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ELECTROCHEMICAL INVESTIGATIONS OF NOVEL ELECTRODE MATERIALS

Progress Report
for period 1 August 1978 - 31 July 1979

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Electrochemical Investigations of Novel Electrode Materials

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Abstract

Electrochemical investigations of the compositional variation of the chemical potential and chemical diffusivity of lithium in Li_xTaS_2 and Li_xTiS_2 have been completed. The experimental results have been used to increase our understanding of the chemical bonding and transport mechanisms of lithium in the layered-structured intercalated disulfides. Our major emphasis during the current year has been to expand our earlier investigations of the co-intercalated disulfides: $Li_xNa_{0.18}TaS_2$ and $Li_xNa_{0.18}TiS_2$. Open-circuit voltage data clearly indicate that these co-intercalated compounds offer exciting possibilities as high-energy-density cathodes in lithium batteries.

Lithium intercalated Group IV, V and VI transition metal disulfides have received considerable attention because of their potential applications as cathode materials in lithium batteries(1-4). The chemical formulas of these intercalated compounds is Li_xMS_2 where M is usually Ti, V,or Ta and x can vary from 0 to 1.0. We have completed our electrochemical investigations of the compositional variation of the chemical potential and chemical diffusivity of lithium in Li_xTaS_2 and Li_xTiS_2. The experimental results have increased our understanding of the chemical bonding and transport mechanisms of lithium in these layered-structured intercalated disulfides.

However, our major emphasis during the past year has been to expand our earlier electrochemical investigations(5) of the co-intercalated disulfides: $Li_xNa_{0.18}TaS_2$ and $Li_xNa_{0.18}TiS_2$.

The variation of the open-circuit cell voltage with composition x of the co-intercalated cathodes has been measured using cell (A) at 303^oK.

$$Li(s)/Li^+(LiClO_4 \text{ in propylene carbonate})/Li_xNa_{0.18}TaS_2 \text{ or } Li_xNa_{0.18}TiS_2 \qquad (A)$$

The $Na_{0.18}TaS_2$ cathodes in cell (a) were prepared using a sodium naphthalide solution in tetrahydrofurane to intercalate sodium into TaS_2 particles, which had been previously annealed to obtain the stoichiometric 2H polytype structure of TaS_2. A coulometric titration technique was used to intercalate sodium into TiS_2 to prepare the $Na_{0.18}TiS_2$ cathodes. The sodium-intercalated powders were pressed to form the cathode pellets. Freshly cut lithium was used as the anodes in cell (A). Preparation of the propylene carbonate electrolyte and the cell design were similar to that described elsewhere(3,6).

All cell measurements were conducted inside a controlled atmosphere glove box at ambient temperature. The lithium composition x of the cathode was increased by discharging the cell at a constant current of ~ 0.3 mA/cm^2 for a specific time period. After each discharge stage, the cell was held until the open circuit voltage was essentially constant (± 0.001 V over 2-3 days). This discharge procedure was repeated to obtain data at other compositions. Cathode reversibility was established by reversing the current (charging the cell). Within 0.02 V the same voltage value was obtained on charging as on discharging. X-ray diffraction patterns of the $Li_xNa_{0.18}TaS_2$ and $Li_xNa_{0.18}TiS_2$ cathodes used in cell (A) were obtained using a Debye-Scherrer camera with copper k_α radiation.

The variation of the open-circuit voltage of cell (A) with the composition, x, of the $Li_xNa_{0.18}TaS_2$ and $Li_xNa_{0.18}TiS_2$ cathodes is shown in Figs. (1) and (2), respectively. Data for the Li_xTaS_2(6) and Li_xTiS_2(7,8) cathode cells are also shown for comparison. Although the individual data points for the co-intercalated cathodes are connected by a smooth curve in Figs. (1) and (2), more data are necessary to establish precisely the exact voltage-compositional relationships. However, the data shown in Figs. (1) and (2) clearly indicate that these co-intercalated materials offer exciting possibilities as high-energy density cathodes in lithium batteries.

