

The study of surface films formed on SnO anode in lithium rechargeable batteries by FTIR spectroscopy

Jingze Li, Hong Li, Zhaoxiang Wang, Liquan Chen, Xuejie Huang*

Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China

Received 5 July 2001; received in revised form 5 September 2001; accepted 25 September 2001

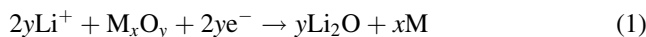
Abstract

Fourier-transform infrared (FTIR) spectra of nanometer SnO anodes at different charge/discharge states in lithium rechargeable batteries were recorded. Solvent decomposition reaction that generally presents on the surface of carbon or alkali metal is also presented on SnO anode. The surface film is composed of Li_2CO_3 and ROCO_2Li . In addition, FTIR data indicates that absorption bands of ROCO_2Li are changed below 0.7 V, which is believed to be related to the change of the surface layer of SnO anode around 0.7 V versus Li/Li^+ during the first discharge process. © 2002 Published by Elsevier Science B.V.

Keywords: SnO; Nanometer; Lithium rechargeable batteries; FTIR; Passivating layer

1. Introduction

Oxide anodes have been widely studied in lithium rechargeable batteries because of their high reversible capacity and a different discharge/charge mechanism compared with carbonaceous materials [1,2]. A two-step mechanism for the reaction of lithium with various tin oxides has been confirmed [1–4]: lithium reacts irreversibly to form a nanocomposite of Sn and Li_2O , then followed by subsequent electrochemical alloying/de-alloying of nanosized Sn. It indicates that the reversible capacity relates to an alloying process instead of intercalation process, and the irreversible capacity comes mainly from the replacement reaction of metal oxide. It has been confirmed that some metal oxides besides SnO and SnO_2 also have the same reaction mechanism with lithium described as following [1,5]:



It is well known that electrolyte decomposition reactions always occur on the surface of carbon or lithium electrodes and lead to the formation of a passivating layer, which attributes the major part of the capacity loss in these cases.

The passivating layer is an ion conductor, named as a solid electrolyte inter-phase (SEI) [6], which mainly consists of Li_2CO_3 and different lithium alkyl carbonates (ROCO_2Li) [7–11]. As for carbonaceous and lithium electrode, active materials are good conductors. Hence, solvents can easily accept electrons from electrodes. The situation for tin oxide anode is different. The original active material is a semiconductor with low electric conductivity. Once the replacement reaction occurs, metal and alloy clusters are dispersed into insulated amorphous Li_2O matrix [1–5,12,13]. In fact, a perfect shell was observed on nanometer SnO particles at deep discharge state in lithium rechargeable batteries by high-resolution transmission electron microscopy (HRTEM) [4]. Similar images were also recorded by Retoux et al. [12] and Hightower et al. [13], the amorphous layer on the surface of the discharged SnO_2 was made of carbon and oxygen as analyzed by EDAX [12]. Our preliminary FTIR measurements have revealed that the surface species on the SnO anode is mainly constituted of Li_2CO_3 and ROCO_2Li [4,14]. It was also found that the electrochemical performance of the SnO anode was also sensitive to the components of electrolytes, similar with the cases of carbon anodes [14].

However, the formation process of the SEI on tin oxide anodes was still not well understood. In addition, the components of the surface species have not been clearly identified. Hence, the aim of this work is to study the variation of the surface composition of this passivating film as a function of electrode discharge/charge states by FTIR spectroscopy.

* Corresponding author. Tel.: +86-10-82649050;
fax: +86-10-82649050.
E-mail address: xjhuang@aphy02.iphys.ac.cn (X. Huang).

2. Experimental

Nanometer-scale SnO powders (100 nm) were obtained after mechanical ball milling the commercial α -SnO used (250 meshes, AR, 99%) for 12 h under an argon atmosphere using agate balls in the shearing mode. The weight ratio of balls to sample powder was 4:1.

