

Electrochemical characteristics of $\text{Sn}_{1-x}\text{Si}_x\text{O}_2$ as anode for lithium-ion batteries

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Abstract

Fine powders of tin oxide doped with traces of silicon in combination with highly dispersed amorphous silicon oxide have been synthesized by an advanced ultrasonic spray method. The mixtures have been analyzed by XRD and IR. The electrochemical results showed that addition of silicon decreases the tin oxidation state, and, hence, reduces the irreversible capacity during the first discharge/charge cycle. SiO_2 and Li_2SiO_3 appeared during the first discharging as confirmed by IR spectroscopy. Furthermore, a reversible capacity of 900 mA h/g to 950 mA h/g for these composites has been found, which is even higher than the theoretical value (783 mA h/g according to the $\text{Li}_{4.4}\text{Sn}$). The chemical diffusion coefficients of lithium in the Li–Sn alloy phases formed ($\text{Li}_{0.4}\text{Sn}$, LiSn , Li_3Sn_7 , $\text{Li}_{3.5}\text{Sn}$ and $\text{Li}_{4.4}\text{Sn}$) have been measured by galvanostatic intermittent titration technique (GITT). Below a Li content corresponding to Li_3Sn_7 , a reduced voltage polarization as well as an increased lithium chemical diffusion coefficient were observed. This improved performance is due to an enhanced interfacial diffusion caused by highly dispersed inert second phases, i.e., SiO_2 and Li_2SiO_3 . © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin oxide composite; Inert second phase; Li–Sn alloy; Lithium chemical diffusion coefficient

1. Introduction

A new generation of lithium-ion batteries was born in early 1997, initiated by Fuji Photo Film Celltec. [1,2], whose anodes comprised amorphous tin-based oxides instead of carbon. This new material is reported to have a four (two)-fold theoretical volumetric (gravimetric) capacity than carbon. According to Courney and Dahn's [3,4] recent results, the mechanism of this tin-based oxide reacting with lithium cannot be described by a simple intercalation–deintercalation process. In this case, initially an irreversible reaction takes place, i.e., the formation of Li_2O and metallic Sn, followed by an alloying process between Li and Sn, which successively proceeds until a maximum of $\text{Li}_{4.4}\text{Sn}$ has been reached. A systematic in-situ XRD study of the composition versus the open voltage in a lithium cell as well as cycling behavior have been reported.

In this paper, we will report on the electrochemical characteristics of a new kind of tin oxide composite doped with traces of silicon and some highly dispersed silicon oxide synthesized by an advanced ultrasonic spray method.

2. Experimental aspects

2.1. Synthesis of the materials

The samples studied here were prepared by an advanced ultrasonic spray method, i.e., flame-assisted ultrasonic spray pyrolysis (FAUSP), using SnCl_4 , SnCl_2 and appropriate amounts of $\text{Si}(\text{OMe})_4$ (all Aldrich products). The precursors were dissolved in ethanol (99.9%), stabilized with a small amount of nitric acid. An aerosol of the solution was generated by an ultrasonic generator, which allows to react immediately with oxygen assisted by a flame. The powders were collected on a stainless steel plate. Details of the FAUSP method are reported in Ref. [5,6].