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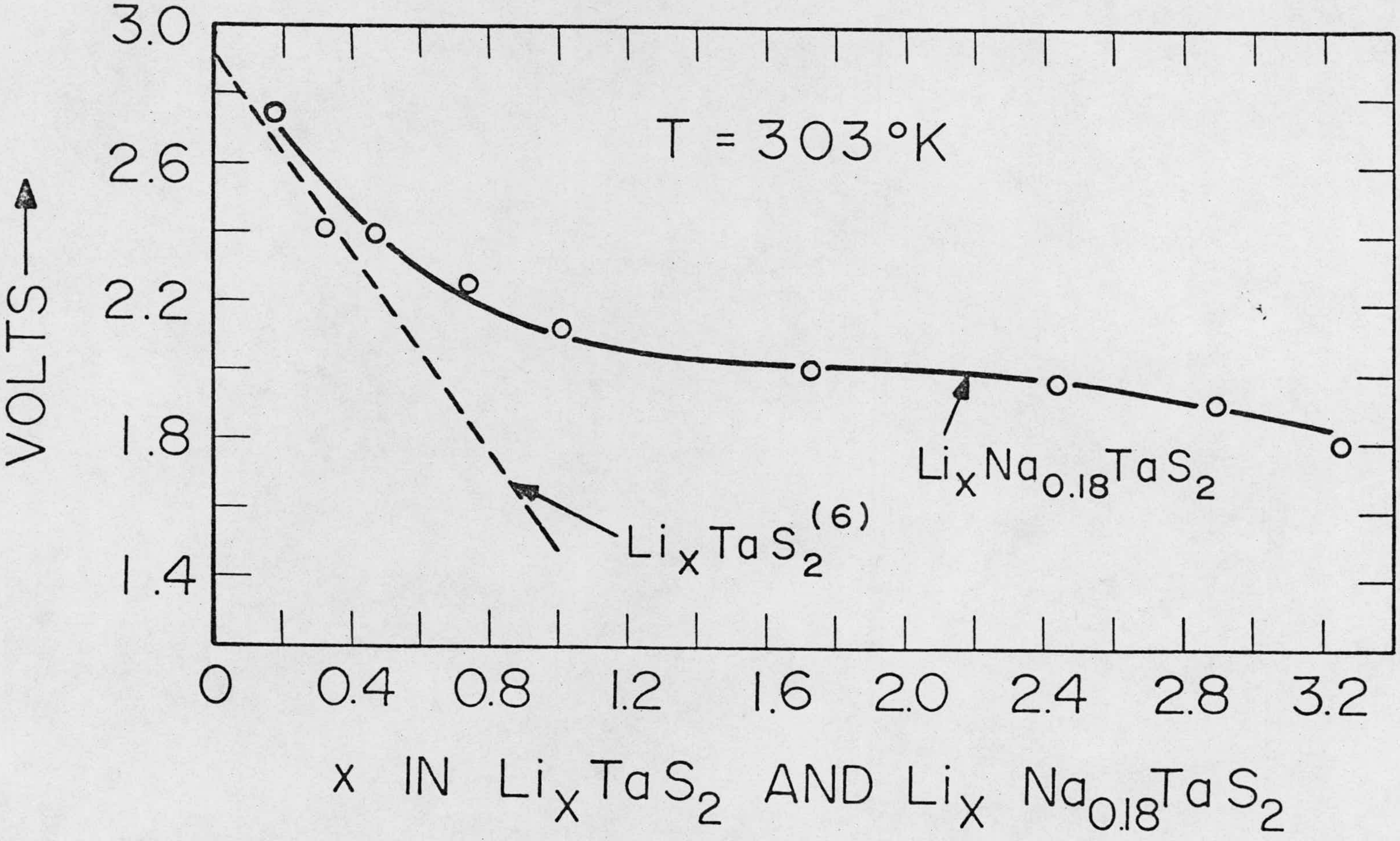

Fig. 1. Variation of the open-circuit voltage of cell (A) with composition, x, of the Li_xTaS_2 and $Li_xNa_{0.18}TaS_2$ cathodes.

