Cation Effect on the CdSe-Liquid Junction

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ABSTRACT

The effect of cation on the CdSe/polysulfide photoelectrochemical (PEC) solar cell has been investigated. The current-potential response of the polysulfide electrolyte on a platinum electrode was measured as a function of the alkaline metal cation in solution. There was a ~33 mV shift in the redox potential and an increase in the current when the cation was changed from Na+ to Cs+. The performance of the CdSe/polysulfide PEC cell with both polycrystalline and single-crystal semiconductor electrodes increased in the open-circuit potential, the short-circuit current, the fill factor, and the energy conversion efficiency when Cs polysulfide was used as compared with K or Na polysulfide. Impedance measurements were made on the electrodes in polysulfide solutions and polysulfide solutions with the different cations. The results for both electrolytes showed a negative shift in the flatband potential, an increase in the apparent charge-carrier concentration, and an increase in the frequency dispersion of the measurements with the addition of Cs+. The impedance measurements also showed a dependence on the orientation of the CdSe crystal. The effects above are related to a combination of a change in the solution and the surface of the semiconductor. The stoichiometric distribution of the polysulfide species changes with the addition of Cs+ and the surface of the semiconductor changes, facilitating charge transfer across the semiconductor/electrolyte interface.

Initial work on the cadmium chalcogenide/polysulfide PEC solar cell was published by Gerischer1 and Ellis et al.2 A great deal of work has been performed since those original studies on improvements to the semiconductor, the surface condition of the semiconductor electrode, and the electrolyte. CdS, CdSe, CdTe and mixed CdSeTe,3,4,5,6,7,8,9,10 have been investigated to increase the energy-conversion efficiency and stability of the PEC cells. Several researchers have investigated cadmium chalcogenide PEC solar cells using polycrystalline electrodes. Long-term stabilities have been demonstrated with conversion efficiencies up to 5% for polycrystalline CdSe.10 The semiconductor/liquid junction solar cell is particularly well suited to low cost polycrystalline electrodes.

Changes in the make-up of the polysulfide electrolyte have a large effect on the performance of the solar cell; the effect of hydroxide ion concentration and the sulfide-to-sulfur ratio have been investigated by some researchers.11-15 Both the hydroxide ion and the sulfur-to-sulfide ratio affect the equilibrium concentration of the electroactive species, the stability of the solution, and the light absorption by the solution. Changing the cation in the solution leads to changes in the performance of the cell.16,17 The cation is not involved directly in the redox reactions at the semiconductor electrode but the performance of the cell increases significantly when the cation in solution is changed from Na+ or K+ to Cs+. The improvement is in the stability of the semiconductor, the open-circuit photovoltage ($V_{oc}$) and the photocurrent response. The flatband potential ($V_{fb}$) also shifts negative with the addition of Cs+; yet the only difference between the cations is the ionic radius and thus the charge density. The change in cation can affect the surface of the semiconductor by altering the degree of adsorption, or by incorporation into the semiconductor itself; or by changing the activity of the species in solution, or the distribution of the polysulfide species.

The CdSe/polysulfide system is examined here. First, the current-potential response of polysulfide on a platinum electrode was measured. Impedance measurements were made to determine how the change in cation affects the band energies and charge-carrier concentration of the semiconductor. The measurements were made in a variety of systems to separate the different effects: CdSe single-crystal electrodes in hydroxide electrolytes with the different cations, CdSe single-crystal electrodes in polysulfide with the different cations, and with CdSe polycrystalline electrodes in polysulfide. The impedance measurements indicate changes in the performance of both single-crystal and polycrystalline CdSe/polysulfide PEC cells with the different cations.

Polysulfide Electrolyte

Polysulfide solutions have been studied extensively in the pulp and paper industry. The equilibrium relationships of the solution species are presented in Table I.16 Lessner et al.17 demonstrated that active species participating in the reduction at the cathode is supersulfur, [S$_n^-$]. The concentration of [S$_n^-$] is maintained in the solution by the dissociation of [S$_{n+1}$]$^-$ by reaction 7. In those studies on platinum, the rate of reduction was limited by both the charge-transfer reaction and the homogeneous chemical reaction maintaining the supersulfur concentration. These findings were confirmed in studies of the influence of aprotic solvents on the current-potential response. Giggenbach and others have shown that with the addition of dimethyl formamide (DMF), the equilibrium of reaction 7 was shifted in favor of [S$_4^-$].18,19 Lessner showed that the addition of DMF in the polysulfide solutions increased the current density, again indicating that it was tied directly to the concentration of [S$_4^-$] at the cathode.16