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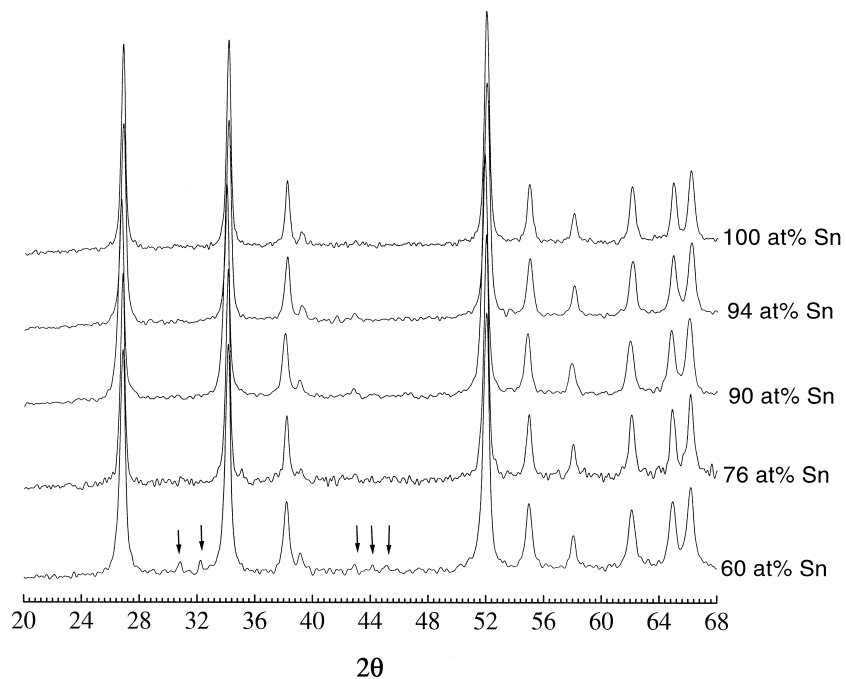


Fig. 1. XRD spectra of the prepared samples with different nominal composition.

2.2. Structure determination

The structures were determined both by XRD with a Philips PW1840 diffractometer using $\text{CuK}\alpha$ radiation and IR spectroscopy (Perkin Elmer FTIR spectrometer 1000).

2.3. Electrochemical testing

Electrodes for electrochemical testing were prepared by the doctor-blade coating technique using copper foils, with PAN (polyacrylonitrile)-based binder (95:5 by weight).

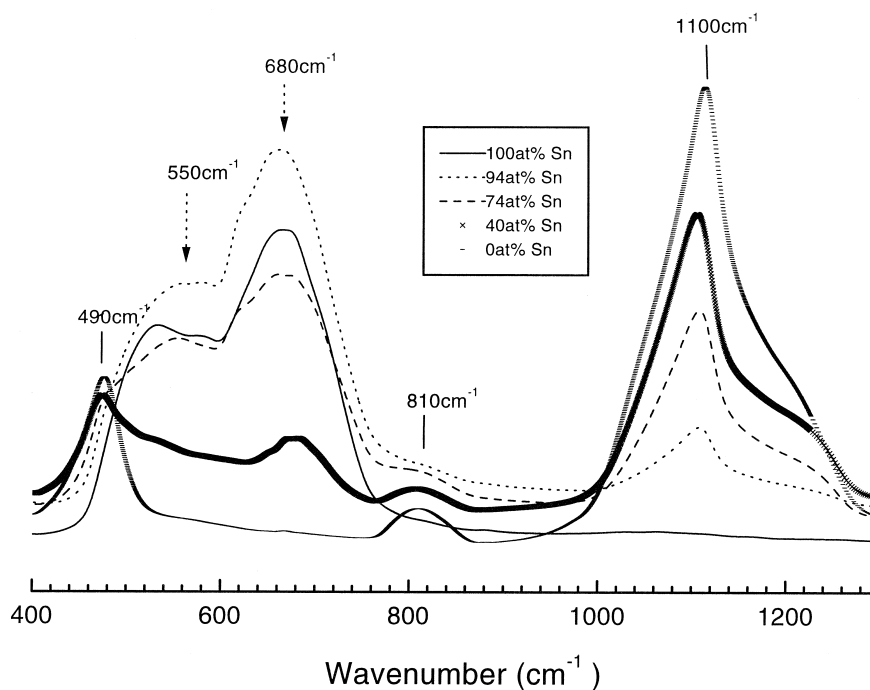


Fig. 2. FTIR spectra of the prepared samples with different nominal composition.

