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Lithium Intercalation into $SnS_2\{CoCp_2\}_x$

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The search for suitable lightweight rechargeable batteries has included an extensive examination of lithium intercalation compounds.[1,2] Lithium's low atomic weight and high reducing potential have stimulated this examination. For a material to be considered as an electrode in such a system, it must be able to participate in a lithium intercalation reaction. A variety of solid state host lattices satisfy this requirement: TiS_2, $Fe_2P_2S_6$, and V_2O_5 to name but a few.[3–5] In this communication, we report the lithium intercalation into $SnS_2\{CoCp_2\}_x$. This is a significant observation because, in this material, the charge is transferred not to the host lattice but to a different intercalated species.

Pure SnS_2 is conveniently prepared from the elements.[6] Large single-crystal boules can be grown from the elements in a simple zone refiner. In addition to the boule, a good yield of thin single-crystal platelets is realized in the cool region of the quartz reaction tube above the melt. It is these crystals which were used in the experiments described here. They are orange/yellow, transparent, approximately 1 × 1 × 0.05 cm, and of high quality. These crystals were intercalated with cobaltocene using a 0.05 M acetonitrile solution at a temperature of 120 °C for 3 weeks or by using a 0.19 M monoglyme solution at room temperature for 25 days.[7,8] The results reported in this communication are independent of these experimental details. All manipulations were performed in an inert-atmosphere drybox because of the oxygen and water reactivity of cobaltocene. The resulting product is lustrous, opaque, and noticeably swollen. These results are consistent with earlier reports of cobaltocene intercalation into SnS_2.[7]

In our recent work using FTIR spectroscopy to probe the redox characteristics of cobaltocene intercalation reactions, we observed only cobaltocenium, $CoCp_2^+$, within the van der Waals gap of cobaltocene-intercalated SnS_2.[6] Hence one could express the resulting material as

$$[SnS_2]^{x-}[CoCp_2^{\ +}]_x$$

emphasizing that the host SnS_2 has served as the oxidizing agent. Parkinson et al. have explicitly identified the oxidizing agent as the Sn^{4+} component of the host using ^{119}Sn Mössbauer.[7]

The cobaltocene-intercalated SnS_2 will be expressed as $SnS_2\{CoCp_2\}_x$, where x has previously been determined to be approximately 0.4 for a fully intercalated crystal.[7] By recording the mass of the crystals with a microbalance before and after the reaction, the final stoichiometry was calculated to be

$$SnS_2\{CoCp_2\}_{0.29\pm0.05}$$

where the cobaltocene is all in the form of cationic cobaltocenium, $CoCp_2^+$, based on our previous ESR and FTIR study.[7] Several of these crystals were then lithiated by soaking them in a 0.060 M solution of *n*-butyllithium in hexane containing an accurately known amount of solute. The SnS_2:*n*-butyllithium mole ratio was 1:15, and the reaction was carried out at 50 °C for 13 days. As with the cobaltocene intercalation reactions, all manipulations with lithium were performed in an Ar atmosphere drybox. Reactions were carried out in sealed glass ampules. At the conclusion of the 13-day period, no visible changes in the crystals were evident: the crystals remained opaque and lustrous with no apparent additional swelling. These twice intercalated crystals are, however, significantly more brittle than $SnS_2\{CoCp_2\}_x$. The amount of *n*-butyllithium remaining in the solution was found by adding an excess of 0.0048 M HCl and then back titrating with 0.0047 M NaOH.[9] The final stoichiometry was then determined to be

$$Li_{0.34\pm0.10}SnS_2\{CoCp_2\}_{0.29\pm0.05}$$

where it was verified that no significant amount of cobaltocene deintercalated during the lithiation by comparison of the crystal masses before and after lithiation. Using a similar procedure, lithiation of pure unintercalated SnS_2 crystals was also attempted, but for comparable reaction times, the amount of lithium intercalated into the SnS_2 was only one-fifth that realized in the $SnS_2\{CoCp_2\}_x$ case. For the case of *powdered* SnS_2, lithium intercalation via *n*-butyllithium has recently been reported.[10] For the powdered case, a maximum of 2 lithiums/tin atom was observed.

