Layered Oxysulfides $Sr_2MnO_2Cu_{2m-0.5}S_{m+1}$ ($m = 1, 2,$ and 3) as Insertion Hosts for Li Ion Batteries

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Materials capable of inserting lithium are widely studied as potential electrode materials in high-voltage rechargeable batteries. While the first cathode materials studied as intercalation hosts about three decades ago were layered dichalcogenides, such as TiS_2,[1] with the development of the SONY cell in 1990, more recent work has focused on the study of oxides.[2]

The layered oxysulfides $Sr_2MnO_2Cu_{2m-0.5}S_{m+1}$ ($m = 1-3$) (Figure 1)[3] consist of alternating perovskite-type Sr_2MnO_2 layers and layers which resemble fragments of the Cu_2S anti-fluorite structure[4] and consist of single, double, or triple layers of CuS_4 tetrahedra for the $m = 1, 2,$ and 3 materials, respectively. Intergrowths of these structures are also possible, and a material with alternating single and double copper sulfide layers has also been prepared.[3,5] Previous work by some of us has shown that these materials can be chemically lithiated using n-butyllithium,[6] with Li^+ replacing Cu^+ ions in the MS_4 tetrahedra, and extrusion of elemental copper. Similar processes have been observed during Li insertion in $Cu_xMo_6S_8$, Cu_3P, layered copper vanadates, and $CuTi_2S_4$[7] and as in these materials the Cu−Li exchange in the oxysulfides appears to be reversible: partial copper reinsertion occurs on exposing the lithiated samples to air, accompanied by the formation of LiOH.[6] Here we demonstrate that this process can be performed electrochemically and reversibly, and we use NMR to probe the Li environments and mobility.

Figure 2 shows the first galvanostatic discharge for the $m = 1-3$ samples versus Li. A long sloping plateau is seen between 1.8 and 1.3 V for all three samples. This plateau ends at a Li content, x, of approximately 1.5, 3.5, and 5.5 for the samples with $m = 1, 2,$ and 3, respectively, corresponding to the initial Cu contents, suggesting that this plateau corresponds to complete Li−Cu exchange.

The ^7Li MAS NMR spectra of the $m = 1-3$ samples following discharging to a voltage of 1.1 V (Figure 3) are similar to those of samples prepared using n-BuLi (Figure S1), indicating that the (local) structures of the chemically and electrochemically prepared compounds are similar. The spectra of all three samples show a peak at about 0 ppm (labeled B), due to diamagnetic impurities (e.g., electrolyte salts and $LiOH/Li_2CO_3$ impurities). The most intense resonance (A), assigned to Li^+ in the sulfide layers, occurs at quite different shifts in the three compounds (385, 211, and 131 ppm for $m = 1, 2,$ and 3, respectively). The $m = 1$ resonance A, at 385 ppm, is extremely broad, and a large fraction of the intensity is contained in its spinning sidebands. The ^6Li A resonance has much weaker spinning sidebands and dominates the ^6Li NMR spectrum (Figure 3a, inset), confirming that this resonance results from the major Li environment. Both the $m = 1$ ^7Li and ^6Li NMR spectra contain a third peak at 213 ppm (C), with a shift that is essentially identical to that of the main resonance found for $m =$

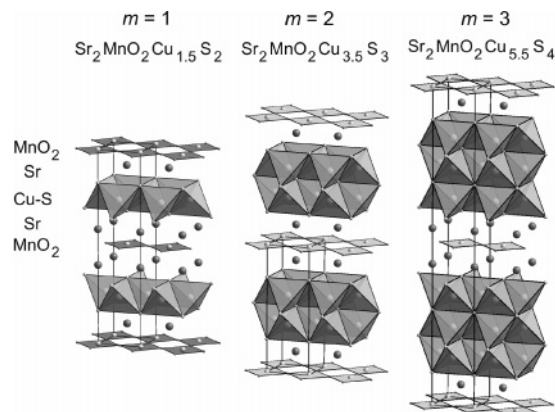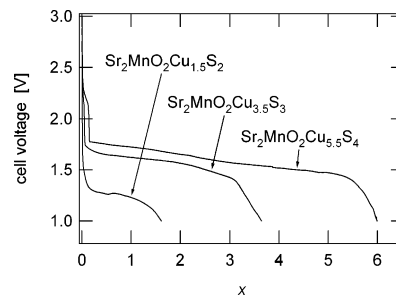**Figure 1.** Structures of $Sr_2MnO_2Cu_{2m-0.5}S_{m+1}$ ($m = 1-3$).

