eₜₜ, of WSe₂, obtained by different techniques are compared. The specific effect of iodide on the onset photopotentials of layer-type compounds is compared with Vₚₚ obtained by capacitance measurements. We also discuss the performance of several solar cells composed of n-MoSe₂ and (halogen/halide) redox couples.

Experimental

The semiconductors used, n-MoSe₂, n- and p-WSe₂, were single crystals generously donated by Dr. Barry Miller and Dr. Frank DiSalvo, Bell Laboratories. The detailed procedures for selecting, mounting, cleaning, and etching the single crystals and preparing the ohmic contacts are similar to those previously reported (4). The electrodes studied here showed mirror-like surfaces with no obvious edges and pits on the surfaces when examined at a magnification of 100X. They produced negligibly small dark oxidation currents (< 1 μA cm⁻²) in 0.5M Na₂SO₄ between -0.5 and 1V vs. SCE. Typically, the electrode areas of the semiconductors were 0.03-0.2 cm². If not otherwise mentioned, the exposed surface is the van der Waals surface (C-axis).

A conventional three-electrode, single-compartment cell was used for all experiments. The electrochemical cell (volume ~ 25 ml) contained Pt disk and semiconductor working electrodes and was fitted with a flat Pyrex window for illumination of the semiconductor electrode. A platinum foil (~ 40 cm²) was used as the counterelectrode in the voltammetric and impedance measurements. An aqueous saturated calomel electrode (SCE) was used as the reference electrode.

The voltammetric experiments and the solar cell measurements were performed with the same apparatus and procedures as reported previously (4). The light source used in the study of the PEC effect was an Oriel Corporation (Stamford, Connecticut) 450W Xe lamp. Experiments designed for specific wavelengths employed an Oriel 7240 grating monochromator with a 20 nm bandpass. A red filter (590 nm cut-on) was used with the Xe lamp. The radiant intensity was measured with an EG & G (Salem, Massachusetts) Model *Electrochemical Society Active Member.

Key words: capacitance, voltammetry, impedance, photoelectrochemical behavior, solar cells.

1 A solar power conversion efficiency of 10.2% has been reported for a cell based on n-WSe₂ and I⁻/I₃⁻ systems (5).

All impedance measurements were carried out with an aqueous 0.5M Na₂SO₄ solution, if not otherwise mentioned. The electrical circuit allowed the application of a variable potential at the semiconductor electrode with respect to the reference electrode. The impedance was measured between this working electrode and a large (~40 cm²) counterelectrode. The applied potential was controlled potentiostatically, and the capacitance was measured as the 90° quadrature signal from a lock-in amplifier (Princeton Applied Research, Model HR-8) with excitation by an external a-c generator via the potentiostat. The amplitude of the sinusoidal wave superimposed on the d-c bias potential was ~5 mV. The measured capacitances were calibrated by replacing the electrochemical cell by a set of standard capacitors. The quantity measured was the equivalent series capacitance, C, since the dissipation factor øRC, where ø is the angular frequency and R is equivalent series resistance, was much smaller than unity for all systems studied here, as shown in the results below. The measured impedance values were not changed when the counterelectrode was partially lifted out of the solution; thus the counterelectrode did not contribute significantly to the reported capacitances. All impedance measurements were performed in the dark.

Reagent grade chemicals were used without further purification. All solutions were prepared from triply distilled water and were deoxygenated for at least 30 min with purified nitrogen before each experiment. All experiments were carried out with the solution under a nitrogen atmosphere.

Results

Impedance measurements.—The capacitance of an electrode as a function of frequency and potential was a useful indicator of the electrode quality. The n-MoSe₂ and n-WSe₂ electrodes were subjected to impedance measurements in supporting electrolyte solutions, if not otherwise mentioned, at d-c bias potentials where the residual currents were negligibly small (<1 μA cm⁻²). Thus the measured value of C is the equivalent differential capacitance of the interface, with no faradaic contribution. If the presence of the oxidized form of a redox couple was required, its concentration was kept as low as possible to prevent substantial reduction current, which might distort the Mott-Schottky plots.

