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ENGINEERING EVALUATION OF SOLID TRANSITION-METAL SULFIDE ELECTRODES FOR USE IN HIGH ENERGY-DENSITY BATTERIES

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Abstract
Solid electrode materials exhibiting anomalously high alkali ion diffusivities through layered structures were studied for application in high energy-density, fast discharge-rate batteries. The maximum storage capacity and maximum discharge rates were studied theoretically for a spectrum of transition metal sulfides which crystallize in the CdI₂ and MoS₂ structures. Simple criteria were established for screening potentially important solid electrode materials for battery applications.

NOMENCLATURE
D₂: Chemical diffusivity of i, cm²/s
D₀: Diffusivity constant, cm²/s
Eₐ: Activation energy for diffusion, J
k: Boltzmann constant, J/°K
i: Electrode thickness, cm
N₀: Surface concentrations of alkali ions, cm⁻²
T: Temperature, °K
t: Time, s
y: Surface normal coordinate, cm

INTRODUCTION
There is currently a strong interest in high energy density batteries for use in electric vehicles and off-peak energy storage, cf. Salman 1. Several important criteria must be applied in selecting a suitable electrode material for these purposes. Among them are the maximum electrical-energy storage capacity, the discharge rate, the cell voltage range of stability and the limitations on dimensional stability.

One class of compounds of particular interest is the dichalcogenides of the group IV, V, and VI transition metals. Due to their layered structure, many of these compounds exhibit anomalously high alkali metal diffusivity. The transition metal dichalcogenides as solid cathodes in batteries containing liquid electrolytes are studied with regard to the above criteria.

STRUCTURE OF TRANSITION METAL DICHALCOGENIDES
Many transition metal dichalcogenides (MX₂) are found to take the CdI₂ or MoS₂ structures. Compounds with this structure are shown in Table I. These structures consist of layers of M and X atoms in particular stacking sequences. The coordination of X is either trigonal prismatic, shown in Fig. 1b, or octahedral, Fig. 1a. The fact that the layers of X are held together by weak van der Waals bonding is the outstanding feature of these compounds which allows as this weak bonding allows alkali ions to enter the lattice in the planes between chalcogen layers. The weak bonding to the alkali ions gives rise to high ionic mobility on these planes.

Chianelli et al. [3], have shown that alkali-TiS₂ intercalation compounds can assume three polytypes according to the location of alkali ions: (I) trigonal antiprisms occupation of octahedral sites, (II) trigonal prismatic occupation of interstitial sites in every other S-S layer, and (III) occupation of less than one quarter of the S-S layers. In addition, polytype I was found to have two stacking sequences, (a) CABCAB and (b) BBACC. The polytypes exhibited by alkali-TiS₂ compounds are summarized in Table II.

The structure of TiS₂ has been shown by Chianelli et al. [3] to be nearly the ideal CdI₂ structure. Riekel and Schöllhorn [4] found the same result for metal-rich TiS₂ₙ. In Li₂TiS₂, however,
Table II

<table>
<thead>
<tr>
<th>Polytypes of Alkali-TiS₂ Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
</tr>
<tr>
<td>Li₄xTiS₂</td>
</tr>
<tr>
<td>Na₄xTiS₂</td>
</tr>
<tr>
<td>K₄xTiS₂</td>
</tr>
<tr>
<td>Rb₄xTiS₂</td>
</tr>
<tr>
<td>Cs₄xTiS₂</td>
</tr>
</tbody>
</table>

The maximum discharge rate can be determined from the permeability of alkali ions in solid electrodes having a planar geometry. The most important quantity required is the chemical diffusivity of the alkali ions through a given layered lattice, which can be deduced theoretically by considering diffusion to occur by an activated process along a path between adjacent octahedra in the sulfur-sulfur layers.

The activation energy for diffusion is then determined from calculations of the lattice energies of interstitial ions at octahedral and trigonal sites.

Table III

| Maximum Alkali-Ion Mole Fraction in Disulfides, Relative to TiS₂ |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                        | Li              | Na              | K               | Rb              | Cs              |
|                        | 1.0             | 1.0             | 1.0             | 1.0             | 1.0             |
| A                      | 0.72            | 0.72            | 0.72            | 0.72            | 0.72            |
| M₂                   | 0.462           | 0.462           | 0.462           | 0.462           | 0.462           |
| T₄                   | 0.71            | 0.71            | 0.71            | 0.71            | 0.71            |
| Hf                   | 0.457           | 0.457           | 0.457           | 0.457           | 0.457           |
| Zr                   | 0.700           | 0.700           | 0.700           | 0.700           | 0.700           |
| Nb                   | 0.453           | 0.453           | 0.453           | 0.453           | 0.453           |
| Ta                   | 0.457           | 0.457           | 0.457           | 0.457           | 0.457           |
| W                   | 0.452           | 0.452           | 0.452           | 0.452           | 0.452           |

The chemical diffusivities in alkali compounds were calculated using the relationship,

\[ D = D_0 e^{-E_a/kT} \]  

The activation energy for displacements between adjacent sites on the diffusion plane was determined by summing the attractive, repulsive and polarization energies to determine the activation energy for diffusion through a compound as a function of mobile ion radius.

The results of the calculation are exemplified for lithium as shown in Table IV.

