Investigation of lead tin fluorides as possible negative electrodes for Li-ion batteries

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Abstract

Lead tin fluorides are well known fast ion conductors. In this study the electrochemical behaviour of materials as negative electrodes in lithium rechargeable batteries was investigated. The initial reduction with lithium occurs at much higher potentials for fluorides than oxides. This correlates well with the standard energies of formation of metals and lithium oxide/fluoride on lithium insertion. Lead rich compounds present a greater degree of crystallinity than tin rich materials and it is also observed that fluoride matrices exhibit greater crystallinity after cycling than their oxide counterparts. Tin oxide exhibits the best cycling performance and this seems to correlate with the low degree of crystallinity observed in this system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tin composite oxides have been the subject of considerable investigations as possible new negative electrodes in lithium-ion batteries [1–3]. They show larger reversible capacity, over 550 mAh/g, compared to carbonaceous materials such as graphite which has a theoretical capacity of only 372 mAh/g. Tin oxide based anodes have entirely different discharge and charge mechanism compared to carbonaceous anodes. A two step reaction mechanism of tin oxides with lithium was proposed and confirmed by considering the results of in situ XRD, Raman and HRTEM [2–4]. In the first step, lithium reacts irreversibly with oxide to produce amorphous Li_2O and metallic Sn, then Sn reacts with more lithium to form Li–Sn alloys. In this study, we have investigated a series of tin fluorides associated with high anionic mobility, following on from earlier phase equilibria and solid state electrochemical studies of this system.

$PbSnF_4$ is a well known fluoride ion conductor exhibiting one of the highest ionic conductivities at room temperature of any material. Ionic conductivities, $>10^{-2}$ s/cm at 300 K and activation energies <0.2 eV have been observed. $PbSnF_4$ exhibits three principal polymorphs, α, β, γ. The γ-form has the cubic fluorite structure and is isomorphous with β-PbF_2. The α- and β-forms have distorted fluorite-related structures with different tetragonal modifications. The cubic fluorite polymorph (β-PbF_2 or γ-$PbSnF_4$) is observed to exist at high temperatures from 0 to 80% SnF_2 and is stabilised to room temperature between ∼15 and ∼30 mol% SnF_2. The α- and β-forms of $PbSnF_4$ are found in the vicinity of 50 mol% SnF_2. The α-form is only found over a narrow range of composition and is not stable at temperatures above 543 K. The β-form is stable over a much wider range of temperatures and compositions. In this study we have investigated the possibility of using these materials as bases for Sn-based negative electrodes.

2. Experimental

2.1. Synthesis and characterisation

Starting materials were synthesised by solid state reaction from stoichiometric mixtures of PbF_2, SnF_2, PbO and SnO (Aldrich). Reaction mixtures were placed in an electrical tube furnace and initially heated at 473 K for a few hours under inert or fluoridising atmosphere and then subjected to further grinding and annealing treatments at temperatures between

473 and 703 K depending on composition. Materials were characterised by X-ray diffraction, simultaneous TGA–DTA, quenching and ac impedance spectroscopy techniques.

2.2. Preparation of the electrodes

Porous "Bellcore"-type electrodes [5] were utilised in electrochemical testing. A slurry was produced by grinding 11.6% active material, 1.4% Super S carbon together, and then adding 5.5% polyvinylidene fluoride (PVDF), 9.5% propylene carbonate and 72% acetone. This slurry was stirred for 4 h at 323 K in a water bath to dissolve the binder and form a disperse mixture. The mixture was then spread on a glass plate. Applying the meniscus principle, a sharp metallic bar was passed over the slurry in order to form a thin film of about 50–70 μm thick. Disks of the anode material were cut and immersed in ether to remove the propylene carbonate, dried under vacuum before they were put into an argon filled glove box.

Electrodes were weighed and then soaked in electrolyte (1 M $LiPF_6$ in ethylene carbonate–dimethylene carbonate (2:1 v/o), Merck) for a few minutes, before being assembled into a 2325 coin cells (NRC Canada). Lithium was used as the counter and reference electrode. The cells were completed with one polypropylene or glass fibre separator, a 11 mm diameter lithium foil disk, one or two stainless steel spacers and springs.

Test cells were charged using a Macpile II system (Biologic, Claix, France). Two different electrochemical experiments were carried out in this study, either in a current controlled or in a potential controlled mode. Galvanostatic experiments were carried out by applying a constant current between 0.05 and 0.15 mA/cm^2 and recording the evolution of cell voltage with composition (number of lithium atoms inserted).