The value of the flatband potential, VFB, was determined from the intercept of the plot of 1/C² vs. V potential according to the Mott-Schottky equation (9)

\[
\left( \frac{1}{C} \right)^2 = \frac{2}{\varepsilon_0 \varepsilon_r n_D} \left( \frac{kT}{|V - V_{FB}|} - \frac{1}{e} \right)
\]  

In this equation ε is the dielectric constant of the semiconductor, ε₀ is the permittivity of free space, n is the donor density, nD, for n-type and the acceptor density, nA, for p-type semiconductors, ε₀ is the absolute value of the charge of the electron, T is the absolute temperature, and k is the Boltzmann constant.

n-MoSe₂.—As shown in Fig. 1a, at frequencies between 1 and 10 kHz, a linear C⁻² vs. V relationship was observed over a considerable potential range. Since the capacitance at these potentials is frequency independent, the intercept of the Mott-Schottky plot gives the flatband potential after correction for the thermal term in Eq. [1] and the potential drop across the Helmholtz double layer (i.e., for the contribution of capacitance of the Helmholtz layer). The flatband potential of this n-MoSe₂ electrode was ~0.0 V vs. SCE at pH 4.5.

If we take the dielectric constant perpendicular to the C-axis, ε', as 6.8 (10), the slope of the Mott-Schottky plot yields nD ~ 1.2 × 10¹⁷ cm⁻³. With this value of the donor density of the MoSe₂ single crystal, the location of conduction band edge, E_c, was calculated from Eq. [2] (9), assuming that the donor impurities are completely ionized. Since N_c >> n_D (see below)

\[ n_D = N_c \exp \left[ \frac{-(E_F - E_c)}{kT} \right] \]  

in which E_F is the Fermi energy and N_c is the density of the effective states in the conduction band, which is given by

\[ N_c \approx \frac{2}{h^2} \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} \]  

where h is the Planck constant and M* is the effective mass of electrons in the conduction band. With the assumption M* ~ M₀ (11), in which M₀ is the mass of a free electron, N_c was estimated to be ~ 2.5 × 10¹⁵ cm⁻³. Thus, E_c was ~0.14 eV above the Fermi level energy, i.e., the conduction band edge is located at a potential ~0.14 V vs. SCE.

The frequency independence of the capacitance implies that no oxide layer was on the surface of MoSe₂. The presence of an oxide layer often leads to frequency dispersion in the measured capacitance values because of dielectric relaxation in this layer.

As shown in Fig. 1b, the flatband potential of the n-MoSe₂ electrode was independent of pH, at least in the range studied (0-8). This finding further confirms the absence of an oxide layer on the electrode surface.

The flatband potential of the n-MoSe₂ electrode shifted to a more negative potential when iodide was present in the solution (Fig. 2a). Moreover, addition of a small amount of triiodide (0.25 mmole) shifted VFB to an even more negative potential. However, bromide had no effect on VFB (Fig. 2b). These results parallel those obtained by the voltammetric measurements which are described later. We can also estimate the resistivity, ρ, of this n-MoSe₂ electrode from the mobility, μ, of electrons and the free electron density, nₑ, based on Eq. [4]

\[ \rho \approx 1/\left( \varepsilon_0 n_e \mu \right) \]  

Here we neglect the contribution from the minority

Notes:

1. The ε value of MoSe₂ was assumed close to that of MoS₂. The ε of MoS₂ has been reported by Evans et al. (10).

2. Here we assume that electrons in MoS₂ have similar effective mass to that in WSe₂ (11).
charge carriers. With $\mu_e = 10 \sim 50 \text{ cm}^2\text{ V}^{-1}\text{ sec}^{-1}$ (12) and the assumption that the donors are completely ionized, $\rho$ can be estimated to be $1 \sim 5 \Omega\text{-cm}$. 

