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ELECTROCHEMICAL INVESTIGATIONS OF
NOVEL ELECTRODE MATERIALS

MASTER

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Co-intercalated transition-metal disulfides in which two alkali metals are incorporated into the lattice are unique and unexplored materials. The major objective of our research program is the determination of the structural and electrochemical properties of lithium co-intercalated disulfides. The TiS_2 compounds have been extensively investigated because of their potential electrode applications in lithium batteries. Progress during the past year is discussed in four sections: preparation of lithium TiS_2 compounds, structural characterization, electrochemical-cell investigations, and external interactions.

Our studies indicate that the maximum intercalated lithium content in TiS_2 can be increased by about a factor of two by the pre-intercalation of another alkali metal such as sodium^(1,2). This increase in lithium content would almost double the calculated energy density of an intercalated TiS_2 electrode in a lithium battery.

A. Preparation of Lithium TiS_2 Compounds

As indicated in our previous research reports, the composition of the TiS_2 significantly affects the amount of alkali-metal intercalation. Titanium atoms in excess of the stoichiometric ratio occupy sites in the van-der-Waals gap between the weakly bonded sulfur layers of TiS_2 and decrease the alkali-metal intercalation. Our results indicate that the titanium to sulfur ratio of TiS_2 should be 1.01/2.0 or less to insure maximum intercalation. The TiS_2 , which is prepared in our laboratory by annealing a mixture of titanium and sulfur at 530°C under a sulfur pressure of $\sim 10^{-0.05}$ atm, has a typical composition of $\text{Ti}_{1.004}\text{S}_2$. The

titanium composition, which is determined by a combustion method, has an uncertainty of ± 0.002 .

Organometallic reagents such as n-butyl lithium and the naphthalides of lithium and sodium have been used to prepare $\text{Li}_x\text{Na}_y\text{TiS}_2$ compounds. The TiS_2 powder (-200 mesh) is equilibrated with the organometallic reagents dissolved in an organic solvent such as anhydrous tetrahydrofuran (THF). The alkali metal concentration of each co-intercalated sample is determined using atomic absorption spectroscopy. Errors due to interference effects between lithium and sodium have been minimized by comparing ion absorbances in mixed-ion solutions with those in standard solutions. Mass-spectrometric analysis indicates that there is no detectable concentration of organic molecules such as naphthalene in the co-intercalated samples. Co-intercalated $\text{Li}_x\text{Na}_y\text{TiS}_2$ compounds in which y varies from 0.04 to 0.50 and x is between 0.1 and 1.9 have been prepared.

A variety of $\text{Li}_x\text{Ca}_y\text{TiS}_2$ compounds have been prepared with y values ranging from 0.01 to 0.45. Intercalation using liquid ammonia solutions is necessary to obtain samples with the higher calcium contents. Lithium is introduced in the Ca_xTiS_2 using organometallic reagents. However, the highest lithium content in $\text{Li}_x\text{Ca}_y\text{TiS}_2$ corresponds to an x value of 1.2.

Several $\text{Ti}_{1-y}\text{V}_y\text{S}_2$ compounds have been prepared to investigate the effect of the transition metal upon the alkali-metal intercalation. X-ray diffraction results indicate that the $\text{Ti}_{1-y}\text{V}_y\text{S}_2$ compounds are isostructural with TiS_2 when y is between 0 and 0.7.

B. Structural Characterization

The $\text{Li}_x\text{Na}_{0.04}\text{TiS}_2$ samples appear to be single phase even with x as high as 1.7. However, when x is greater than 1.5, an Li_2S line appears on the X-ray diffraction pattern. Preliminary studies indicate that the Li_2S forms upon exposure of the samples to humid air. For $\text{Li}_x\text{Na}_y\text{TiS}_2$ samples with y between 0.16 and 0.50, it is necessary to anneal the compounds at elevated temperatures (1 to 3 weeks at temperatures between 140 and 190°C) to obtain equilibrium structures. Many of the $\text{Li}_x\text{Na}_y\text{TiS}_2$ compounds exhibit a two-phase region which is either the same or related to that observed for Na_yTiS_2 in the absence of lithium. However, it is interesting that the $\text{Li}_x\text{Na}_y\text{TiS}_2$ compounds with the highest sodium content ($y = 0.50$) exhibit a single phase structure over the entire lithium concentration range.

