

Novel layered chalcogenides as electrode materials for lithium-ion batteries

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Abstract

Misfit layer compounds of general formula $(\text{PbS})_{1+\delta}(\text{TS}_2)_2$ ($\text{T} = \text{Ti, Ta}$) are evaluated as the alternative intercalation electrodes versus lithium metal and in lithium-ion cells versus LiCoO_2 and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrodes. Galvanostatic cycling experiments of lithium anode cells showed an excellent capacity retention, particularly for the $(\text{PbS})_{1.14}(\text{TaS}_2)_2$ composition. The potential stability range of the intercalation compounds of the sulfides (1.5–3.5 V) allows the use of these materials as the positive electrode versus $\text{Li}_7\text{Ti}_5\text{O}_{12}$ or as the negative electrode versus the 4 V cathode LiCoO_2 . The use of titanium oxide anodes requires a previous in situ electrochemical lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in a three-electrode assembly. Average cell voltages of about 1.0 V were then obtained. The use of LiCoO_2 cathodes allows higher cell voltages (1.3–3.0 V) and capacity retentions during the first 50 cycles up to 80%. © 1997 Elsevier Science S.A.

Keywords: Lithium-ion batteries; Intercalation electrodes; Layered chalcogenides; Misfit layer compounds; Lead titanium sulfide; Lead tantalum sulfide

1. Introduction

Due to safety and efficiency reasons, the use of lithium metal electrodes is limited to rechargeable batteries. From 1990, a significant improvement was achieved by the use of carbon electrodes versus LiCoO_2 in lithium-ion batteries [1]. Irrespective of being more expensive and less available than some carbon electrode materials [2], other inorganic host lattices showed to be suitable anodes [3]. More recently, compounds such as layered TiS_2 [4,5], spinel oxides [6] and spinel chalcogenides [7] have been studied as the negative electrodes versus 4 V electrodes in rocking-chair cells. Layered chalcogenides are well-known host lattices for intercalation reactions. In fact, TiS_2 provided one of the first examples of intercalation electrode in lithium anode batteries [8]. Since the early studies of binary systems, other structurally less simple ternary chalcogenides have been found of interest for these purposes, such as phosphotrichalcogenides [9,10].

Misfit layer chalcogenides of general formula $(\text{MX})_{1+\delta}(\text{TX}_2)_n$ ($\text{M} = \text{Sn, Pb, Bi, rare earth}; \text{T} = \text{V, Cr, Ti, Nb, Ta}$, and $\text{X} = \text{S, Se}$) consist of an intergrowth of one two-atom thick MX slab structurally related to TII and three-atom thick TX_2 slabs similar to those found in the binary transition metal dichalcogenides [10–15]. The two sublattices MX and TX_2 have nonrational axis ratio in one direction leading to the $n/(1+\delta)$ stoichiometry ratio. The chemical and electro-

chemical intercalation of lithium and sodium has been studied in these compounds [16–20], and a better intercalation behaviour was found for $(\text{PbS})_{1+\delta}(\text{TS}_2)_2$ ($\text{T} = \text{Ti, Ta}$) compositions [19,20]. Different sets of sites are potentially available for lithium intercalation in both solids. The PbS-TS_2 gap defines $1+\delta$ pseudotetrahedral sites per formula unit, while the $\text{TS}_2\text{-TS}_2$ van der Waals gap defines one octahedral and two tetrahedral sites per formula unit. Thus, large cell capacities are expected by using these solids as intercalation electrodes.

From the previous knowledge on the intercalation properties of these systems, the aim of this paper is to evaluate the potential use of compounds $(\text{PbS})_{1.18}(\text{TiS}_2)_2$ and $(\text{PbS})_{1.14}(\text{TaS}_2)_2$ as the alternative intercalation electrodes versus LiCoO_2 and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ electrodes in lithium-ion cells.

2. Experimental

Polycrystalline samples of $(\text{PbS})_{1.18}(\text{TiS}_2)_2$ and $(\text{PbS})_{1.14}(\text{TaS}_2)_2$ were prepared from stoichiometric mixtures of the elements heated at 800–900 °C in evacuated silica ampoules. LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were prepared by the conventional ceramic procedures described in Refs. [21,22]. Phase purity was determined in the powder products by X-ray diffraction (Siemens D500) and electron microscopy (JEOL 200CX).