The electrodes for FTIR analysis were prepared by pressing the nanometer SnO powder into pellets so as to avoid the interference of binder and additives. These pellets were dried at 120 °C for 8 h before assembling into Li cells in an argon-filled glove box. The electrochemical cells were constructed by using Cellgard 2300 sheet as separator, 1 M LiPF₆, ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 v/v) as electrolyte, a lithium foil as counter electrode and nano-SnO pellet described above as working electrode. The cells were discharged and charged at a constant current of 0.05 mA/cm² and dropped off to different preset voltage, then potentiostat at corresponding voltage for 48 h to reach equilibrium before spectroscopy tests.

The nano-SnO pellets at different discharge/charge states were taken out from the cells and mixed with anhydrous KBr in glove box, then pressed into pellets for FTIR tests. IR spectrum for nano-SnO at initial state was recorded using a Perkin-Elmer Model 983G infrared spectrophotometer. FTIR for nano-SnO pellets at different discharge states were performed with a Bio-Rad FTS6000 spectrophotometer. Each spectrum was scanned for 128 times with resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Identification of Li₂CO₃ and ROCO₂Li in FTIR spectra of nano-SnO anode

Fig. 1 shows IR spectrum of nano-SnO at initial state, two peaks at 515 and 334 cm⁻¹ are observed. It is consistent with

the literature's report [15]. For the sake of comparison, a typical FTIR spectrum of electrolyte used in the cells are shown in Fig. 2. Peaks at 1020, 849, 559 cm⁻¹ are attributed to LiPF₆ based on our data and [7].

Fig. 3(a) presents FTIR spectrum of SnO electrode as directly discharged to 1.2 V. It is obvious that FTIR spectrum of SnO electrode is entirely different from that of pure sample. Despite that the interference of residual electrolyte (as marked with * in Fig. 3), it is easy to recognize the typical peaks of Li₂CO₃ at 1510 cm⁻¹ (ν CO₃²⁻), 1431 cm⁻¹ (ν CO₃²⁻) and 866 cm⁻¹ (δ CO₃²⁻) [7–11]. The other absorption bands appearing at 2934 cm⁻¹ (ν CH), 2891 cm⁻¹ (ν sCH₃), 2851 cm⁻¹ (ν CH), 1044 cm⁻¹ (δ CH₂), are assigned to lithium alkyl carbonates C₂H₅OCO₂Li, which has proved to be the dominant reduction product of DEC [7–11].

While at 0.9 V, the spectrum is very similar to that at 1.2 V (Fig. 3(b)). The “shoulder” band located at about 868 cm⁻¹, on the high frequency side of the strongest absorption peak at 845 cm⁻¹ (P–F vibration of PF₆⁻), can be distinguished. This indicates the existence of Li₂CO₃ [7,14]. The peaks attributed to C₂H₅OCO₂Li are also visible as shown in Fig. 3(b).

However, it is found that IR spectra of SnO anode discharged from 0.7 to 0.0 V are obviously different from the above IR data (shown in Fig. 3(c) and (d)). The absorption bands at 868, 1435 and 1508 cm⁻¹ are easily identified. This result clearly proved that one of the surface species is Li₂CO₃. The unambiguous change is related to ROCO₂Li. In CH stretching vibration region, the relative absorption intensity is greatly increased, meaning that the ratio of alkyl carbonates to Li₂CO₃ is increased. Moreover, the central peaks move to 2963, 2920, 2851 cm⁻¹. As reported, ROCO₂Li presents a series of lithium alkyl carbonates. Organic functional group R is related to the solvents in electrolyte and the reduction reaction processes occurred on the surface of electrodes [7,8,16]. It is clear that the difference among spectral data is caused by the different R of ROCO₂Li.