The electroactive species and rate-limiting step at the photoanode have been the subject of several papers.14-24-26 It
was thought that the rate of sulfur dissolution was the rate-limiting step. Winnick et al., in a survey of measurements of the peak current decay with varying sulfur-to-sulfide ratios in the electrolyte, showed that the performance depends on the [S$_2^-$] concentration. Ardon, in another study on the temperature dependence of the short-circuit current, demonstrated that the activation energy was approximately 71 kJ/mol while that for sulfur dissolution was 10.5 kJ/mol. It was shown that the higher activation energy was tied to the equilibrium reaction between [S$_2^-$] and [S$^2$]-, a combination of reactions 3 and 4 in Table I:

\[
2S^2- + \frac{4}{3} H_2O \rightarrow \frac{2}{3} S_2 + \frac{4}{3} HS^- + \frac{4}{3} OH^- \quad [8]
\]

At the photoanode, disulfide is oxidized to supersulfide, with the disulfide concentration maintained by the homogeneous reaction of [S$_2^-$] to [S$^2$]-. At the cathode, the reduction of [S$_2^-$] to [S$^2$]- takes place, with the [S$^2$]- maintained by the homogeneous dissociation of [S$_2^-$] to [S$^2$]-. The polycrystalline surface is a nonideal semiconductor-liquid interface because of the grain boundaries, dislocations, and inclusions present in the material. To better understand the performance improvements with Cs$^+$, the semiconductor/electrolyte interface was simplified. Experiments were conducted on n-Cds single crystals with different crystal faces exposed to the electrolyte. To separate the different effects, impedance experiments were performed in both polysulfide and hydroxide electrolytes with the different cations.

### Experimental

The solutions were 3M in the hydroxide, 1M in H$_2$S, and 1M in sulfur. They were prepared by bubbling H$_2$S through the appropriate hydroxide solutions. NaOH, KOH, CsOH, and tetraethylammonium hydroxide were used. The mass of H$_2$S added to the hydroxide solution and the pH change depended on the [S$_2^-$] concentration. 14 Ardoin, in another study on the temperature dependence of the short-circuit current, demonstrated that the activation energy was approximately 71 kJ/mol while that for sulfur dissolution was 10.5 kJ/mol. It was shown that the higher activation energy was tied to the equilibrium reaction between [S$_2^-$] and [S$^2$]-, a combination of reactions 3 and 4 in Table I:

<table>
<thead>
<tr>
<th>K</th>
<th>Reaction</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Range (°C)</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_1$</td>
<td>H$_2$S $\leftrightarrow$ H$^+$ + HS$^-$</td>
<td>-1158</td>
<td>-3.10</td>
<td>15-35</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$</td>
<td>HS$^-$ $\leftrightarrow$ H$^+$ + S$^2$-</td>
<td>-1426</td>
<td>-12.0</td>
<td>15-270</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_3$</td>
<td>S$_2^-$ + H$^+$ + OH$^-$ $\leftrightarrow$ 2S$^2$- + H$_2$O</td>
<td>-4.2</td>
<td>0.35</td>
<td>20-140</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_4$</td>
<td>2S$^2$- + H$^+$ + OH$^-$ $\leftrightarrow$ 3S$^2$- + H$_2$O</td>
<td>-1.75</td>
<td>0.35</td>
<td>20-140</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_5$</td>
<td>3S$^2$- + H$^+$ + OH$^-$ $\leftrightarrow$ 4S$^2$- + H$_2$O</td>
<td>3.6</td>
<td>0.25</td>
<td>20-140</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_6$</td>
<td>4S$^2$- + 8 OH$^-$ + H$_2$O $\leftrightarrow$ 2S$_2$O$^2$- + 10 HS$^-$</td>
<td>-48,168</td>
<td>-0.2855</td>
<td>261.2</td>
<td>0.90</td>
<td>150-210</td>
<td>6</td>
</tr>
<tr>
<td>K$_7$</td>
<td>S$^2$- $\leftrightarrow$ 2S$^2$-</td>
<td>-4533</td>
<td>6.42</td>
<td>100-250</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The CdSe was illuminated through a quartz window with a 650 W tungsten-halogen lamp. The distance from the electrode to the light was calibrated with a pyrometer to give 100 mW/cm$^2$ of incident energy. The current-potential measurements were made with a PAR 362 (Princeton Applied Research, Princeton, NJ) potentiostat.

Impedance measurements were made by superimposing a 5 mV sinusoidal signal on the dc bias. The current response from the cell was separated into the in-phase and out-of-phase elements with an lthaco 391A lock-in amplifier. The phase shift and magnitude of the response were used to determine the impedance of the cell.

CdSe crystals were obtained from Cleveland Crystals (Cleveland, OH); they were oriented on the (0001) and (1120) planes. The crystals were mounted so that the Cd face (0001), the Se face (0001), or the mixed face (1120) would be exposed to the solution.