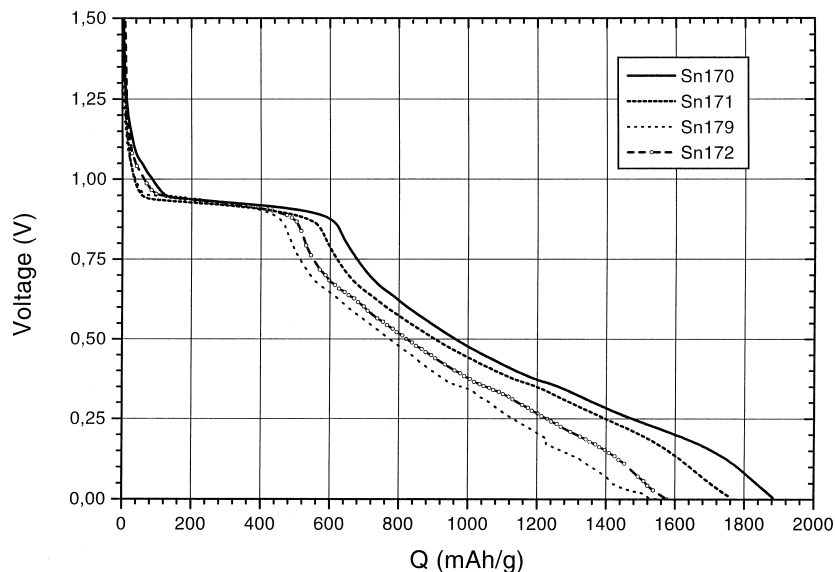


Fig. 3. The first discharge profiles at a discharge current rate of 0.1 mA.

After pressing and drying, the thus made electrode foils were transferred into a glove box filled with He gas. Finally, state-of-the-art two electrode cells were assembled, with 1 M LiPF_6 -EC-DMC as electrolyte, and fresh Li foil as both reference and counter electrode.

All cells were initially discharged and charged at a constant current density of $100 \mu\text{A}/\text{cm}^2$ between 10 mV and 2.5 V for three times, till the capacity efficiency is more than 90%. Then the cells were discharged at a current density of $20 \mu\text{A}/\text{cm}^2$ to obtain the reversible capacity within the set voltage range. The chemical diffusion coefficient D_{Li} was measured by the galvanostatic intermittent titration technique (GITT) method [7]. All electrochemical measurements were controlled and recorded automatically by a MACCOR battery tester.

3. Results and discussions

3.1. Structure

Fig. 1 presents the XRD spectra of the powders synthesized. The major phase obtained in all powders is rutile-type

SnO_2 , showing a shift of the lattice parameters of SnO_2 upon Si addition, suggesting that traces of silicon dissolved in the SnO_2 rutile structure to form a solid solution. However, it is very unlikely that SnO_2 can accept 25% of Si in its lattice ($\text{Sn}/\text{Si} = 2.8$). The 1108 cm^{-1} peak in the IR spectra (Fig. 2) confirms the presence of an amorphous SiO_2 phase.

Hence, a second phase mixture has been found of a solid solution $\text{Sn}_{1-x}\text{Si}_x\text{O}_2$ with amorphous SiO_2 highly dispersed in the former. The results are in line with previous measurements with EDX and XPS [6].

3.2. Electrochemical measurements

It has been reported that the tin-based oxide anodes consume Li initially by a reaction with oxygen originally bonded to tin, leading to Li_2O and leaving metallic tin [3]. But for the SiO_2 , the Si–O bond is too strong to be broken up by Li, and, so, the SiO_2 remains intact not leading to an irreversible reaction.