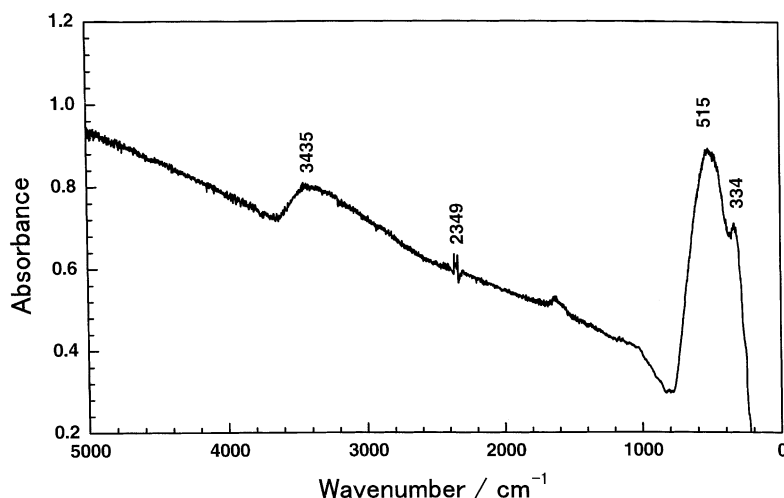


Fig. 1. IR spectrum of nanometer SnO mixed with KBr measured by a PE 983G spectrophotometer.

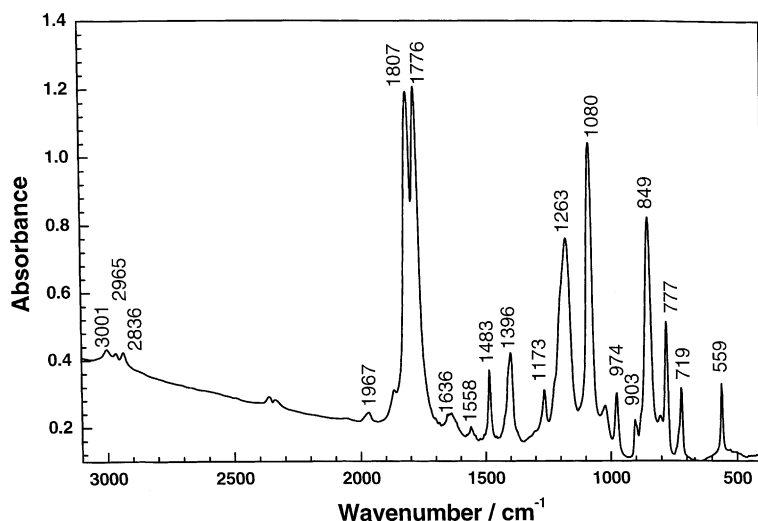


Fig. 2. FTIR spectrum of electrolyte: 1 M LiPF₆, EC-DEC (1:1 v/v). The pellet for IR was prepared by mixing a droplet with KBr in glove box.

Especially, for the spectrum recorded at 0.7 V, the interference from the solvent can be neglected because the absorption bands around 1800 cm⁻¹ disappear. Only trace LiPF₆ is visible, e.g. weak peak on 599 cm⁻¹. Therefore, the well-defined absorption bands, located at 1261, 1651, 1800, 826 and 806 cm⁻¹, can be attributed to solvent reduction product ROCO₂Li [7–10,15,16]. It is found that the absorption peaks at 2963 (νCH), 2920 (νCH), 1651 (ν_{as}C=O), 1404 (δCH₂), 1304 (ν_sC=O), 1082 (ν_sC–O) and 826 cm⁻¹ (δOCO₂⁻), are well in agreement with the standard IR spectrum of (CH₂OCO₂Li)₂, which has been proved to be the reduction of EC by several techniques [7,8]. It is well known that EC is a highly reactive solvent, and apt to produce highly protective passive films due to its cyclic structure, high polarity and dipole moments [7–11,16]. Therefore, even the amount of EC is comparable to that

of DEC, its reduction dominates the surface chemistry of SnO anode. Therefore, Fig. 3(d) shows no pronounced peaks of C₂H₅OCO₂Li. It is consistent with previous reports. They claimed that the formation of the passive film is mainly caused by the decomposition of EC in the EC/DEC binary system [7–11,14,16].