The electrochemical measurements were alternatively carried out in two-electrode Swagelok and three-electrode glass cells. A typical electrode consisted of about 6 mg of active material mixed with graphite (Merck), acetylene black (Strem) and polytetrafluoroethylene (PTFE) binder in a 70:10:10:10 mass ratio. The mixtures were compacted in 7 mm diameter pellets onto stainless-steel mesh current collectors by pressing at 200 MPa. The electrolyte consisted of 1 M solutions of LiClO_4 in anhydrous propylene carbonate (PC), pure or in a 1:1 mixture with ethylene carbonate (PC+EC). A MacPile multichannel potentiostat/galvanostat system was used. Unless otherwise specified, galvanostatic experiments were carried out at 0.05 mA. For the temperature-controlled measurements a Haake thermostat and specially designed glass cells were used.

3. Results and discussion

Open-circuit voltage and galvanostatic discharge curves of the lithium anode cells, $\text{Li}/\text{LiClO}_4(\text{PC})/\text{sulfide}$, (see Fig. 1) revealed that the misfit layer compounds may intercalate a number of lithium atoms per formula unit larger than unity, as a consequence of the above discussed number of available sites ($4 + \delta$). However, extended cell discharges resulted in a progressive loss of long-range order, as evidenced in the X-ray diffraction patterns, particularly for the $(\text{PbS})_{118}(\text{TiS}_2)_2$ composition. This, in turn, revealed that reversible intercalation/extraction process was only observed for less than three lithium atoms per formula unit. The lithium cells were cycled galvanostatically in the potential interval 1.5–3.5 V and 1.5–2.5 V for the tantalum and titanium compounds, respectively. An excellent capacity retention was observed (see the inset in Fig. 1), particularly for the $(\text{PbS})_{114}(\text{TaS}_2)_2$ composition (about 68% in 100 cycles) [20].

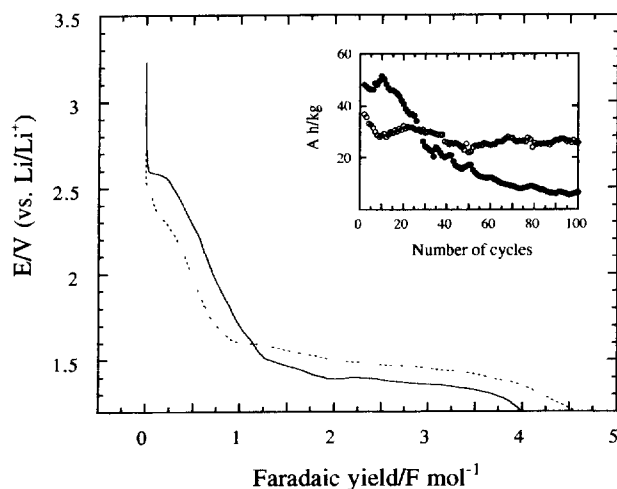
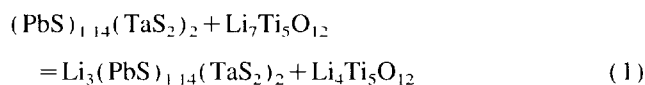


Fig. 1. Galvanostatic discharge curves of $\text{Li}/\text{LiClO}_4(\text{PC})/\text{misfit layer sulfide}$ cells: (· · ·) $(\text{PbS})_{118}(\text{TiS}_2)_2$ cathode, and (—) $(\text{PbS})_{114}(\text{TaS}_2)_2$ cathode. Inset, cycling performance of the cells: (●) $(\text{PbS})_{114}(\text{TaS}_2)_2$ cathode, and (○) $(\text{PbS})_{118}(\text{TiS}_2)_2$ cathode.

The intermediate potential stability range of the lithium intercalation compounds observed for both sulfide compositions versus lithium metal allows that these materials can be used either as anode or cathode in lithium-ion batteries. The use as the positive electrode requires an anode with moderate potential. The defect spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was recently shown to insert reversibly lithium up to $\text{Li}_7\text{Ti}_5\text{O}_{12}$ at a voltage of 1.55 V [22] and will be considered here. Alternatively, both misfit layer sulfide electrodes can be used as the negative electrode versus 4 V cathodes, such LiCoO_2 , the first example of cathode material in commercial lithium-ion batteries [1].

As the initial sulfides have no lithium in their composition, the counter-electrode should contain all lithium to be moved back and forth during cell charge and discharge. While this is true for LiCoO_2 electrodes, the use of the titanium spinel oxide electrodes versus the chalcogenide required a first in situ electrochemical lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the three-electrode assembly used in the study of the lithium-ion cells. After this preliminary step, the cells were allowed to start the cycling experiment by the discharge process without previous charge. The best results for this type of cells were obtained with the tantalum misfit layer compound. The ideal reaction for full utilization of this type of cell is then



in which the maximum capacity (105 and 65 Ah/kg , as referred to the mass of active cathode material, and the total mass of electrode, respectively) is expected for an electrode mass ratio $r^+/r^- = 1.60$.