$n$-WSe$_2$—The general behavior for $n$-WSe$_2$ electrodes was similar to that of the $n$-MoSe$_2$ electrode described above. At frequencies between 0.2 and 2 kHz, a linear $C^{-2}$ vs. $V$ relationship was obtained over a considerable potential range and the capacitance was essentially frequency independent (see Fig. 3). Thus, $V_{FB}$ of this $n$-WSe$_2$ electrode was $\sim -0.32\text{V vs. SCE}$. Assuming that $\varepsilon_e \sim 10$ for WSe$_2$ (13), we estimate a donor density of this electrode of $\sim 2.0 \times 10^{19} \text{ cm}^{-3}$. According to Hicks (11), $M_e^* \sim M_h^* \sim M_e$; hence $N_e$ was $\sim 2.5 \times 10^{19} \text{ cm}^{-3}$ and $E_c$ was $\sim 0.12 \text{ eV}$ beyond the $V_{FP}$ Fermi level energy. With $\mu_e = 100 \sim 150 \text{ cm}^2\text{ V}^{-1}\text{ sec}^{-1}$ for the $n$-WSe$_2$ single crystals (12), the resistivity of this $n$-WSe$_2$ is $0.1 \sim 0.2 \Omega\text{-cm}$. 

$p$-WSe$_2$—As shown in Fig. 4a, $p$-WSe$_2$ electrodes show quite different capacitance-potential curves from their $n$-counterparts. With potentials positive of $0.05\text{V vs. SCE}$, a linear $C^{-2}$ vs. $V$ relationship was observed at frequencies of 1-10 kHz (Fig. 5a). For potentials more negative than $0.05\text{V vs. SCE}$, frequency dispersion of capacitance occurs. The capacitance at $-0.2\text{V vs. SCE}$ for $p$-WSe$_2$ follows a (frequency)$^{-2}$ dependence at frequencies $> 2 \text{ kHz}$. The origin of this frequency dispersion is still not clear, but might involve the presence of interface states or the onset inversion coupled with a faradaic process. Further investigations are required to explain this behavior.

ASSUMING THAT $\varepsilon_e \sim 10$ FOR WSe$_2$ (13), WE ESTIMATE A DONOR DENSITY OF THIS ELECTRODE OF $\sim 2.0 \times 10^{19} \text{ CM}^{-3}$. ACCORDING TO HICKS (11), $M_e^* \sim M_h^* \sim M_e$; HENCE $N_e$ WAS $\sim 2.5 \times 10^{19} \text{ CM}^{-3}$ AND $E_c$ WAS $\sim 0.12 \text{ eV}$ BEYOND THE $V_{FP}$ FERMI LEVEL ENERGY. WITH $\mu_e = 100 \sim 150 \text{ CM}^2\text{ V}^{-1}\text{ SEC}^{-1}$ FOR THE $n$-WSe$_2$ SINGLE CRYSTALS (12), THE RESISTIVITY OF THIS $n$-WSe$_2$ IS $0.1 \sim 0.2 \Omega\text{-CM}$.

4 An approximate value was taken here since the exact dielectric constant at the frequency range studied is unknown (13).
Since frequency dispersion is found only at potentials negative of 0.0V vs. SCE which is well negative of V_{FB}, it has essentially no effect on the Mott-Schottky plots as shown in Fig. 5a. V_{FB} of this p-WSe₂ electrode was thus ~ 0.72V vs. SCE. If $\varepsilon = 10$ for WSe₂, the acceptor density of this electrode can be estimated as ~ $5 \times 10^{18}$ cm⁻³. The density of effective states in the valence band of WSe₂, $N_v$, the energy of the valence band edge, $E_v$, and the resistivity of this p-WSe₂ are shown in Table I. As found with n-MoSe₂, V_{FB} of p-WSe₂ is pH independent (Fig. 5b) in the pH range studied.

The capacitance-potential plots which correspond well to that expected of the semiconductor space charge capacitance (e.g., well-behaved Mott-Schottky plots and frequency independence) found with edge-free electrode material (e.g., Fig. 4a for n-WSe₂) can be contrasted with that found with material which contains some edges and discontinuities on the surfaces (designated "type E" in previous studies (4c)). For type E n-WSe₂ electrodes, discontinuities are seen in the capacitance plots (Fig. 4b) as well as hysteresis effects and frequency dispersion. Thus capacitance plots are useful in distinguishing electrode material which produces low dark currents and efficient PEC cells from less efficient (type E) material.