Electrical contact was made on the back of the crystal with a gallium-indium alloy. The electrodes were etched in a concentrated solution of HCl/HNO$_3$ to remove defects from the surface. The crystals then were dipped in a hot 10% KCN solution to dissolve any elemental selenium formed on the surface of the semiconductor in the previous step. The CdSe and CdS crystals were then photoetched in 6M HCl by short-circuiting the electrodes with a platinum foil and illuminating with 100 mW/cm$^2$.

The current-potential measurements were made with a PAR Model 273 potentiostat under the control of an IBM PC/30 computer. A three-electrode configuration was used: the counterelectrode was a 2 cm$^2$ platinum foil, and the reference was a saturated calomel electrode (SCE) or a platinum wire. The cell was illuminated with the same 650 W tungsten-halogen lamp used in the polycrystalline experiments. The impedance measurements were made using a PAR 5301 lock-in amplifier in conjunction with the 273 potentiostat.

### Results

The current-potential behavior of solutions containing Na$^+$, K$^+$, and Cs$^+$ as the counterion was measured at a platinum electrode (Fig. 1). The oxidation and reduction currents were higher for the polysulfide solution containing the Cs$^+$. The oxidation current, from 50 to 100 mV overpotential, for Cs$^+$ was double that of K$^+$ which was double that of Na$^+$. The reduction current with Cs$^+$ was larger than that of K$^+$ and Na$^+$, which were approximately equal.

The redox potential, $E_{redox}$, was measured on platinum with respect to a SCE reference. The $E_{redox}$ in Cs$^+$ polysulfide was the most negative, at $-0.738$ V vs. SCE; in K$^+$ polysulfide it was $-0.771$, and in Na$^+$ polysulfide it was $-0.753$ V vs. SCE. This result agrees closely with the measurements made by Licht: $-0.755$, $-0.786$, and $-0.748$ V vs. SCE for Cs$^+$, K$^+$, and Na$^+$, respectively.

Solar cell performance measurements were made in three different polysulfide solutions with Na$^+$, K$^+$, and Cs$^+$ as the cation. The results of these measurements are shown in Fig. 2 with the important differences enumerated in

Table I. Equilibria in aqueous polysulfide solutions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>B</th>
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<td></td>
</tr>
</tbody>
</table>
Table II where \( V_{oc} \) is the open-circuit potential, \( I_{sc} \) is the short-circuit current, \( FF \) is the fill factor, and \( \eta \) is the energy-conversion efficiency. There is an increase in both the open-circuit potential and the short-circuit current with Cs\(^+\) as the cation in the polysulfide electrolyte. The trend in \( I_{sc} \) is Cs\(^+\) >> K\(^+\) >> Na\(^+\). The \( V_{oc} \) for Na\(^+\) and K\(^+\), however, within the limits of error are equal and are about 30 to 40 mV less than that with Cs\(^+\). \( \eta \) for the three different polysulfide electrolytes shows the same trend with Cs\(^+\) >> K\(^+\) >> Na\(^+\). The fill factors, however, for the three different electrolytes are approximately equal.

The performance was measured for the cell with single-crystal CdSe in either K\(^+\) polysulfide or Cs\(^+\) polysulfide for the three different orientations of the CdSe crystal, (0001), (0001), and (1120). The performance curve for the (0001) face is shown in Fig. 3, and the characteristics for each system are given in Table III. The addition of Cs\(^+\) gave the highest performance for each of the different crystal faces. The improvement was achieved with an increase in the fill factor for each of the different faces. Only for the Se face, (0001), was there an improvement in \( V_{oc} \). \( I_{sc} \) was approximately equal for the different polysulfides with each of the different crystal faces. Licht\(^1\) reported similar results at CdSe crystals where the short-circuit current changed only marginally, from 20.8 mA/cm\(^2\) for K\(^+\) polysulfide to 21.3 mA/cm\(^2\) for Cs\(^+\) polysulfide. In that study, the fill factor showed an increase to 0.647 with Cs\(^+\) from 0.624 for K\(^+\). This is different from the polycrystalline experiments where the fill factor remained approximately the same; however, \( V_{oc} \) and \( I_{sc} \) increased when Cs\(^+\) was the cation in the polysulfide.

The (0001) Se face with Cs\(^+\) was the most effective orientation for the solar cell, with the efficiency close to 12%. \( V_{oc} \) for the (0001) face was slightly greater than with the (0001) face, but the short-circuit current was smaller. The (1120) face was the least effective face overall, the largest improvements with Cs\(^+\) were with the Se (0001) face. The efficiency increased from 5% with K\(^+\) to almost 12% with Cs\(^+\). With the (0001) face, the improvement was from 9.6 to 10.6%, and with the (1120) face it was from 5.1 to 6.6%.