Figure 2. The first discharge of $Sr_2MnO_2Cu_{2m-0.5}S_{m+1}$ for $m = 1-3$ versus a $Li|Li^+$ negative electrode, with a discharge rate of $C/20$ (i.e., all the Cu ions are replaced by Li within 20 h); x denotes the number of Li ions inserted per formula unit.

2. This suggests, based on integration of the ^6Li NMR spectrum, that about 3% of the sulfide slabs in the $m = 1$ sample are double thickness. This is consistent with either an $m = 2$ impurity (although none was detected by powder X-ray diffraction measurements) and/ or intergrowths of the $m = 2$ phase, as in the $m = 1/m = 2$ ordered intergrowth phase.[3,5] The large shifts of the resonances are ascribed to the Fermi contact interaction of the Li nuclear spins with unpaired spin density associated with the manganese ions.[8] This interaction becomes weaker with increasing thickness of the sulfide layers, that is, as m increases, presumably because the (average) number of Mn ions nearby Li decreases. Neutron diffraction results for the $m = 1$ compound indicate that each Li ion is tetrahedrally coordinated by four S ions, each directly bonded to Mn.[3] For $m = 2$, only two S atoms per LiS_4 tetrahedron are coordinated to Mn, accounting for the reduction of the Fermi contact shift by approximately 50%; thus one Mn ion in the Li first cation coordination shell results in a shift of approximately $101(\pm 5)$ ppm. This assignment is confirmed by measurements on the $m = 1/m = 2$ intergrowth material $Sr_2MnO_2Cu_{2.5}S_{2.5}$ (Figure S2), where the NMR
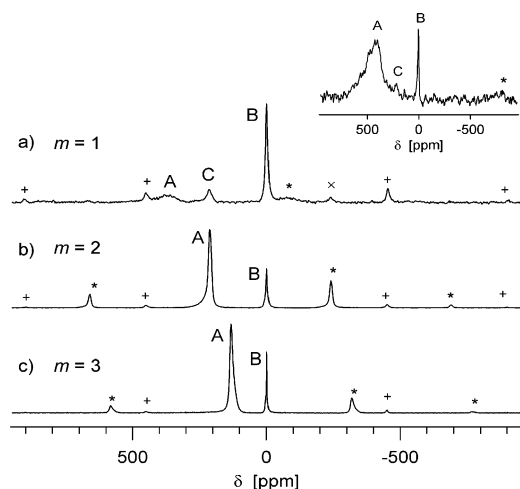
Figure 3. ^{7}Li (4.7 T) MAS NMR room temperature spectra of the lithiated (a) $m = 1$ ($x = 1.2$) (inset = ^{6}Li spectrum), (b) $m = 2$ ($x = 3.3$), and (c) $m = 3$ ($x = 6.1$) materials. Spinning sidebands of A, B, and C are marked with $*$, $+$, and $\times$, respectively. Spinning speed = 35 kHz.

Figure 4. The charge and discharge capacities of $Sr_2MnO_2Cu_{2m-0.5}S_{m+1}$, $m = 1-3$, and Cu_2S as a function of cycle number, between 2.7 and 1.1 V. Full symbols: discharge; empty symbols: charge; crosses: Cu_2S.