**Volatmetric behavior.**—Electrochemical and PEC behavior of n- and p-WSe₂ electrodes have been reported previously (4). The following results mainly involve n-MoSe₂ electrodes. The voltammetric behavior of iodide at n-MoSe₂ and Pt is shown in Fig. 6. With or without $I^-$ in the solution, in the dark a negligibly small background current was observed (curves a and b). Under illumination, with slowly chopped light (wavelength ~ 590 nm), an anodic photocurrent commencing at 0.5V vs. SCE (curve c) was observed in the supporting electrolyte containing 0.5M H₂SO₄. No cathodic photocurrent was found, as expected for an n-type material. In the presence of 1.0M NaI, the onset photopotential, V_{on}, shifted to a much more negative potential (~ -0.26V vs. SCE) (curve d). The addition of iodine (0.10M) to the solution shifted V_{on} to slightly more negative potentials (~ -0.30V vs. SCE) (curve e). Note that the specific effects of iodide and triiodide on V_{on} parallel their effects on the V_{FB} determined from impedance measurements. The current-potential curves on Pt (curve f) and n-MoSe₂ in an I⁻/I₃⁻ solution yield an "underpotential" for I⁻ photo-oxidation at n-MoSe₂ (V_{on} ~ -0.50V). This value agrees fairly well with the experimental open-circuit voltage, V_{oc}, of an n-MoSe₂/I₂⁻/Pt PEC cell described below.

The voltammetric data and photopotentials of other redox couples on n-MoSe₂ electrodes are summarized in Table II. For redox couples with standard potentials, Vₖ, much more negative than V_{FB}, no photoeffect was observed. The V_{oc} for the redox couples with V_{FB} < V₀ < 0.25V vs. SCE (except for I⁻/I₃⁻) are nearly independent of the redox couples and are close to V_{FB} (~ 0.0V vs. SCE). For redox couples with 0.50V < V₀ < 1.0V vs. SCE, V_{on} depended on the particular species and varied from ~ 0.25V for Br⁻ to ~ 0.50V for background oxidation. The photo-oxidation of compounds with V₀ more positive than for water oxidation is uncertain because of the background photoreaction. It is interesting to compare the reduction of various oxidants on n-MoSe₂ electrodes in the dark. As shown in Fig. 7, reduction of bromine (curve a) and Fe²⁺ (curve b) occurs at potentials negative of 0.5V vs. SCE.
Fig. 6. Voltammetric curves of n-MoSe₂ and Pt in 0.5M Na₂SO₄ and 0.5M H₂SO₄. Scan rate, 10 mV/sec. Light source, 450W Xe lamp with a 590 nm cut-on filter. (a) Dark cyclic voltammogram on n-MoSe₂. (b) Dark cyclic voltammogram on n-MoSe₂. Solution contained 1.0M NaI. (c) Voltammetric curve under illumination by chopped red light on n-MoSe₂. No iodide or iodine in solution. (d) Current-potential curve under illumination by chopped red light on n-MoSe₂. Solution contained 1.0M NaI. (e) Same conditions as in (d) but solution contained 1.0M NaI and 0.10M iodine. (f) Cyclic voltammogram on Pt. Solution contained 0.10M NaI. Initial potential at +0.10V vs. SCE.

Fig. 7. Voltammetric curves in the dark on n-MoSe₂ electrode in 0.50M Na₂SO₄. Scan rate, 10 mV/sec. (a) Solution contained 1.0M NaBr and 0.02M bromine. (b) Solution contained 0.10M Fe²⁺, 0.02M Fe³⁺, and 0.50M H₂SO₄. (c) Solution contained 1.0M NaI and 0.10M iodine. (d) Solution contained 0.1M Fe(CN)₆⁴⁻ and 0.1M Fe(CN)₆³⁻.

by immersing the semiconductor electrode and a suitable counterelectrode in an aqueous solution containing the appropriate redox couple.