IR spectrum of SnO anode, which was discharged to 0.0 V after cycled between 0 and 2.0 V for four times is presented in Fig. 3(e). The difference is small compared with that of SnO directly discharged to 0.0 V. Only one of the stretch modes has a blue shift from 2963 to 2970 cm⁻¹. The other weak difference is caused by the residue electrolyte. It may indicate that the components of the SEI film did not vary at following cycles.

Taking into account the above results, it is certain that SnO was covered with a film consisting of ROCO₂Li and

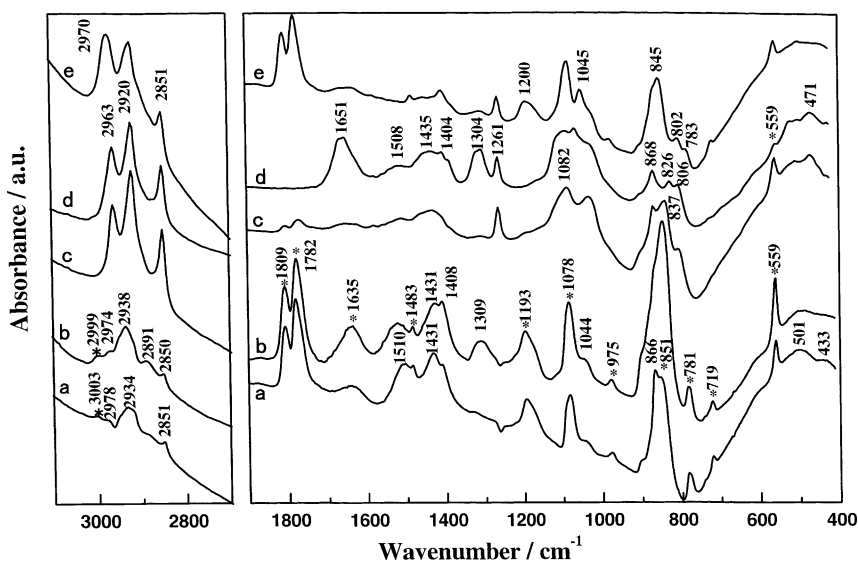


Fig. 3. FTIR spectra obtained from reacted SnO after discharge to (a) 1.2 V, (b) 0.9 V, (c) 0.7 V, (d) 0.0 V and (e) cycled four times between 0 and 2.0 V, then discharged to 0.0 V in Li/1 M LiPF₆, EC-DEC/SnO cell.

Li_2CO_3 . The formation of SEI can be briefly described as follows. While discharged to 1.2 and 0.9 V, the electrolyte is irreversibly reduced on the surface of SnO anode. The main product is Li_2CO_3 , accompanying with small amount of ROCO_2Li . As further discharged to 0.7 V, not only the amount of ROCO_2Li is increased in comparison with Li_2CO_3 , but also the component of ROCO_2Li is changed. After the first cycle, the structure and the component of the SEI film are stable gradually.

Recently, an organic coating surrounding discharged Cu_2O anode was found to be composed of Li_2CO_3 and ROCO_2Li despite that the reversible mechanism with Li is partly different from tin-base oxides [17]. This finding supports that solvent decomposition reactions occur on the surface of oxide electrodes.

3.2. The formation mechanism of Li_2CO_3 and ROCO_2Li

Aurbach has reported that the solvent reduced products on graphite electrodes in 1 M $\text{LiPF}_6 + \text{EC/DEC}$ (1:1 v/v) are ROCO_2Li and trace Li_2CO_3 [7]. It was suggested that ROCO_2Li is formed by radical termination reactions and Li_2CO_3 is mainly formed by the reaction of ROCO_2Li with trace water, but not excluding the possibility of a direct reduction from EC or DEC [7,8,16]. However, according to the results of EELS and FTIR, Naji et al. proposed a mechanism of EC reduction at the surface of graphite electrode in the presence of LiClO_4 . Li_2CO_3 is formed at potential above 0.8 V by a direct two-electron reduction from EC. But, a two-step radical termination reaction lead to the formation of lithium alkyl carbonate below 0.8 V [9,10].