Impedance measurements were made with the polycrystalline electrodes in K\(^+\)-polysulfide and Cs\(^+\)-polysulfide at frequencies ranging from 500 to 1000 Hz. The capacitance was used to determine the flatband potential from the Mott-Schottky (M-S) equation:

\[
\frac{1}{C_{sc}^2} = \frac{2}{qN_v e \varepsilon_0 A} \left( U - U_{fb} - \frac{kT}{q} \right)
\]

where \( C_{sc} \) is the semiconductor capacitance, \( N_v \) is the doping density, \( A \) is the area, \( \varepsilon \) is the dielectric constant, and the other symbols have their usual meaning. Plots of \( 1/C_{sc}^2 \) vs. \( V \) were linear with some dispersion of lines between the frequencies, but the separate lines converged to the same \( x \)-intercept. Figure 4 shows a comparison of the M-S plots for CdSe in K\(^+\)-polysulfide and the Cs\(^+\)-polysulfide as the electrolyte. The same CdSe electrode was used in this measurement to compare the slopes. The Cs\(^+\)-polysulfide gave a smaller slope, \( 5.1 \times 10^{10} \text{cm}^2/(\text{F}^2\text{V}) \) compared to \( 9.6 \times 10^{10} \text{cm}^2/(\text{F}^2\text{V}) \) for the K\(^+\)-polysulfide. This difference corresponds to a greater apparent concentration of charge carriers when Cs\(^+\) was the cation. The absolute value of the charge-carrier concentration was not determined because of the surface roughness of the polycrystalline electrode.

When the term \( kT/q \) is negligible, the \( x \)-intercept of the M-S plots gives the flatband potential from the M-S plots but not the intercept. The \( V_{fb} \) in Cs\(^+\) polysulfide was \(-1.533 \pm 0.01 \text{ V vs. SCE} \) and in the K\(^+\)-polysulfide is \(-1.441 \pm 0.02 \text{ V vs. SCE} \). The negative shift in \( V_{fb} \) increases the maximum photovoltage attainable by the cell.

To understand the nature of the semiconductor-electrolyte interface in the absence of faradic charge transfer, impedance measurements were made with the single-crystal semiconductors in four hydroxide solutions, NaOH, KOH, CsOH, and (C\(_2\)H\(_5\))\(_4\)NOH (Fig. 5) for the CdSe (0001) face in 1M NaOH. A linear regression of the data is shown. The results for the CdSe (0001) face in KOH were similar, but in CsOH an increase in slope with increase in frequency was observed. The flatband potential for the (0001) CdSe

Table II. Polycrystalline CdSe performance.

<table>
<thead>
<tr>
<th>Element</th>
<th>( V_{oc} ) (mV)</th>
<th>( I_{sc} ) (mA/cm(^2))</th>
<th>FF</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.632</td>
<td>11.9</td>
<td>0.365</td>
<td>2.74</td>
</tr>
<tr>
<td>K</td>
<td>0.629</td>
<td>13.9</td>
<td>0.356</td>
<td>3.16</td>
</tr>
<tr>
<td>Cs</td>
<td>0.672</td>
<td>16.9</td>
<td>0.356</td>
<td>4.04</td>
</tr>
</tbody>
</table>

Fig. 1. Polysulfide current response on platinum with alkali metal-polysulfide solutions: Cs\(^+\) (solid); K\(^+\) (dashed); Na\(^+\) (dotted).

Fig. 2. Polycrystalline CdSe performance curves with Na, K, and Cs polysulfides. Illuminated at simulated AM1 spectrum with 100 mW/cm\(^2\).

Fig. 3. CdSe (0001) performance with K and Cs polysulfide. Illuminated at simulated AM1 spectrum with 100 mW/cm\(^2\).
Table III. Single-crystal CdSe performance.

<table>
<thead>
<tr>
<th>(0001)</th>
<th>K</th>
<th>650</th>
<th>37.0</th>
<th>0.27</th>
<th>8.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>670</td>
<td>37.5</td>
<td>0.51</td>
<td>11.86</td>
<td></td>
</tr>
</tbody>
</table>

Table V is a summary of the $V_{fb}$ measurements compared with the measurements of $V_{oc}$ for the single-crystal CdSe electrodes in the different polysulfide solutions. The measurements were made for the polycrystalline electrodes and values from the literature are included.

The etched CdSe (0001) face, listed on the third line of Table V, showed no negative shift with Cs+ polysulfide as compared with Na+ or K+ polysulfide in either $V_{oc}$ or $V_{fb}$. The slopes of the M-S plots between the different cations for the (0001) face were not significantly different. This finding parallels the results with the CdSe (0001) face in the different hydroxide solutions. Consistent through all the other data presented in Table V is a large increase in both $V_{oc}$ and $V_{fb}$ when the cation is changed to Cs+ from Na+ or K+. $V_{oc}$ and $V_{fb}$ for Na+ and K+, however, showed no difference between the two cations.