The n-MoSe₂/iodide, triiodide/Pt system.—Photovoltaic cells were set up with an n-MoSe₂ photoanode and a platinum foil cathode immersed in a solution containing 1.0M I⁻, 0.025M I₃⁻, and 1.0M H⁺. The action spectrum of the short-circuit photocurrent, iₚ, is shown in Fig. 8. The bandgap of WSe₂ and MoSe₂ can be determined from the (νhν)² vs. hν plot (for a direct transition) or the (νhν)² vs. hν plot (for an indirect transition) near the bandedge region (14). E₀ here is the quantum efficiency (proportional to iₚ) and hν is the photon energy. As shown in Fig. 9, both (νhν)² vs. hν and (νhν)² vs. hν plots give fairly good straight lines. The nature of the fundamental optical transition is thus ambiguous as simply determined from the action spectrum. However, the determination of E₁ from the capacitance measurements, as discussed later, is helpful in deciding on the value of E₀.

The i-V characteristics of this cell under irradiation, shown in Fig. 10, yields a fill factor of 0.53. The light intensity dependence of the open-circuit photovoltage and the short-circuit photocurrent of the cell is shown in Fig. 11. Irradiation of the n-MoSe₂ crystal with the full visible (longer than 590 nm and infrared filtered) output (150 mW/cm²) from a 450W Xe lamp focused onto the photoelectrode surface yielded a constant iₚ ~ 50 mA/cm² and an open-circuit photovoltage ~0.59V. The photocurrent and photovoltage were essentially the same and the electrode surface showed no apparent change during the experimental period (~8 hr).

Table II. Voltammetric data, onset photopotential* and underpotential at n-MoSe₂

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>V* (V vs. SCE) **</th>
<th>V₁ (V vs. SCE)</th>
<th>ΔV = V₁ − V* (V)</th>
<th>Experimental underpotential, **</th>
<th>Theoretical underpotential, ***</th>
<th>ΔV' = Vₓ − V* (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻/Cl₂</td>
<td>1.12</td>
<td>0.99</td>
<td>-0.13</td>
<td>-0.29</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>H₂O/O₂</td>
<td>0.99</td>
<td>0.99</td>
<td>-0.00</td>
<td>-0.00</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>Br⁻/Br₂</td>
<td>0.53</td>
<td>0.30</td>
<td>-0.23</td>
<td>-0.33</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>Fe(II)/Fe(III) (1N H₂SO₄)</td>
<td>0.22</td>
<td>0.22</td>
<td>-0.00</td>
<td>-0.00</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>Fe(II)-EDTA/Fe(III)-EDTA (pH = 5)</td>
<td>-0.15</td>
<td>-0.15</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>HV²/H₂O²⁺</td>
<td>-0.48</td>
<td>-0.48</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
<tr>
<td>MV²⁺/MV⁴⁺⁸⁻</td>
<td>-0.66</td>
<td>-0.66</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
<td>No photoeffect</td>
</tr>
</tbody>
</table>

* The onset photopotential, V₁, here is defined as the potential at which 1% of the limiting or maximal photocurrent is observed.

** V* = standard potential.

*** Vₓ is based on that obtained from the impedance measurement. It is -0.3V vs. SCE for iₚ and 0V for other redox couples.

† HV = heptyl viologen (1,1'-dlheptyl-4,4'-bipyridyl).

‡ MV⁺ = methyl viologen (1,1'-dimethyl-4,4'-bipyridyl).

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The n-MoSe₂/bromide, bromine/Pt system.—When a solution containing 1.0M Br⁻, 0.02M Br₂, and 1.0M H⁺ was used as the electrolyte, a lower open-circuit photovoltage (0.52V), and a lower fill factor (0.25) were found (Fig. 10) (15). However, the short-circuit photocurrent was higher (~60 mA/cm²) under the same intensity irradiation. This difference is probably attributable to the lower light absorbance by the Br⁻.

Solar cells with higher fill factors but lower open-circuit voltages have been reported by Ang et al. (15).