Fig. 2 shows the experimental galvanostatic cycling profiles of a cell in which the electrode mass ratio was optimized to obtain maximum cell capacity and cycling performance. The deduced r^+/r^- value was 3.0, which involves an incomplete intercalation of the misfit layer compound, as compared with Eq. (1). The first-cycle capacity of this cell was 25 Ah/

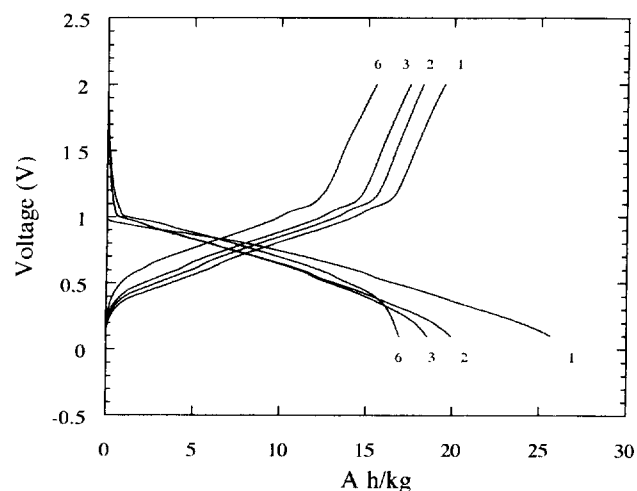
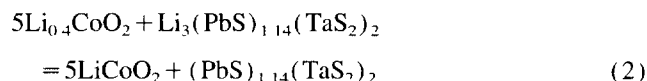


Fig. 2. Galvanostatic cycling of the $\text{Li}_7\text{Ti}_5\text{O}_{12}/\text{LiClO}_4(\text{PC} + \text{EC})/(\text{PbS})_{114}(\text{TaS}_2)_2$ cell after in situ lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The capacity refers to that delivered by the cathode only (misfit layer compound).

kg, as referred to that delivered by the total mass of active electrode material, and represents a 40% utilization of the theoretical value. This value decreased in about 30% after six cycles. An average cell voltage of about 1.0 V was found, which implies a moderate value of energy density (25 Wh/kg total mass). For some applications, these values could be appropriate [6].

LiCoO₂ was used alternatively as the positive electrode in lithium-ion cells using the misfit layer chalcogenide and as the active material of the negative electrode. In the latter case, higher voltages than in the Li₇Ti₅O₁₂ case were observed and the cells required previous charge as in other commercial lithium-ion batteries. A particularly good behaviour was found for the cell based in the following ideal reaction



This reaction has ideal $r^+/r^- = 0.64$ and a theoretical capacity of 64 Ah/kg (total mass) and 164 Ah/kg (cathode only). A maximum experimental capacity of about 55% of this value was obtained for a cell with $r^+/r^- = 0.56$, indicative of an incomplete use of the misfit layer sulfide anode, although closer to the ideal mass ratio than the Li₇Ti₅O₁₂ cell previously described. Fig. 3 shows the capacity retention during the first 100 cycles of a similar cell cycled in a 1.3–2.8 V window.

The effect of several factors on the performance of this cell were examined. First, on increasing simultaneously both limits of the potential window from 1.0–2.5 V to 2.0–3.5 V, the cell capacity increased monotonically from 14 to 35 Ah/kg, while the capacity retention after 100 cycles reached a maximum for the 1.3–2.8 V interval. The initial capacity value under these conditions was 20 Ah/kg and the average energy density took a value of 40 Wh/kg total mass.