The CdSe (0001) and (0001) faces were tested after operating in K+-polysulfide and Cs+-polysulfide solar cells for 20 min. The electrodes were biased at -0.4 V vs. the counter electrode while illuminated at 100 mW/cm². That potential was close to the optimum as measured in the performance curves shown earlier. The impedance was then measured as before without illumination. For all the crystal orientations the frequency dispersion increased once the CdSe electrode was exposed to illumination and current was passed. The slopes for the M-S plots were smaller than before running in the cell.

After operating in the cell, the flatband potential for CdSe (0001) in both the K+ and Cs+-polysulfide shifted to more negative potentials. $V_{fb}$ for the CdSe (0001) in Cs+ polysulfide shifted 200 mV more negative from -1300 to -1500 mV. $V_{fb}$ for the CdSe (0001) in K+ polysulfide shifted only approximately 60 mV negative from -1350 to -1410 mV. These values are much closer to those for the CdSe (001). Thus, after a short period of operation in the cell, the CdSe (0001) also demonstrated a negative shift in $V_{fb}$ with change to Cs+.

Discussion

Several changes in the electrode-electrolyte interface for hydroxide and polysulfide solutions with Na+ or K+ to Cs+ cations have been observed: the oxidation current and, to a lesser extent, the reduction current on platinum, increased when the potential was scanned. The redox potential shifted to more negative values with Cs+ cations, the open-circuit potential increased, and the flatband potential shifted to more negative values. The slope of the M-S plots decreased and showed more frequency dispersion with Cs+ than with K+ or Na+.

The cation is not involved directly in the electrode reactions; however, its charge density affects several solution and surface equilibria. The smaller cations have a larger hydration shell, with Li, K, Na, and Cs having primary hydration numbers of 5 ± 1, 4 ± 1, 3 ± 2, and 1 ± 1 respectively. In the experiments with the polysulfide solutions on platinum, $E_{redox}$ changed a total of -30 mV when the cation was changed from Na+ to Cs+. A change in the equilibrium concentrations of the redox species. The electroactive species in the charge-transfer reactions are disulfide, [S2]⁻, and polysulfide, [Sx]⁻ which are maintained by the reactions listed in Table I. The basicity of the solution affects the distribution of polysulfide species in solution.

An increase in the activity of the hydroxide solutions when the cation is changed to larger alkali metal cations has been reported previously. For 3 molal solutions, the hydroxide ion activity was 1.48, 2.35, and 3.24 for LiOH, NaOH, and KOH, respectively; data are not available for the CsOH solutions at these concentrations. Assuming that the change in activity in the polysulfide solutions behaves the same, there would be an approximately 40% increase in the activity of OH⁻ from Na+ to K+.

The change in the distribution of species with a change in the OH⁻ activity can be estimated using the equilibrium relationships listed in Table I. An increase in the activity of OH⁻ increases the concentration of the smaller chain poly-
sulfide species, $[S_2]^{2-}$ and $[S_3]^{2-}$, and decreases the concentration of the longer chain $[S_4]^{2-}$ and $[S_5]^{2-}$. The concentration of supersulfide, $[S_2]^{2-}$, is maintained by the dissociation of $[S_4]^{2-}$ and decreases with an increase in the OH$^-$ activity. Thus, the $E_{\text{redox}}$, as given by the Nernst equation, shifts approximately -7 to -10 mV when sodium is replaced by potassium, due to the changes in reactant and product activities. The measured change in $E_{\text{redox}}$ is -18 mV, which is within the error in the measurements and equilibrium data.

Also evident from the different polysulfide solutions on platinum is an increase in the current density with a change to Cs$^+$. The oxidation current for Cs$^+$-polysulfide at an overpotential of 80 mV is more than 4 times that of the Na$^+$-polysulfide. There was also a slight increase in the reduction current with a change to Cs$^+$ as the cation.

The current-potential measurements in this study agree with those of Lessner et al. on platinum electrodes. In that study, it was determined that the rate expression for the charge transfer reaction coupled with the homogeneous chemical reactions could be written as in Eq. 10

$$\frac{i}{nF} = k_s[S_2]^{2-}[^2]_i[OH]^{1-}[^2][HS]^{1-}[^2]_i - k_s[S_2]^{2-}[^2]_i[OH]^{1-}[^2]_i$$

[10]

The change in the current is caused by either an increase in the charge-transfer rate constants, $k_s$ and $k_o$, or a change in the activities of $[S_2]^{2-}$, $[OH]^{1-}$, $[HS]^{1-}$, and $[S_4]^{2-}$.