Discussion

The (n-MoSe₂/solution) interface.—A model for the behavior of the n-WSe₂/solution interface in aqueous electrolyte has been discussed previously (4). A similar model, i.e., the recombinative model, is applicable to explain the voltammetric behavior of n-MoSe₂ in various redox electrolytes. Vₒ of the n-MoSe₂ electrode determined from the impedance measurement is ~0.0V vs. SCE. When no specific adsorption occurs, the expected most negative Vₒ value was obtained for redox couples with 0 ≤ Vₒ ≤ 0.5V vs. SCE. (The I⁻/I₃⁻ couple involves adsorption effects and is discussed later.) For redox couples with Vₒ more positive than 0.5V, however, Vₒ occurs at more positive potentials. This can be ascribed to the effects of dark reduction of the oxidized form of redox couples. Recall that considerable dark reduction of the Fe(CN)₆³⁻ takes place at a potential ~0.3V positive of Vₒ (Fig. 7). The reduction of I₃⁻ occurred at more negative potentials probably because the bandedges shift with specific adsorption as suggested by the impedance measurements and the voltammetric experiments. For the couples with Vₒ more positive than 0.5V vs. SCE, e.g., Fe³⁺/ Fe⁷⁺ and Br⁻/Br₂, the reduction occurred at a potential ~0.5V vs. SCE. This positive shift of the zero current or onset potential might involve induced positive surface charges. The positive shift of Vₒ is attributed to the dark reduction of photogenerated species. There are several different mechanisms by which such dark reduction can occur at an n-type material at potentials significantly positive of that for Vₒ (i.e., of the energy of the conduction bandedge) in the supporting electrolyte.
lyte solution. One involves a recombination model and the existence of filled surface states or intermediate levels at energies within the bandgap which can be emptied by electron donation to solution oxidants (or by photogenerated holes in the valence band) (16). The lack of detection of such states in the capacitance plots and the lack of significant dark anodic current implies that such states are very "slow" with respect to emptying via the conduction band. An alternative mechanism involves positive charge injection into the surface states (via solution species or photogenerated holes) causing a shift in the conduction band edge toward more positive potentials and allowing electron transfer directly from the conduction band. This latter mechanism should result in a shift in $V_{FB}$ in the presence of the redox couple; determination of such a shift by capacitance measurements are made difficult by the interference of faradaic reactions in determination of the actual space charge capacitance. Inversion could also cause such a shift in the bandedge (8); however, the location of the $Fe^{3+}/Fe^{2+}$ couple is such that inversion would not occur at these potentials. A schematic representation of the energetic situation at the n-MoSe$_2$/solution interface, neglecting any band bending and specific surface interactions, is shown in Fig. 13. A direct-transition bandgap of 1.4 eV$^8$ is taken here based on the agreement of $E_g$ determined from the action spectrum and the capacitance measurements for WSe$_2$ electrodes, discussed later.

Photovoltaic cells based on n-MoSe$_2$ electrodes.—The n-MoSe$_2$/I$^-$/I$_3^-$/Pt system shows a $V_{oc}$ of 0.59V which is identical to the value predicted either from the experimental, $\Delta V$, or the theoretical, $\Delta V'$, underpotential 0.59V, as shown in Table II. For the n-MoSe$_2$/Br$^-$, $^8$An indirect transition bandgap of 1.1 eV has been reported (8c). An $E_g$ of 1.4 eV has also been reported (7).
discrepancy can be attributed to the dark reduction processes or to a shift in the bandedges toward positive potentials because of induced positive surface charges. Besides this striking difference in Voc between the two systems, we also note that the fill factors for these two systems were also quite different, probably again because of the effects discussed above.

Eg of WSe2—As shown in Table I, Ev and Ec of WSe2 in aqueous solution correspond to 0.93 V and –0.44 V vs. SCE, respectively. The uncertainty of Ev and Ec due to the uncertainties in the dielectric constant taken over a wide pH range is about 0.05 eV. This agrees fairly well with the direct transition bandgap determined from the action spectrum of the photocurrent.

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