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Locating redox couples in the layered sulfides with application to $Cu[Cr_2]S_4$

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ABSTRACT

Use of $LiPF_6$ in EC:DEC as electrolyte has allowed electrochemical extraction of Li from $LiV_{1-y}M_yS_2$ and $LiTi_{1-y}M_yS_2$ ($M = $ Cr or Fe). The data show access not only to the Ti(IV)/Ti(III) and V(IV)/V(III) redox couples, but also to the V(V)/V(IV) and Fe(III)/Fe(II) couples in these layered sulfides. However, the Cr(IV)/Cr(III) couple could not be accessed. The concept of redox-couple pinning is outlined and applied to the V(V)/V(IV) and Fe(III)/Fe(II) couples, which are pinned at the top of the *S*-3*p* bands. Holes associated with the "pinned" couples occupy orbitals of dominant *S*-3*p* character, but they have sufficient cation-3*d* character to prevent condensation of the holes into *p*–*p* antibonding states of disulfide bonds. Strong covalent bonding in the pinned couples creates itinerant-electron states in the partially occupied couples. Application to the metallic, ferromagnetic thiospinel $Cu[Cr_2]S_4$ favors location of the itinerant holes in states of a pinned Cu(II)/Cu(I) couple having primarily *S*-3*p* character.

1. Introduction

With the discovery [1] that reversible electrochemical extraction of Li from $LiVS_2$ is possible with $LiPF_6$ in ethylene/diethyl carbonate (EC/DEC) as electrolyte, we report a reinvestigation of electrochemical extraction of Li from $LiV_{1-y}M_yS_2$ and from $LiTi_{1-y}M_yS_2$ with $M = $ Cr or Fe. The original studies [2–5] of these systems were frustrated by the irreversibility of electrochemical extraction of Li with $LiClO_4$ in propylene carbonate (PC) as electrolyte. Although these early authors were able to extract Li chemically with I_2/I^- in acetonitrile, the oxidation states of the atoms in the delithiated compounds has remained controversial. In particular, the possibility of oxidation of Cr(III) and Fe(II) in these layered sulfides and, by implication, in other sulfides, remains unresolved. Since these early studies, the concept of "pinning" of a redox couple at the top of anion-*p* bands has been proposed [6], and we use this concept not only to interpret our findings, but also to revisit an old controversy concerning the atomic oxidation states in the metallic, ferromagnetic spinel $Cu[Cr_2]S_4$.

2. Experimental methods

2.1. Synthesis

Polycrystalline nominal $LiM_yM'_{1-y}S_2$ (M or $M' = $ Ti, V, Cr, Fe) were obtained from 2-g batches of Li_2S (Aldrich, ≥98.0%) and appropriate elements, Ti (Alfa, 99.9%), V (Alfa, 99.5%), Cr (Alfa, 99.95%), Fe (Alfa, 99.998%), and S (Aldrich, 99.99%). They were mixed, ground together, placed inside a pre-dried, carbon-coated quartz tube inside an Ar glove box, and then sealed under vacuum. The sealed tube was heated slowly over 20 h to 750 °C, held for 40 h, and then cooled to 250 °C over 10 h followed by quenching in air. The samples were removed to an Ar glove box where they were thoroughly ground and pelletized. Then they were treated again under the above process. Since these compounds are moisture-sensitive, they were always handled in an Ar atmosphere once they were removed to the glove box.

2.2. Electrochemical analysis

Since the samples are sensitive to moisture, the electrode disks and cells were prepared in the Ar glove box. The electrodes were fabricated from a 70:20:10 (wt%) mixture of active material:acetylene black as a current conductor:polytetrafluoroethylene (PTF). The active material and acetylene-black conductor were mixed completely first, the PTF binder was then added and then mass mixed again. The mixture was rolled into thin sheets and punched into 7-mm-diameter circular disks as electrodes. The typical electrode mass and thickness were 5–10 mg and 0.03–0.08 mm, respectively. The electrochemical cells were prepared in standard 2016 coin-cell hardware with lithium-metal foil as both the counter and reference electrodes. The electrolyte used for analysis was 1 M $LiPF_6$ in 1:1 ethylene carbonate/diethyl carbonate (EC/DEC). The sealed cells were taken out of the glove box and placed in a battery-testing system (Arbin BTS-2043); they were aged for 5 h before the first discharge (or charge) to ensure full absorption

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of the electrolyte into the electrode. A ten-minute rest period was employed between the charge and discharge steps.

3. Results

The XRD patterns of the $LiV_{1-y}M_yS_2$ and $LiTi_{1-y}M_yS_2$ ($M =$ Cr, Fe) were all in good agreement with published data [4,5]. The hexagonal structure of the $LiV_{1-y}M_yS_2$ and $LiTi_{1-y}M_yS_2$ ($M =$ Cr, Fe) consists of hexagonal-close-packed sulfur with M and Li atoms in alternate octahedral-site (001) planes. On removal of Li, the MS_2 layers are held together by van der Waals bonding. However, high-temperature synthesis commonly gives a ratio $Li/M<1.0$ in the layered chalcogenide compounds [1,3]. The as-prepared samples in this work were also found to be slightly Li-deficient.