Fig. 3 shows the first discharge curves of the cells. The plateau above 0.85 V observed for all samples corresponds

Table 1

The specification, nominal composition, structure, irreversible and reversible capacity of the prepared samples

Sample	Precursor	Phase	Capacity (mA h/g)	
			Q_{ir} (0.9 V)	Q_{r} (0–0.9 V)
Sn172	SnCl_2	SnO_2^{a}	450	795
Sn170	SnCl_4	SnO_2^{a}	600	860
Sn171	$\text{SnCl}_4 + \text{Si}(\text{OMe})_4$ (Sn:Si = 0.94:0.06)	$\text{Sn}_{1-x}\text{Si}_x\text{O}_2^{\text{a}} + \text{SiO}_2^{\text{b}}$	580	936
Sn179	$\text{SnCl}_4 + \text{Si}(\text{OMe})_4$ (Sn:Si = 0.74:0.26)	$\text{Sn}_{1-x}\text{Si}_x\text{O}_2^{\text{a}} + \text{SiO}_2^{\text{b}}$	420	910

^aCrystal phase (rutile structure).

^bAmorphous phase.

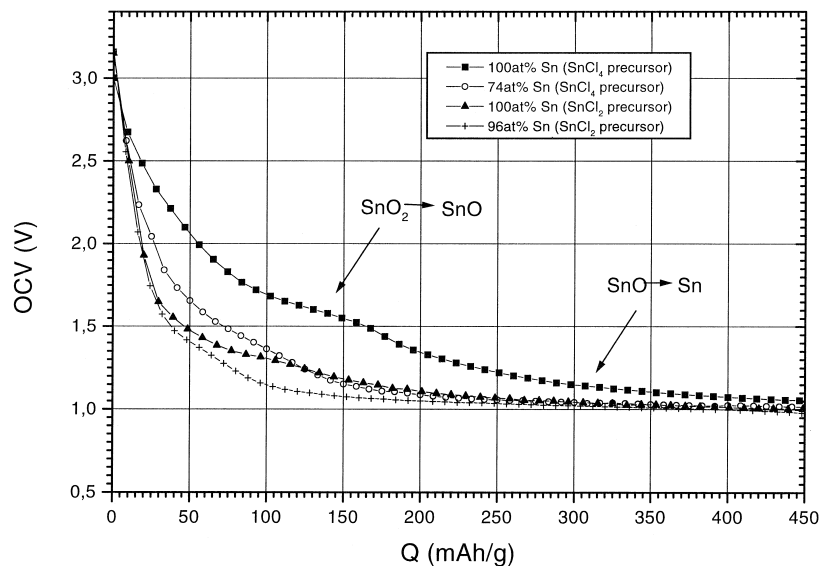


Fig. 4. The OCV titration curves obtained by discharging 0.5 h ($I = 0.1$ mA) followed by 3 h resting.

to the initial irreversible reaction as mentioned above. The samples Sn172 and Sn179 have a shorter plateau, which is attributed directly to the difference of oxygen content as well as the Sn oxidation state in the samples. The specification and capacity data are listed in Table 1. It is noteworthy that upon addition with enough Si, the irreversible reaction capacity, as well as the oxidation state of Sn, reduces significantly.

It has even been found that when the silicon content in the precursor was high enough, there appear some metallic tin in the product as identified by XRD. This means that

addition of some $\text{Si}(\text{OMe})_4$ in the precursor will reduce the oxygen content of the final product. Since the oxygen bound to Sn is responsible for the observed irreversible capacity, a low oxidation state is highly beneficial for this anode material.