The increase in oxidation current also can be related to the increase in [OH$^-$] activity discussed above, with the change in $E_{\text{redox}}$. At high anodic overpotentials (e.g., 80 mV), the cathodic back reaction can be neglected. The increase in current with change in cation can be estimated using the equilibrium relationships in Table I. The change in polysulfide species concentrations assuming a 40% increase in the OH$^-$ activity with change from sodium to potassium leads to an increase in the current by a factor of 1.8 to 1.8. This is close to the measured difference between the current with Na$^+$ and K$^+$, an increase by a factor of 2.

The reduction current, however, also shows a small increase in magnitude. The shift in the distribution of the polysulfide species described above does not predict this increase but rather a small decrease in the magnitude of the reduction current by 2 to 3%. Thus, we must conclude that in addition to the change in activity of the polysulfide species, there is a change in the rate constants. Others working with the ferricyanide-ferrocyanide redox couple on platinum have found that the current increases with a change in cation in the order of Li$^+ <<$ Na$^+ <<$ K$^+ <<$ Rb$^+ <<$ Cs$^+$. The rate constants that Kuta and Yeager calculated for the ferricyanide-ferrocyanide couple in the different alkali metal chloride electrolytes on a gold electrode are 0.014, 0.02, 0.03, and 0.05 cm/s for NaCl, KCl, RbCl, and CsCl, respectively. The increase in the rate constant appears related to the cation size and is sufficient to explain the increase in reduction current density.

Licht et al. also measured the I-V response of the different polysulfide solutions of Cu$_2$S and found that the current increased in the order of Li$^+ <<$ Na$^+ <<$ K$^+ <<$ Cs$^+$. They
related the increase in the magnitude of the current to an increase in the bulk conductivity in the polysulfide solutions with the larger cations which they measured as 0.23, 0.265, 0.365, and 0.372 S/cm for Li⁺, Na⁺, K⁺, and Cs⁺, respectively. However, here the cell was configured so as to reduce the effect of the solution resistance and the bulk resistance of the solution is small, less than 5Ω. For the currents measured on platinum in this experiment (<50 μA) this would be an IR drop of less than 0.3 mV at anodic overpotentials of 80 mV. The solution IR drop does not contribute significantly to the overall polarization and it is unlikely that the increase in bulk conductivity can explain the current differences on platinum with the different cations.

The results from this study indicate that the two mechanisms, a change in the activities of the polysulfide species and an increase in the charge-transfer rate constant with Cs⁺ affect the current-potential response on platinum in an additive way. Increasing the activity of the hydroxide in the polysulfide solution also changed the distribution of the polysulfide species. This change in the solution shifts Erdox mechanisms, a change in the activities of the polysulfide species

Table IV. VFe in hydroxide solutions.

<table>
<thead>
<tr>
<th>(mV vs. SCE)</th>
<th>(0001)</th>
<th>(0001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>-0.84</td>
<td>-0.72</td>
</tr>
<tr>
<td>KOH</td>
<td>-0.84</td>
<td>-0.72</td>
</tr>
<tr>
<td>CsOH</td>
<td>-0.97</td>
<td>-0.73</td>
</tr>
<tr>
<td>(C₂H₅)₂NOH</td>
<td>-1.32</td>
<td>-0.85</td>
</tr>
</tbody>
</table>

Small fill factor is a consequence of low current densities at potentials close to Vₚₙ where the cathodic back reaction, the reduction of [S₂]⁻ to [S₀]²⁻, limits the net oxidation. The shift in the distribution of the species in the polysulfide solution favors an increase of [S₂]⁻ and a decrease in the concentration of [S₈]²⁻ with Cs⁺.

The negative shift in Vₒ, and the subsequent increase in Vₛ are due to a change in the surface of the semiconductor. The values for both parameters are approximately equal for Na⁺ and K⁺ while there is a consistent improvement with Cs⁺. This pattern is observed also for the polycrystalline photoanodes, and the (0001) and (1120) single-crystal photoanodes in the polysulfide and hydroxide electrolytes.

In addition, the observation that these effects are dependent on the crystal orientation strongly indicates that this is a surface-related effect. The change in the surface is facilitated by the presence of chalcogenide (e.g., S or Se) atoms on the surface of the crystal. The CdSe (0001) face when cleaved is cadmium; the (0001) face is selenium. It is acknowledged that the surfaces may change with the etching and cleaning of the surfaces prior to testing. The difference in the measurements remain however with all but the orientation of the face held constant. The difference in the findings for the two faces is tied to the behavior of surface atoms on a compound semiconductor. The different atoms in a mixed semiconductor behave as Lewis acid and base sites.

The decrease in slope of the Mott-Schottky plots with the addition of Cs⁺ cations as does the short-circuit current with the polycrystalline electrodes. This result probably is due to limitations in charge transport within the semiconductor at the higher currents.

A frequency dispersion in the slope of the M-S plots was observed. One effect of faradaic current with the CdSe-polysulfide cell is the formation of a CdS film by exchange with the solution ions.