Fig. 1 shows the voltage profiles for the first 10 charge/discharge cycles of Li extraction from and intercalation into $Li_{1-x}V_{1-y}Cr_yS_2$. The as-prepared samples all tended to be deficient in Li, so the first charge (extraction of Li) had a smaller capacity than the subsequent charging curves for $y = 0, 0.25$, and 0.5. Fig. 2 shows the voltage profiles for the second charge of $Li_{1-x}V_{1-y}Cr_yS_2$. The small steps in the $y = 0$ voltage profile of Fig. 2 occur [1] in the compositional ranges of the different phases identified chemically by Murphy et al. [2] Addition of 0.25 Cr(III) for V(III) removes the steps in the voltage profile, increases the capacity, and raises the voltage further; but the capacity decreases with increasing y for $y \geq 0.5$. By $y = 0.75$, a flat $V(x)$ curve in the interval

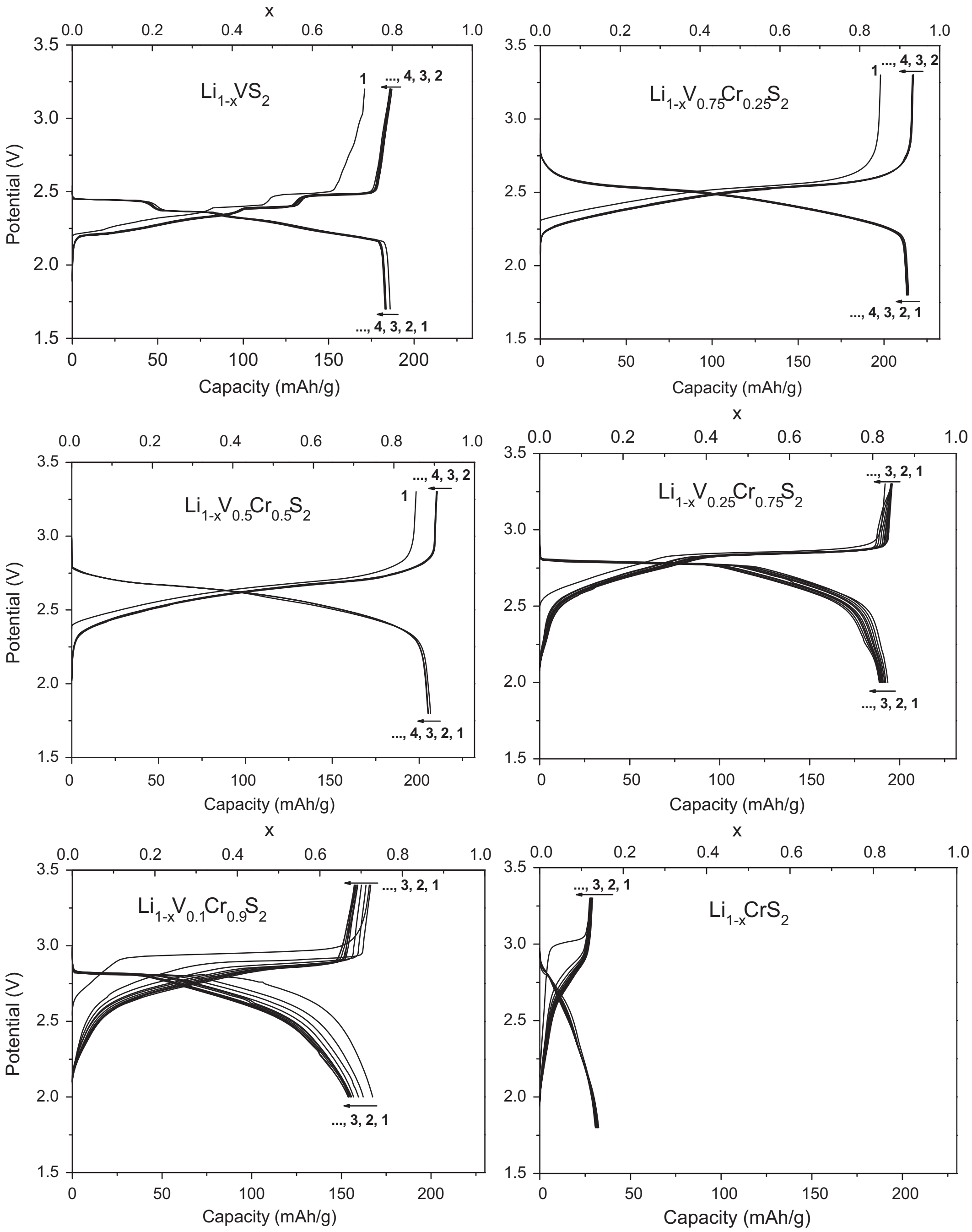

Fig. 1. The voltage profiles for the discharge and charge curves on cycling of Li intercalation into $Li_{1-x}V_{1-y}Cr_yS_2$ at the rate of 0.1 mA/cm^2.