To investigate the irreversible reaction process, OCV titration measurements were performed and the important parts of the OCV profiles were shown in Fig. 4. The two plateaus observed correspond to the SnO_2 to SnO and SnO to metallic Sn transitions while reacting with Li. It is interesting to notice that there are some differences be-

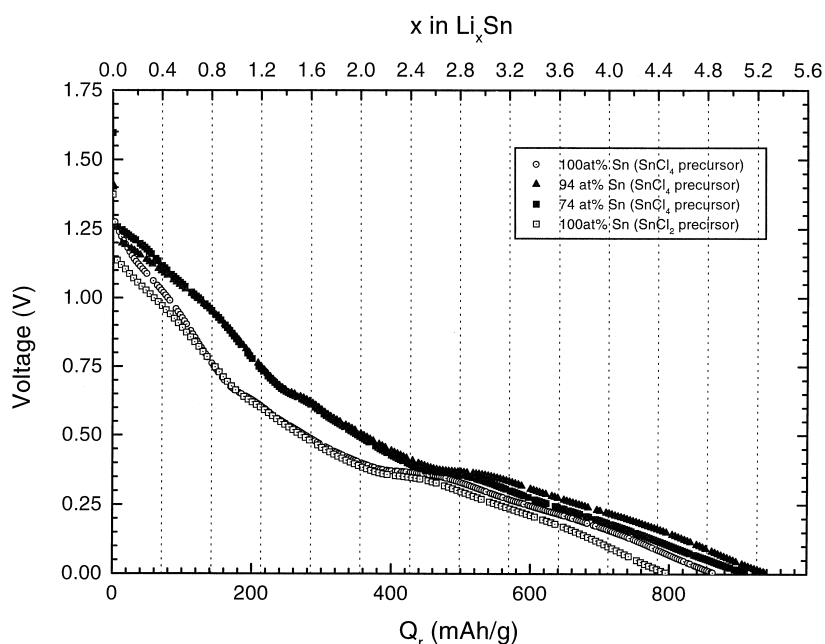


Fig. 5. The discharge profiles at a current rate of 0.02 mA after three cycles at a current rate of 0.1 mA.

tween the samples with and without silicon addition at the initial part of the profile, i.e., the SnO₂ to SnO reduction. The plateaus were lowered and replaced by a slope to some extent, which may be related to the reaction of the by-product Li₂O and amorphous SiO₂ in the original sample and may have formed another amorphous phase, i.e., Li₂SiO₃. Compared with IR spectra of sample Sn171 before and after discharge, there exist some typical Li₂SiO₃ peaks. Therefore, it is reasonable to state that once the first irreversible step is finished the working electrode (Sn171 and Sn179) becomes metallic tin with highly dispersed amorphous Li₂O, Li₂SiO₃ and SiO₂ as inert phases.

Following by the above irreversible reactions, metallic tin reacts with Li to form various Li–Sn alloys with different compositions [8]. From the reversible capacity according to the voltage profile (Fig. 5), it can be seen that a similar trend and peak position occur corresponding to the successive phase transitions of Li_{0.4}Sn, LiSn, Li_{2.3}Sn, Li_{3.5}Sn and Li_{4.4}Sn. Besides a decreased voltage polarization, the specific gravimetric capacity increased with the added silicon content. Furthermore, the reversible capacity of Sn171 and Sn179 reached 900 to 950 mA h/g, which is much higher than the theoretical value (783 mA h/g corresponding to Li_{4.4}Sn) at room temperature. The improved capacity can be explained by the formation of even Li₆Sn which is known to exist only at 400°C [9]. The enhanced performance is possibly due to the stabilization of Li₆Sn by the presence of Si in either the lattice or as second phase oxide.

In order to establish the suitability of the electrode candidate for practical application, it is important to understand its kinetic properties, as well as the thermodynamic characteristics. The Li chemical diffusion coefficient, therefore, is an important factor as it is directly related to the battery charge/discharge rate. With the GITT method, the lithium chemical diffusion coefficient D_{Li} was measured. For sample Sn179 D_{Li} is almost two orders of magnitude higher than for Sn172, especially before the Li₃Sn₇ phase has been formed (viz. Table 2). This result is consistent with the discharge curve, where a lower chemical diffusion coefficient leads to a higher voltage polarization.