Table V. Comparison of Vₛ and Vₒ results with literature.

<table>
<thead>
<tr>
<th>Na</th>
<th>K</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vₑ</td>
<td>Vₒ</td>
<td>Vₑ</td>
</tr>
<tr>
<td>-1.31</td>
<td>-1.32</td>
<td>-1.44</td>
</tr>
<tr>
<td>-1.41</td>
<td>-1.35</td>
<td>-1.42</td>
</tr>
<tr>
<td>-1.30</td>
<td>-1.45</td>
<td>-1.35</td>
</tr>
<tr>
<td>-1.36</td>
<td>-1.38</td>
<td>-1.37</td>
</tr>
<tr>
<td>-1.38</td>
<td>-1.53</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

* Fresh etched crystal.
* Aged.
* pH 12.

The decrease in slope of the Mott-Schottky plots with the addition of Cs⁺ as does the short-circuit current with the polycrystalline electrodes. This result probably is due to limitations in charge transport within the semiconductor at the higher currents.
a range of time constants, $RC$, for charging and discharging. The apparent concentration of charge carriers changes for different frequencies as the number of surface states able to respond at a particular frequency changes. That the addition of Cs⁺ causes a frequency-dependent slope gives further evidence that the surface is undergoing a change.

The effect of cation in the solution has been explained as a shift in the distribution of the active species due to the increased hydroxide ion activity with the addition of Cs⁺. The changes in the CdSe surface with the addition of Cs⁺ are expected, particularly the negative shift in the $V_n$ with the addition of Cs⁺. The addition of the sulfide anion and its subsequent adsorption on the surface shifts the flat-band potential negative; $V_n$ shifted negatively by about 600 mV with the sulfide compared to the hydroxide electrolyte. The adsorption of a cation on the surface of the semiconductor is expected to shift $V_n$ and the band energy levels in the positive direction. If the Cs⁺ were adsorbed more easily than the other cations, the excess positive charges on the surface of the semiconductor would have shifted the band edges and the $V_n$ positive.

The adsorption of alkali metal atoms on the surfaces of metals and semiconductors has been shown to cause this effect; however, the work function of the surfaces of semiconductors and metals is reduced with the adsorption of alkali metals. 44 An increase in work function results in a negative shift in the band edges and $V_n$. The reduction in work function is dependent on the extent of coverage of the alkali metal on the surface and which alkali metal cation.

It has been demonstrated on several different metallic surfaces, Ta, W, Fe, Ag, Ni, and on Si that there is a larger reduction in the work function with Cs⁺ as opposed to Na⁺ or K⁺. 45 There is an approximately 1 eV greater reduction of the work function with Cs⁺ adsorption as opposed to Na⁺.

The mechanism for this change in the work function and band energies has been related to the chemisorption of the alkali metal with the material surface. 46–48 The chemisorption leads to a rearrangement of the surface states in the semiconductor which reduces the work function. This result correlates well with the data presented here. In the M-S plots there was an increase in the charge-carrier concentration which could be an increase in the surface states, additionally there was increased frequency dispersion in the slope with Cs⁺ as the cation indicating the possible increased presence of surface states. Goldstein and Van De Mark also theorized that the Cs⁺ cations act as more efficient charge transfer centers in their experiments with the ferrocyanide couple.

**Summary**

The changes in the semiconductor-electrolyte interface with the nature of the alkali-metal cation in polysulfide have been identified. The improvement in the performance of the CdSe/polysulfide solar cell with the addition of Cs⁺ reported by other researchers has been confirmed. The performance improvement occurs through both an increase in the current and in the $V_n$ with Cs⁺ polysulfide as compared to the other polysulfides.

The effect with Cs⁺ is a combination of solution effects and semiconductor surface effects. There was a shift in the $E_{\text{red}}$ of $-33$ mV with a change in cation from K⁺ to Cs⁺ as measured on platinum. This change is accounted for by a shift in the distribution of the polysulfide redox species, with a change in charge density and activity of the cation. The major component of the large increase in the anodic oxidation current on platinum has been attributed to the same shift in the polysulfide species. The $i$-$V$ behavior of the CdSe/polysulfide cell under illumination shows an increase in current with the addition of Cs⁺ also due to the shift in the polysulfide species.

The orientation of the crystal. The slopes of the M-S plots with Cs⁺ in both polysulfide and hydroxide solutions were lower, indicating an increase in charge-carrier concentration in the semiconductor. There is larger frequency dispersion of the M-S plots with Cs⁺ as the cation, indicative of a surface effect.