The maximum electrical-energy storage capacity of TiS₂ electrodes is determined by several factors. Assuming that alkali ions occupy octahedral sites between X layers, then the theoretical maximum filling of such sites by alkali ions is limited by the total number of such sites in the lattice. In MX₂ the ratio of octahedral sites to X atom sites is 2 so that the limiting formula of the alkali-intercalated MX₂ lattice is AₓM₁₋ₓX₂.

If, however, the A ion is so large that two of them in adjacent sites would overlap, this limiting formula becomes H₀.₅M₁.₀X₂.₀. Octahedral site overlap was found to occur only for Cs in disulfides of Nb, Ta, Mo, W, and di-selenides of Nb and W.

A more important limitation is the maximum for which a trigonal prismatic coordination of alkali ions is maintained. For example, intercalation of Na into TiS₂ causes an irreversible phase transformation for X<0.40, therefore the limiting fill is given by the formula Na₄₀TiS₂. Table II summarizes the maximum alkali ion mole fractions in transition metal sulfides. The storage capacity of TiS₂ is 239 amper-hr/kg. Similar trends were obtained for the maximum alkali ion mole fraction in metal diselenides.
Table IV

Chemical Diffusivities of Lithium in Metal Disulfides Relative to Na\(_{0.4}\)TiS\(_2\)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
<th>Nb</th>
<th>Ta</th>
<th>Mo</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, x=0</td>
<td>0.564</td>
<td>0.739</td>
<td>0.874</td>
<td>0.482</td>
<td>0.477</td>
<td>0.310</td>
<td>0.312</td>
</tr>
<tr>
<td>Li, x=1</td>
<td>0.491</td>
<td>0.672</td>
<td>0.618</td>
<td>0.410</td>
<td>0.403</td>
<td>0.278</td>
<td>0.312</td>
</tr>
</tbody>
</table>

The calculated diffusivities were utilized with Eq. 2 to determine discharge rates for different electrodes. Highest discharge rates were predicted for TiS\(_2\) containing sodium as the mobile ion. This result is a consequence of the high diffusivities calculated for Na in TiS\(_2\).

The chemical diffusivity of Na in NaTi\(_{1+y}\)S\(_2\) has been measured experimentally by Winn [7] using the electrochemical cell:

\[
\text{Na | NaI-saturated propylene carbonate | Na}_{x}\text{Ti}_{1+y}\text{S}_2 \quad (3)
\]

The measured values of D\(_{Na}\) were found to be on the range from 10\(^{-6}\) to 10\(^{-7}\) cm\(^2\)s\(^{-1}\) for \(x<0\), and \(x<0.45\). The measured values were lower by several orders of magnitude, however, when \(y\) was increased to 0.05 [8].

There is a critical dependence of the chemical diffusivity on stoichiometry of \(Na_{x}M_{1+y}X_2\) compounds which can be explained by the experimental evidence that any excess in the transition metal atoms tends to fill octahedral sites in the van der Waals gap between X-ion layers, thereby stiffening the lattice and tending to block the diffusion of the alkali ions. Both the group IIIB and VB disulfides show a tendency to form metal-rich compounds. The excess metal must be carefully avoided for maintaining high discharge rates in battery electrodes.

**ELECTRODE STABILITY**

A criterion for electrode stability is that no phase transformation take place. The concentration of diffusion ion at which a transition occurs limits the concentration range allowed. The storage capacity and the discharge range all depend on the alkali ion mole-fraction range. It can be expected that alkali metals cause lattice distortion when critical mole fractions are exceeded. There is no good way to predict this behavior, however, and little experimental data is currently available.

**VOLTAGE STABILITY**

Another important problem to be investigated in evaluating an electrode material is cell voltage stability. The only study to date is that of Winn and Steele [9] on \(Na_{x}Ti_{1+y}\)S\(_2\) when \(x\) was below 0.45. At values of \(x=0.45\) the voltage was ~2 volts, but dropped rapidly to 1.4-1.5 volts as \(x\) tended to 1.0. A similar drop in cell voltage can be expected for other systems owing to the dependence of the alkali-ion activity on alkali mole fraction, but further study is necessary.

**CONCLUSION**

A simple set of calculation procedures has been devised to determine the suitability of transition metal chalcogenides with the CdI\(_2\) and MoS\(_2\) structures for use as electrode materials in high energy-density, fast-discharge batteries.

The MoS\(_2\) and CdI\(_2\) structures of transition metal dichalcogenides contain van der Waals planes which allow anomalously high alkali ion diffusivity.

The theoretical maximum storage capacity of various transition metal sulfides was determined for elements of the alkali metal series, from which the maximum electrical storage capacity was determined. The solid electrode compound exhibiting the highest electrical storage capacity in this class of compounds is TiS\(_2\), owing to its low molecular weight. A simple potential function allowed the calculation of the activation energy for diffusion of alkali metals in transition metal dichalcogenides, from which the discharge rates could be compared. TiS\(_2\) containing Na showed a higher discharge rate than all other electrodes examined. The alkali ion discharge range is limited by shape-stability requirements and by electrode voltage variation with mole fraction.

**ACKNOWLEDGMENT**

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**REFERENCES**


REFERENCES (cont.)


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Fig. 1 Structure and stacking sequence for NaTiS$_2$. 

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