3. Results and discussion

3.1. SnF₂, Pb₀.₁₅Sn₀.₈₅F₂, Pb₀.₄₇₅Sn₀.₅₂₅F₂ and SnO

SnF_2 and $Pb_{0.15}Sn_{0.85}F_2$, have similar voltage profiles (Fig. 1). An initial reduction using 2Li per formula unit occurs
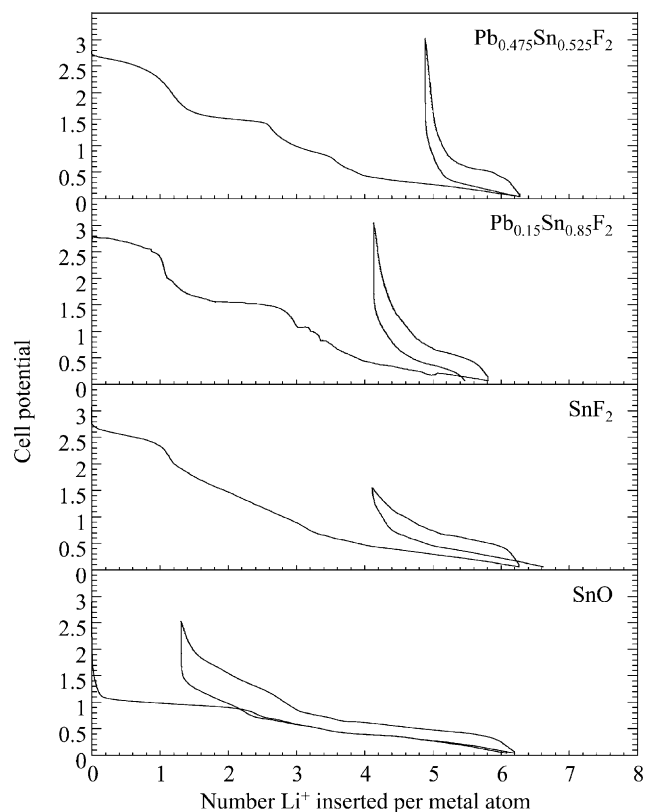

Fig. 1. Evolution of cell voltage vs. composition obtained when cycling cells with the following configuration: Li ‖ $Pb_{0.475}Sn_{0.525}F_2$, Li ‖ $Pb_{0.15}Sn_{0.85}F_2$, Li ‖ SnF_2 and Li ‖ SnO.

in two steps, between 2.8 and 1.5 V corresponding to the formation of 2LiF per formula unit. Significant lithium insertion (alloying) occurs below 1.5 V. For both compounds a reversible capacity of 300 mAh/g was observed (Table 1). For $Pb_{0.475}Sn_{0.525}F_2$, initial reduction with 2Li occurs in two steps, between 2.7 and 1.4 V. Lithium insertion occurs below 1.4 V. A reversible capacity of 195 mAh/g was observed. The electrochemical behaviour of SnO has been reported previously [6] and our results agree with this previous work. A large plateau at 0.92 V is observed and this plateau is related to the formation of one Li_2O per formula unit. Lithium insertion

Table 1
Charge and discharge properties for lead tin fluorides and oxides

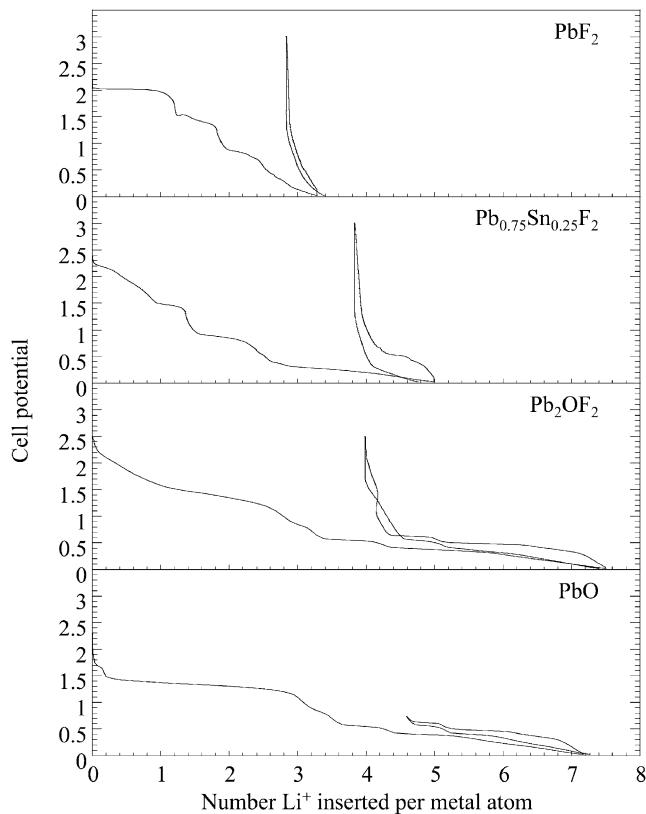| Material	Total capacity observed (mAh/g)	Reversible capacity observed (mAh/g)	Total capacity calculated (mAh/g)	Reversible capacity calculated (mAh/g)
SnO	1230	1030	1273.9	875.8
$Pb_{0.475}Sn_{0.525}F_2$	850	195	863.4	593.6
$Pb_{0.15}Sn_{0.85}F_2$	1025	300	1009.5	694
SnF_2	850	300	1095	752.8
PbO	810	260	768.7	528.5
Pb_2OF_2	858	400	732.6	503.7
$Pb_{0.75}Sn_{0.25}F_2$	600	140	769.2	528.8
PbF_2	360	50	699.8	481.1