spectrum consists of a superposition of those of the $m = 1$ and $m = 2$ materials. Two types of Li local environments are present for $m = 3$: one very similar to that observed for $m = 2$ (i.e., Li nearby two Mn), and a second with no Mn ions in the first cation coordination shell, with relative populations of 2:1, respectively. Two resonances with shifts of approximately 202($\pm$10) (two Mn) and 0($\pm$3) (no Mn) ppm are predicted. Experimentally a single resonance at the weighted average of the two predicted shifts is observed ($\sim$136 ppm predicted; 131 ppm observed). This strongly suggests that, for $m = 3$, the Li ions are hopping between the two Li environments on a time scale faster than the frequency separation between the two resonances (i.e., the jump frequency is greater than 15.7 kHz (= 202 ppm $\times$ 77.8 MHz)). Variable temperature experiments are consistent with this, line broadening of the Li resonance occurring for $m = 3$ on reducing the temperature to -30 °C (Figure S3). Furthermore, the line widths of the A resonances in the $m = 2$ and $m = 3$ spectra are similar, while that for $m = 1$ is much broader. However, on heating the $m = 1$ sample, the resonance sharpens noticeably (Figure S4), suggesting that the Li ions are mobile in all three compounds but are noticeably less mobile for $m = 1$.

The reversibility of the copper extrusion process was evaluated between 2.7 and 1.1 V (Figure 4). This voltage window corresponds to the Cu−Li exchange process and is associated with theoretical capacities of 95.4, 161.6, and 199.1 mAhg^{-1} (for $m = 1$, 2, and 3) for $x = 1.5$, 3.5, and 5.5, respectively. The electrochemical Cu−Li exchange is fairly reversible: the thinner the sulfide layers, the lower the capacity but the higher the capacity retention. The $m = 1$ material shows the largest drop in capacity between the first and second cycle, but the smallest capacity fade in subsequent cycles. Unlike the other two compounds, this material does not contain vacant octahedral holes between the MS_4 tetrahedra; these are likely involved in ion transport, which may enhance the Cu−Li exchange in compounds with thicker sulfide layers, resulting in higher initial capacities. However, the materials with thinner Cu_2S layers are likely less susceptible to structural collapse or rearrangement, accounting for the higher capacity retention. Cycling experiments for the $m = 1/m = 2$ intergrowth ($Sr_2MnO_2Cu_{2.5}S_{2.5}$)^{3,5} show a reversible capacity of 100 mAhg^{-1} (Figure 4), apparently combining
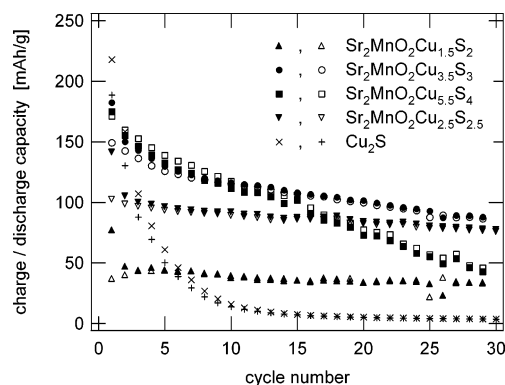
the higher capacity of the $m = 2$ phase with the higher reversibility of the $m = 1$ phase. Cu_2S was tested in order to confirm the role of the Sr_2MnO_2 layers in providing structural stability: its initial capacity is much higher (theoretical, 336.8 mAhg^{-1}; observed, >225 mAhg^{-1}) but drops much more rapidly within the first few cycles, consistent with the results for the oxysulfides, where the highest capacity loss is seen for the material with the thickest sulfide slabs. Such a large capacity loss has also been seen for CuS on cycling.^{9} The voltage profiles of the $m = 2$ and 3 materials show two steps during charging and subsequent discharging (Figure S5) which appear similar to those of Cu_2S and CuS.^{9}

Stabilization of an electroactive structure with poor reversibility (anti-fluorite Cu_2S) by combining it with a rigid perovskite-type fragment yields a structure that can accommodate the structural changes that occur on Li/Cu exchange. This opens up the possibility of designing related structures in which a compromise between stability and capacity is achieved, leading to a wide variety of potential new Li ion battery electrode materials.

Supporting Information Available: Experimental details, voltage profiles on cycling, and variable temperature ^{7}Li NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA064961A