Debye-Scherrer patterns of the chemically prepared Ca_yTiS_2 compounds indicate that the TiS_2 structure is observed when y is between 0.01 and 0.04, the $\text{Na}_{0.22}\text{TiS}_2$ structure is observed when y is between 0.07 and 0.21, and the $\text{Na}_{1.0}\text{TiS}_2$ structure is observed when y is 0.45. The latter observation agrees with an earlier study of $\text{Ca}_{0.5}\text{TiS}_2$ reported by Rouxel. The Debye-Scherrer patterns for the $\text{Li}_x\text{Ca}_y\text{TiS}_2$ compounds are being analyzed.

C. Electrochemical-Cell Investigations

The open-circuit EMF of cell (A) has been measured at 30°C using the $\text{LiC}_2\text{O}_2\text{F}_3$ - polyethylene oxide (PEO) electrolyte. As discussed in last year's progress report this electrolyte can be prepared as a thin film with a typical thickness of 20 to 60 microns.

Lithium/LiC₂O₂F₃-PEO/Li_xNa_yTiS₂ (A)

Results from cell (A) are stable and reproducible.

The structural and EMF data for the Li_xNa_{0.04}TiS₂ compounds indicate a single phase region for x between 0 and 1.8. The cell EMF's are virtually identical to those obtained previously with an Li_xTiS₂ electrode when x is less than 1.0. When x is greater than 1.0 in Li_xNa_{0.04}TiS₂, the cell EMF abruptly decreases from 1.7 to about 1.0 volts.

The EMF data for Li_xNa_yTiS₂ electrodes in which y is between 0.16 and 0.34 are also consistent with the structural data which indicate two-phase regions. However, the Li_xNa_{0.50}TiS₂ compounds have an extensive single-phase region, and the compositional variation of the EMF of cell (A) can be interpreted using our recent thermodynamic model⁽⁴⁾ for alkali-metal intercalated compounds. In moderate compositional ranges, our model predicts that the repulsive interaction energy between intercalated ions and the electron chemical potential are the most significant factors establishing the observed EMF variation with lithium concentration, x. Preliminary data indicate that the interaction energy between the lithium ions in the single-phase co-intercalated Li_xNa_yTiS₂ compounds is nearly the same as that in Li_xTiS₂.

The electrochemical properties of Li_xCa_yTiS₂ compounds have been investigated using cell (B).

Lithium/LiC₂O₂F₃-PEO/Li_xCa_yTiS₂ (B)

When the calcium content, y, is greater than 0.07, the EMF of cell (B) indicates that there is a larger interaction energy

between the lithium ions in $\text{Li}_x\text{Ca}_y\text{TiS}_2$ than in the Li_xTiS_2 compounds where, calcium is absent. Structural studies of the $\text{Li}_x\text{Ca}_y\text{TiS}_2$ compounds, which are necessary to fully understand the effects of calcium on the lithium-lithium interaction energy, are in progress.

To investigate the effect of the transition-metal on the lithium-lithium interaction energy, the EMF of cell (C) has been measured.

A liquid propylene-carbonate solution of either 1M LiClO_4 or 1M LiAlF_6 is used as the electrolyte in Cell (C). The $\text{Li}_x\text{Ti}_{0.9}\text{V}_{0.1}\text{S}_2$ ($y = 0.1$) and the $\text{Li}_x\text{Ti}_{0.7}\text{V}_{0.3}\text{S}_2$ ($y = 0.3$) electrodes with x between 0 and 1.08 have been investigated. The initial results indicate that the substitution of vanadium atoms for up to 30% of the titanium atoms in Li_xTiS_2 does not significantly change the lithium-lithium interaction energy in the van-der-Waals gap between the sulfur layers.

D. External Interactions

Three publications⁽¹⁻³⁾ summarizing our results have appeared during the past year and reprints of these are enclosed with this report. A paper entitled "Thermodynamic and Transport Properties of Lithium Intercalated Dichalcogenides" was presented at the International Lithium Battery Meeting in Rome in April, 1982. The principal investigator has been invited to present a keynote lecture at the International Conference on Ternary and Multinary Compounds in Italy in September, 1982 and to discuss co-intercalated compounds at a joint U.S.-U.K. solid-state chemistry workshop in England in December, 1982. He has received a Japanese fellowship

to lecture at various Japanese Universities during November, 1982 and a Max-Planck fellowship to collaborate with the solid-state chemistry group at the Max-Planck-Institut in Stuttgart, West Germany. As part of an invitation to establish a collaborative program on intercalated compounds, he has been invited to spend two months at the University of Rome during either 1983 or 1984.

The principal investigator is a consultant for the lithium battery group at the Jet Propulsion Laboratory and for several other industrial laboratories including those at DuPont Chemical Corp., United Technologies, and Westinghouse. He is also chairman of the review committee of the Chemical Engineering Division at Argonne National Laboratory, which has extensive battery research programs.

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