In a previous study on the preparation of LiMn₂O₄, the Li chemical diffusion coefficient was also found to increase when some impurities, such as Li₂MnO₃ or Mn₂O₃ existed in the bulk phase [10]. In an attempt to dope the spinel with silicon, the by-product Li₂SiO₃ plays a similar role in increasing the Li diffusion coefficient [11]. The performance improvement was explained in terms of defects, compositional inhomogeneity at the grain boundaries, and, hence, with the formation of highly conductive interfacial regions between particles of the two phases. For the tin-based oxide as electrode, after the first irreversible reaction, the product is indeed a highly dispersed complex. Therefore, it seems reasonable to apply the same mechanism to explain our present results. The reason sample

Table 2

The chemical diffusion coefficients of lithium in various Li–Sn alloys are obtained by GITT method

Sample	log D (cm ² /s)				
	Li _{0.4} Sn	Li _{0.7} Sn	LiSn	Li ₃ Sn ₇	Li _{4.4} Sn
Sn172	–8.78	–9.24	–9.1	–8.81	–9.04
Sn170	–8.04	–8.9	–8.54	–8.5	–8.76
Sn171	–7.80	–8.57	–8.32	–8.32	–8.76
Sn179	–7.88	–7.85	–7.27	–8.4	–8.96

Sn172 has the lowest diffusion coefficient can be explained by the least dispersed phase, while the other three samples have a higher second phase concentration, and, hence, a higher amount of the highly conductive boundaries. For Sn170, Sn171 and Sn179, although the amount of the inert phases is similar, the later two have more Li₂SiO₃ as second phase, which leads to a higher Li ionic conductivity. Therefore, they showed better kinetic characteristics. It should be kept in mind that too much second inert phase, results in a reduction of the specific gravimetric capacity as well as a reduced average electronic conductivity.

4. Conclusions

The advanced ultrasonic spray synthesis is a good method to prepare composite materials containing a highly dispersed second phase. The product synthesized from a mixture of Sn chloride and Si(OMe)₄ as precursors has a rutile tin oxide structure with traces of dissolved Si in addition to highly dispersed amorphous silicon oxide. The higher the content of silicon, the lower the oxidation state of tin, while the content of the second phase increased.

By doping with appropriate amounts of silicon, the reversible capacity increased to over 900 mA h/g, whereas the irreversible capacity was reduced. Furthermore, the Li chemical diffusion coefficient increased before the Li₃Sn₇ phase has been formed. The improved performance is related to the presence of Si in the lattice and as an oxidic second phase.

References

- [1] Y. Idota, M. Mishima, Y. Miyaki, T. Kubota, T. Miyasaki, Canadian Patent Application, 2134952, 1994.
- [2] Y. Idota, M. Mishima, Canadian Patent Application, 2143388, 1995.
- [3] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (6) (1997) 2045.
- [4] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (9) (1997) 2943.
- [5] F. Yuan, C.H. Chen, E.M. Kelder, J. Schoonman, Solid State Ionics 109 (1998) 119–123.
- [6] H. Huang, E.M. Kelder, L. Chen, J. Schoonman, Solid State Ionics (1999) in press.
- [7] W. Weppner, R.A. Huggins, J. Electrochem. Soc. 124 (10) (1977) 1569.

- [8] R.A. Huggins, *Electrochem. Soc. Proc., Pennington* 97 (18) (1997) 1–18.
- [9] J. Wang, I.D. Raistrick, R.A. Huggins, *J. Electrochem. Soc.* 133 (3) (1986) 457.
- [10] L. Chen, E.M. Kelder, X. Huang, J. Schoonman, *Solid State Ionics* 76 (1995) 91.
- [11] E.M. Kelder, A.A. van Zomeren, M.M. Bakker, F.G.B. Ooms, J. Schoonman, Abstract no. 2162, in the book of *Extended Abstracts, 1997, Joint International Meeting, the Electrochemical Society 192nd Meeting and the International Society of Electrochemistry 48th Annual Meeting, France, August, 1997.*