On the other hand, cell currents were varied from 0.05 to 0.50 mA. As expected, cell capacity decreased with current

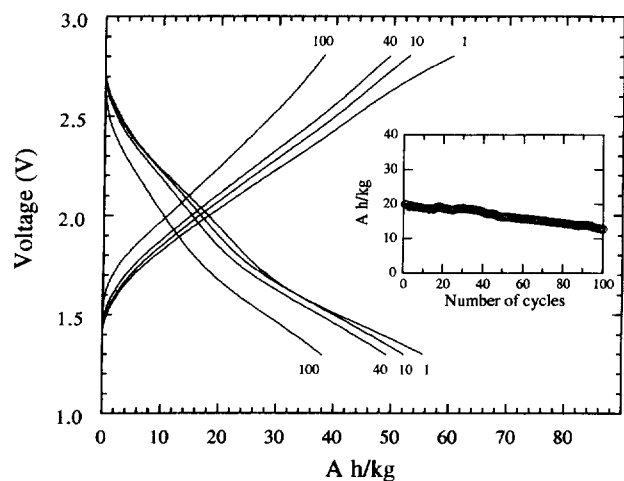
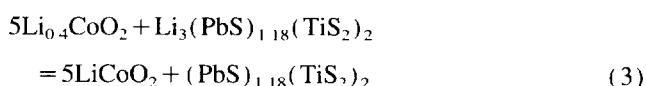


Fig. 3. Galvanostatic cycling of the (PbS)_{1.14}(TaS₂)₂/LiClO₄(PC + EC)/LiCoO₂ cell. The capacity refers to that delivered by the cathode only (lithium cobalt oxide). Inset: cell capacity referred to the total mass of active electrode materials vs. cycle number.

intensity. However, the capacity retention increased with current as a result of the uncomplete use of both active electrode materials during cell charge and discharge. Thus, the results shown in Fig. 3 were obtained with a compromise value of 0.20 mA.

Finally, the effect of working temperature was evaluated in two-electrode thermostated glass cells. For 0.20 mA, $r^+/r^- = 0.56$ and 1.3–2.8 V potential window, the cell capacity increased about 30% from 25 to 35 °C, but the retention of this capacity value decreased markedly with the number of cycles. For the 0.50 mA experiments, the maximum capacity was also observed at 35 °C, and showed little changes at 50 °C.

Similarly, the titanium misfit layer sulfide was used as the negative electrode in a cell described ideally by the reaction



The ideal values for this reaction are $r^+/r^- = 0.96$, cathode capacity = 164 Ah/kg, and total mass capacity = 81 Ah/kg.

The experimental lithium-ion cells using titanium misfit compound anodes were assembled using a mass ratio lower than the theoretical one in order to avoid the loss of long-range order in the chalcogenide for extended discharges, as discussed above. The optimization at the experimental cell was carried out by modifying two additional parameters: the current density and the cycling voltage window.

For the current density, three experiments were carried out at 0.05, 0.1 and 0.2 mA in the 1.5–2.5 V range. A continuous decrease in cell capacity was observed in all cases. Nevertheless, extended charge/discharge cycles at a lower current density showed a higher cell capacity retention. In the case of the voltage window, the new experiments were made in the following ranges, 1.5–2.2 V, 1.5–2.5 V and 1.5–2.8 V at 0.05 mA. Two opposite effects were found. The lower is the

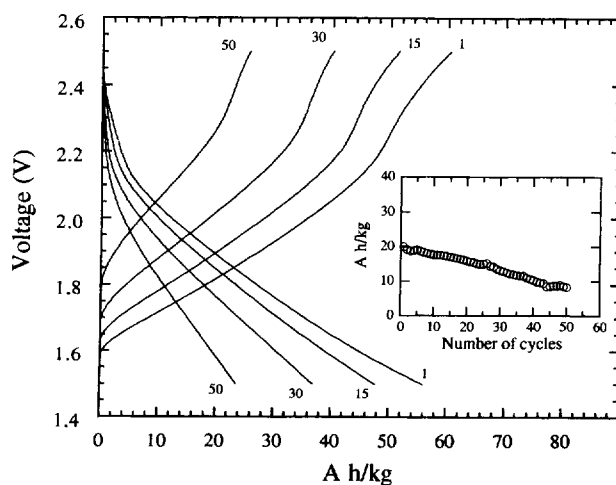


Fig. 4. Galvanostatic cycling of the (PbS)_{1.18}(TiS₂)₂/LiClO₄(PC + EC)/LiCoO₂ cell. The capacity refers to that delivered by the cathode only. Inset: cell capacity referred to the total mass of active electrode materials vs. cycle number.

voltage window the lower is the cell capacity and the higher is the window the lower is the capacity retention.

Hence, we decided that the optimal conditions for the cycling of this cell were 0.05 mA and 1.5–2.5 V. Fig. 4 shows the galvanostatic cycling behaviour of the cell obtained with an optimum r^+/r^- ratio (0.8). Under these experimental conditions, the initial capacity and the capacity referred to cathode mass after 50 cycles took values of about 40 and 18% of those predicted from Eq. (3).

Acknowledgements

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