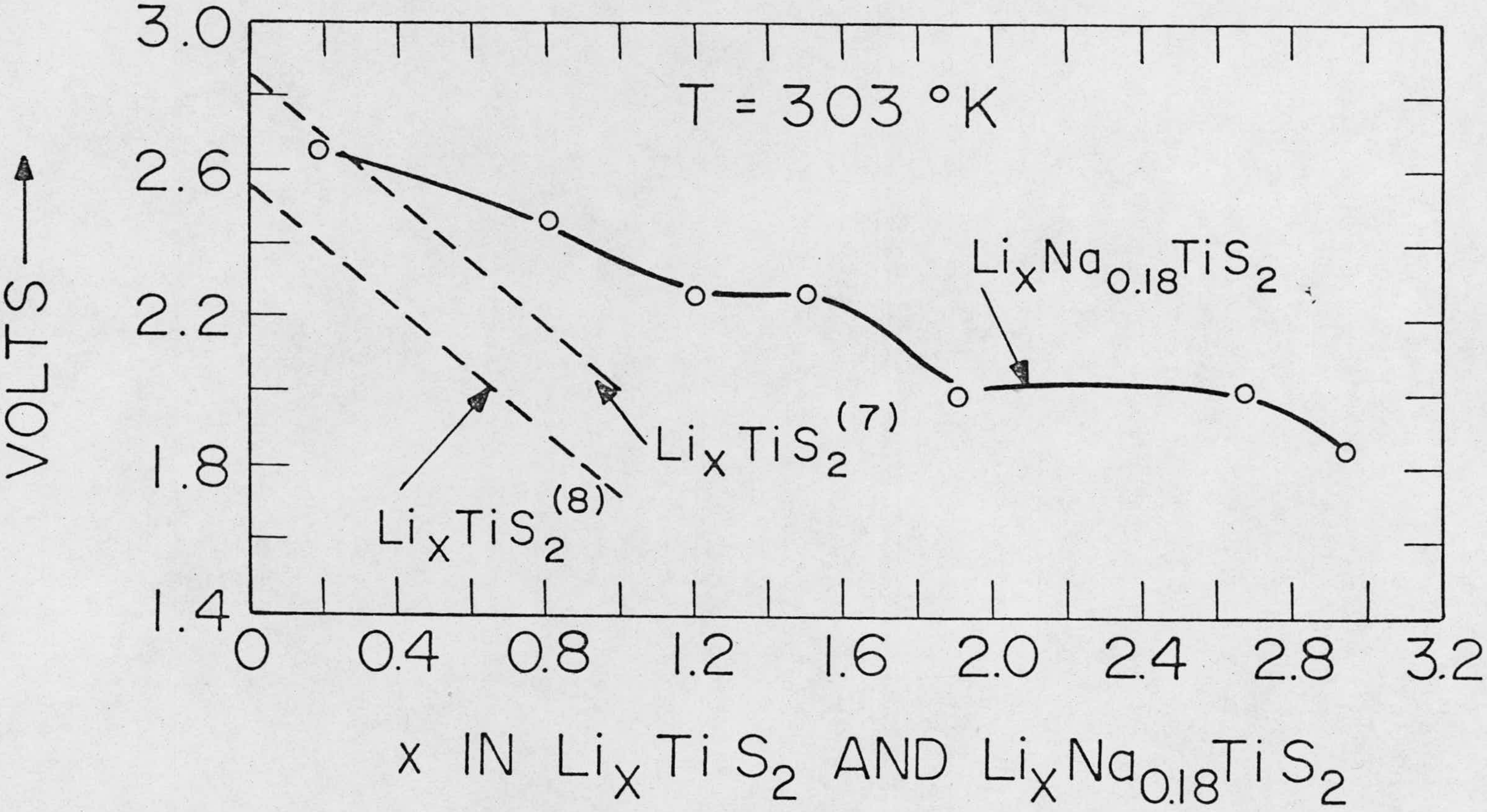

Fig. 2. Variation of the open-circuit voltage of cell (A) with composition, x, of the Li_xTiS_2 and $Li_xNa_{0.18}TiS_2$ cathodes.