Despite the unchanged appearance of $SnS_2\{CoCp_2\}_x$ after lithiation, two pieces of evidence suggest that important changes have indeed occurred. First, the infrared spectrum of the material no longer matches that of cobaltocenium, but instead it matches the infrared spectrum of neutral cobaltocene with a small contribution from some residual cobaltocenium (see Figure 1).[11] This suggests that lithium has intercalated $SnS_2\{CoCp_2\}_x$ with reduction of cobaltocenium to cobaltocene. This material could be represented as

$$[SnS_2]^{x-}[CoCp_2]_xLi_x^{\ +}$$

The second piece of evidence that lithium has intercalated into $SnS_2\{CoCp_2\}_x$ concerns the air stability of the final product. Upon exposure to ambient air, a white microcrystalline material develops around the edge of the intercalated crystal. FTIR results show that, at the same time, the cobaltocenium concentration increases within the lattice. Effectively, an electron is transferred from

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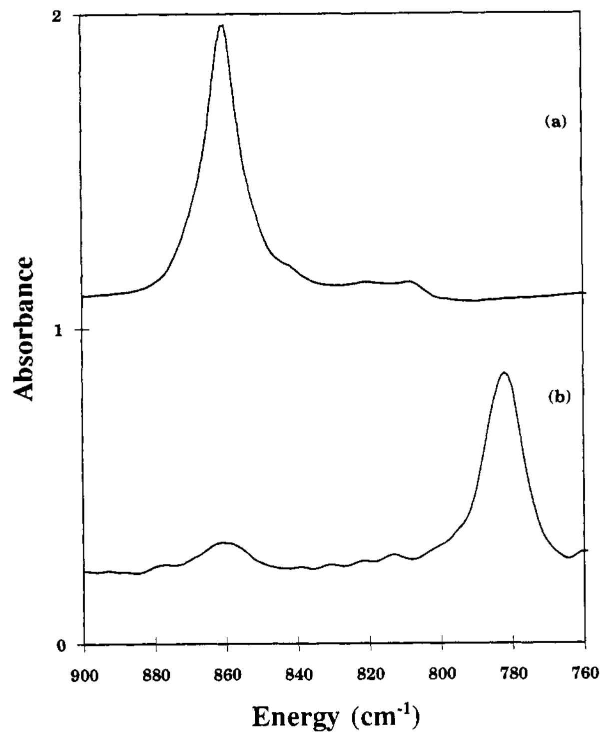

Figure 1. FTIR spectra of (a) $SnS_2\{CoCp_2\}_x$ and (b) $Li_{0.34}SnS_2\{CoCp_2\}_{0.29}$. The cobaltocene intercalation was performed at room temperature from a monoglyme solution. The lithium intercalation was performed using *n*-butyllithium. The peak at 862 cm^{-1} is due to cobaltocenium, $CoCp_2^+$, and the peak at 784 cm^{-1} is due to cobaltocene, $CoCp_2$.

the cobaltocene to oxygen, Li_2O forms, and Li^+ diffuses to the edge of the lattice. No such reaction occurs with SnS_2 or $SnS_2\{CoCp_2\}_x$. Recall that large single crystals of SnS_2 are used in the initial cobaltocene intercalation thus making any edge process such as the formation of white microcrystallites very noticable.

The final product, $[SnS_2]^{x-}[CoCp_2]_xLi_x^+$, does not show an ESR spectrum from neutral cobaltocene (at 4 K) which is consistent with Ammeter and Swalen's detailed work on the ESR properties of cobaltocene.[12] To observe a spectrum, these authors had to dilute the cobaltocene into a diamagnetic host (ferrocene). Pure cobaltocene did not give an observable ESR spectrum, presumably due to strong spin–spin interactions. In the present case, with a fully intercalated $SnS_2\{CoCp_2\}_x$ where essentially all of the cobaltocenium is returned to the neutral state, spin–spin interactions would again render the ESR spectrum broad beyond detection.

The present observations are significant for several reasons. SnS_2 is a convenient material to prepare in single-crystal form given its congruent melting point. Also this lattice has been prepared in epitaxial thin films.[13] If such films displayed the same chemical properties as the bulk material, then the reported observations potentially represent a new way to prepare electrodes for lithium batteries. A final point worth noting is that since both the original host and metallocene can be modified separately, this system should be tunable to produce a final material with desired characteristics. For example, the SnS_2 can be prepared as a solid solution with $SnSe_2$ to give $SnS_{2-x}Se_x$.[14] The metallocene can be substituted at the ring or metal site in order to vary its redox potential.[15]

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