**REFERENCES**

H/D Isotope Effect on Electrochemical Pumps of Hydrogen and Water Vapor Using a Proton-Conductive Solid Electrolyte

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From the standpoint of an H/D isotope effect, the electrochemical pumping of hydrogen or water vapor has been studied using high temperature proton conductor as a solid electrolyte. When a potential was applied to the cell at 1173 K, the pumping rate of deuterium was remarkably smaller than that of hydrogen. During hydrogen pumping, the total current was depressed by replacing H⁺ and D⁺. In addition, an increase in cathodic overpotential was observed by the current-interruption method. Similar behavior was recognized in the pumping of water vapor, except that the transport number of the conducting ion decreased with replacement of D⁺ by H⁺.

High temperature proton-conductive solids are of industrial interest because of their application as solid electrolytes for a solid-oxide fuel cell, for a steam electrolyzer for organic compounds, and for a hydrogen gas sensor. Furthermore, an electrochemical reactor for organic compounds is possible using the proton conductor as a diaphragm. High temperature proton-conductive ceramics based on SrCeO₃, BaCeO₃, CaZrO₃, and SrZrO₃ were first found by us and have been investigated by various authors from different viewpoints. Particularly, the studies regarding the conduction mechanism are being made dynamically and can be summarized as follows: (i) temperature programmed desorption (TPD) spectra of the above oxides indicate that the proton concentration becomes larger as the electronegativities of constituent atoms in oxides decrease, namely, their basicities increase; (ii) infrared spectroscopy indicates that a proton is bound to an oxide ion in the lattice; (iii) decrease in ac conductivity by replacing H⁺ by D⁺ suggests that the conducting ion is not a hydroxide ion but rather a proton and that it migrates via the dissociation of the O-H bond when hydrogen and argon are supplied to the anode and the cathode, respectively, and a direct current is sent to the electrolyte, hydrogen evolves at the cathode. This fact demonstrates that the charge carrier is the proton.

This mechanism indicates a possibility for the separation of tritium-, or deuterium-, species from hydrogen or water vapor as a new application of the proton conductor. The results show that the isotope effect results from the difference in rate of migration in the bulk and/or of the electrode reaction among isotopes. Thus, as the basic research for this separation, we examine here the H/D isotope effect on the pumping of hydrogen or water vapor. Furthermore, the isotope effects on the migration of conducting ions and on their electrode reaction are investigated independently by current interruption.

Experimental

Preparation of SrCe₀.₉₅Yb₀.₀₅O₃-a ceramic.—The ceramic was prepared by a solid-state reaction, followed by sintering. The desired amounts of raw materials (SrCO₃, CeO₂, and Yb₂O₃) were mixed with ethanol and calcined in air at 1673 K for 10 h. The oxide was ground in a ball mill and pressed into the cylindrical pellet at 2 ton cm⁻². The pellet was sintered in air at 1603 K. The density of the ceramic was more than 95% of its theoretical value, and the crystal phase was confirmed to be a single perovskite-type phase by x-ray diffraction.

The electrochemical pump was constructed in the form of disk which was fixed in a stainless steel vessel with an O-ring. Platinum paste also was coated on the side face of the specimen as an electrode material. Porous Pt metal was attached to the top and bottom faces of the specimen as an electrode material. The measurement was carried out in hydrogen, deuterium, or wet air. Wet air was prepared by passing air through a water or heavy water bubbler at 293 K.

Electrochemical pumping of hydrogen or water vapor.—The schematic illustrations of the apparatus are shown in Fig. 2a and b. The ceramic was sliced into a thin disk (thickness: 0.5 mm and diam: 15 mm), as shown in Fig. 2a. Platinum paste was baked on both faces of the disk at 1173 K as an electrode material. Each electrode was attached with two Pt lead wires, one of which was connected to a potentiostat and the other of which was connected to an electrometer to eliminate the ohmic resistance of Pt lead wire. Platinum paste also was coated on the side face of the disk as a reference electrode, and was exposed to the atmosphere with a constant partial pressure of water vapor. On the reference electrode, three equilibria, Eq. 1, 2, and 3, were established simultaneously between the ceramic oxide and the atmosphere, regardless of the anodic or the cathodic reactions:

\[ \frac{1}{2} \text{O}_2 + V_0 = \text{Ox} + 2h^+ \]  
\[ \text{H}_2\text{O} + V_0 = \text{Ox} + 2\text{H}^+ \]  
\[ \text{H}_2\text{O} + 2h^+ = 2\text{H}^+ + \frac{1}{2} \text{O}_2 \]  

where H⁺, h⁺, V₀, and Ox denote the proton, hole, oxygen vacancy, oxide ion on a normal lattice site in the oxide, respectively.

In the experiment of the electrochemical hydrogen pump, 1 atm hydrogen or deuterium and argon were introduced into the anode and the cathode, respectively, at 1173 K. The voltage was applied potentiostatically, and hydrogen or deuterium evolved at the cathode was detected by a gas infra-red spectrometer.