Our results confirmed that the formation process of the SEI film on SnO anode is analogous to the reaction scheme proposed by Naji et al. [9,10]. Above 0.7 V, the two-electron reduction reaction for EC and free radical termination reaction for DEC may occur on the surface of SnO at the same time. EC is electrochemically reduced to Li_2CO_3 , DEC is reduced to $\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$. Around 0.7 V, electrochemistry, XRD, TEM and other techniques have proved that the irreversible replacement reaction which leads to the formation of nanosized Sn dispersed within Li–O matrix terminated around 0.7 V [1–5,12,13]. That is to say, the active material of the anode varies from a semiconductor to a mixture of metallic nanosized Sn and Li–O insulation matrix. The variation of the intrinsic properties of active material may directly influence the reduction processes of the electrolyte on SnO surface [16]. As a result, it may also lead to the formation of different SEI components. For example, the reduction product of EC is $(\text{CH}_2\text{OCO}_2\text{Li})_2$, and

DEC is still reduced to $\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$ below 0.7 V during the first discharge process.

4. Conclusions

FTIR confirms that the SEI film is formed on the surface of oxide anodes, when the SnO anode was discharged to 1.2 and 0.9 V, the main product is Li_2CO_3 , along with a small amount of ROCO_2Li . After further discharge to 0.7 V, not only the amount of ROCO_2Li is increased in comparison with Li_2CO_3 , but also the component of ROCO_2Li is changed. After the first cycle, the structure and the component of the SEI film are stable gradually.

Acknowledgements

This work was supported by NSFC (no. 59972041) and National 863 Key Program.

References

- [1] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [2] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2045.
- [3] W.F. Liu, X.J. Huang, Z.X. Wang, H. Li, L.Q. Chen, *J. Electrochem. Soc.* 145 (1998) 59.
- [4] H. Li, X.J. Huang, L.Q. Chen, *Electrochem. Solid-State Lett.* 1 (1998) 241.
- [5] H. Li, X.J. Huang, L.Q. Chen, *Solid-State Ionics* 123 (1999) 189.
- [6] E. Peled, *J. Electrochem. Soc.* 126 (1979) 2047.
- [7] D. Aurbach, A. Zaban, A. Schechter, Y. Ein-Eli, E. Zinigrad, B. Markovsky, *J. Electrochem. Soc.* 142 (1995) 2873.
- [8] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, *Electrochem. Acta* 45 (1999) 67.
- [9] A. Naji, J. Ghanbaja, P. Willmann, B. Humbert, D. Billaud, *J. Power Sources* 62 (1996) 141.
- [10] A. Naji, J. Ghanbaja, P. Willmann, B. Humbert, D. Billaud, *J. Power Sources* 63 (1996) 33.
- [11] C. Yang, Y. Wang, C. Wan, *J. Power Sources* 72 (1998) 66.
- [12] R. Retoux, T. Brousse, D.M. Schleich, *J. Electrochem. Soc.* 146 (1999) 2472.
- [13] A. Hightower, P. Delcroix, G.L. Caer, C.K. Huang, B.V. Ratnekumar, C.C. Ahn, B. Fultz, *J. Electrochem. Soc.* 147 (2000) 1.
- [14] J.Z. Li, H. Li, Z.X. Wang, X.J. Huang, L.Q. Chen, *J. Power Sources* 81 (1999) 346.
- [15] R.A. Nyquist, R.O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971, p. 210.
- [16] Y. Ein-Eli, *Electrochem. Solid-State Lett.* 2 (1999) 212.
- [17] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizat, J.M. Tarascon, *J. Electrochem. Soc.* 148 (2001) 285.