Fig. 2. Evolution of cell voltage vs. composition obtained when cycling cells with the following configuration: Li ‖ PbF_2, Li ‖ $Pb_{0.75}Sn_{0.25}F_2$, Li ‖ Pb_2OF_2 and Li ‖ PbO.

occurs at 0.55, 0.38 and 0.25 V forming a series of alloy phases. SnO shows an irreversible loss of 18% of the initial capacity and a reversible capacity of 1030 mAh/g (Table 1).

3.2. PbF_2, $Pb_{0.75}Sn_{0.25}F_2$, Pb_2OF_2 and PbO

PbF_2 and $Pb_{0.75}Sn_{0.25}F_2$, have similar voltage profiles (Fig. 2). Initial reaction with lithium occurs in two steps, between 2.4 and 1.5 V corresponding to the formation of 2LiF per formula unit. Limited further lithium insertion occurs and reversibility is poor. The discharge curve for PbO shows a very large plateau at 1.4 V containing about half the initial capacity (350 mAh/g). This plateau corresponds to the formation of Li_2O and LiPb. Further lithiation occurs showing at least three different plateaux at 0.8, 0.55 and 0.38 V. The last two plateaux are still observable in subsequent cycles. The voltage levels of these plateaux match those previously reported by Wang et al. [7] for a coulometric titration at 25°C. Pb_2OF_2 has a similar electrochemical behaviour to PbO but with a higher total capacity of 858 mAh/g and reversible capacity of 400 mAh/g.

Fig. 3 shows the ex situ X-ray diffraction patterns for tin and lead compound electrodes after 2.5 cycles. $Pb_{0.75}Sn_{0.25}F_2$ and $Pb_{0.475}Sn_{0.525}F_2$ showed the presence of Pb and Sn metal. Lead oxide and oxyfluoride showed the presence of Pb and PbLi alloy.

4. Conclusions

The initial reduction with Li occurs at the highest potential for SnF_2 containing compositions. This initial potential follows the trend $SnF_2 > PbF_2 > PbO > SnO$, with SnO exhibiting the largest deviation from that expected from solution redox behaviour. This correlates well with the standard energies of formation of the metals and lithium oxide or fluoride phases, with SnO exhibiting the smallest energy for this reaction. Lead rich compounds present a
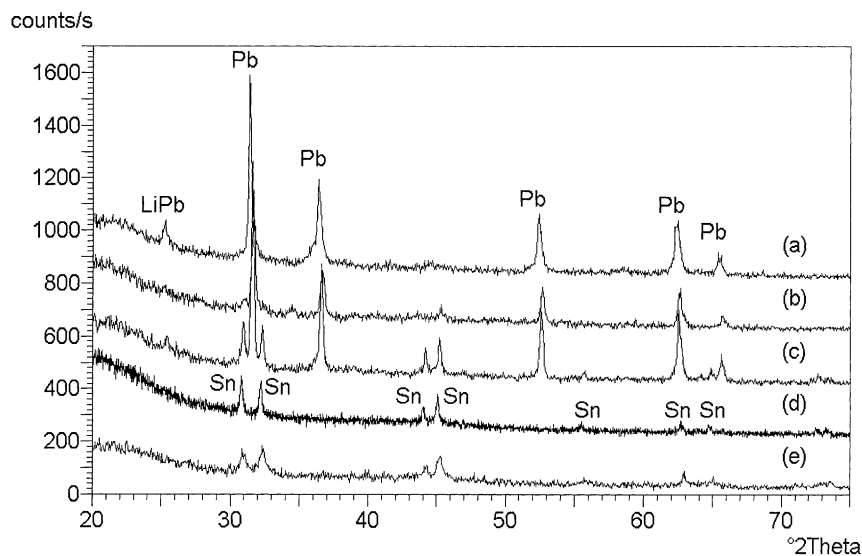

Fig. 3. Ex situ X-ray diffraction patterns after 2.5 cycles for (a) Pb_2OF_2; (b) $Pb_{0.75}Sn_{0.25}F_2$; (c) $Pb_{0.475}Sn_{0.525}F_2$; (d) SnF_2; (e) SnO.

greater degree of crystallinity than tin rich materials and it is also observed that fluoride matrices exhibit greater crystallinity after cycling than their oxide counterparts. Tin oxide exhibit the best cycling performance and this seems to correlate with the low degree of crystallinity observed in this system.

Acknowledgements

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