PERFORMANCE OF SN-CU ALLOY ANODE MATERIALS AT LOW TEMPERATURE

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Abstract

Sn-Cu alloy anode was prepared by pulsed electrodeposition for lithium ion batteries, and its electrochemical performance was tested at low temperature. Four liquid electrolytes of 1M $LiPF_6$ in EC+DMC+DEC (1:1:1), 1M $LiPF_6$ in EC +PC(1:1), 1M $LiPF_6$ in EC+DMC+EMC(1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1) were prepared and their ionic conductivities were measured at the temperature range of -20~20℃. It was found that the liquid electrolyte of 1M $LiBF_4$ in EC+EMC+γBL solution decreased most slowly when temperature decreasing and it had the highest ionic conductivity below -20℃, followed by the electrolyte solution of 1M $LiPF_6$ in EC+DMC+DEC; the alloy anode with electrolyte of 1M $LiBF_4$ in EC+EMC+γBL presented better performance than it did with electrolyte of 1M $LiPF_6$ in EC+DMC+DEC at -20℃, as graphite anode did; and the alloy anode presented much higher capacity retention than that of graphite at -20℃. The Cu-Sn alloy anode in the electrolyte of 1M $LiBF_4$ in EC+EMC+γBL is promising for low temperature application of lithium batteries.

Keywords: Sn-Cu alloy electrode; electrodeposition; low temperature; lithium batteries

Introduction

The increasing demand for higher capacity batteries in electronics devices has promoted an intensive research effort to develop new materials suitable for new high energy capacity lithium batteries. For the anode materials, there is an increasing interest to research other alternative anode materials for rechargeable lithium batteries, because of the graphite, which is used extensively in currently commercialized lithium batteries, has only 10%(372mAh/g) of the theoretical capacity of metallic lithium (3860mAh/g). Many alloy anode materials have been studied to overcome the limited capacity of graphite [1~7]. The Sn-Cu intermetallic compound has been suggested as one of the promising alternative anode materials [1~3, 10].

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The electrolyte plays a key role of low temperature operation of lithium batteries. The low temperature performance of graphite anode was widely studied and the understanding of the poor low temperature performance was briefly summarized in the reference [8, 9]. It was reported that the use of thermally stable $LiBF_4$ salt provided improved low temperature performance of lithium-lion cells with graphite anode over that of state-of-the-art cells using $LiPF_6$ salt, and the excellent performance of cells with graphite anode resulting from the electrolyte of 1M $LiBF_4$ in EC+EMC+γBL(1:1:1) was demonstrated at low temperature [9]. In reference [8], it was concluded that the total resistance of the lithium-ion cells with graphite anode was mainly composed of bulk resistance, solid-state interface resistance and charge-transfer resistance. The last one was linked to kinetics of the electrochemical reaction; it increased most significantly as the temperature decreased. At low temperature, the total resistance of cells was predominated by the charge-transfer resistance; the high resistance resulted in the poor performance of the cells. In a word, the poor performance of the cells with graphite anode was mainly ascribed to the slow kinetics of the electrochemical reaction between the graphite anode and the electrolyte at low temperature. Therefore, the electrochemical reactivity between the electrolyte and the alloy anode should present different result.

So far, all attentions were only focused on the cells with graphite anode, not an alloy anode. Unfortunately, the low temperature performance of alloy anode is still uncultivated. The alloy anode should behave differently for the kinetics of reaction at low temperature.

Pulsed electrodeposition is simple, cost-effective, and widely utilized in plating sector, also used to prepare alloy materials [11], and was adopted to prepared copper-tin alloy negative electrodes for lithium-ion batteries [12]. In reference [12], Sn-Cu alloy was plated on the substrate of nickel by pulsed electrodeposition, which was performed by alternate deposition of Cu and Sn in a single bath.

In this study, the Sn-Cu alloy electrodes were directly prepared by pulsed electrodeposition. The electrodes were obtained by plating tin on a substrate of copper foil, which is normally used as current collector of electrode for lithium batteries, and by annealing. Its low temperature performance in different electrolytes was carried out at -20□. It was found that the alloy anode presented much higher electrochemical performance than that of graphite anode at -20□.

Experimental

Sn-based electrode were prepared in the pH neutral pyrophosphate aqueous solution containing 0.1M $SnCl_2{\cdot}H_2O$, 0.4M $K_4P_2O_7{\cdot}3H_2O$, 0.05 M $C_4H_6O_6$ (Tartaric Acid), and 0.01M gelatin with a small quantity of antioxidant and surfactant. Anode was tin metal in electrodeposition bath, and electrochemically dissolved into electrolyte to keep concentration of Sn ions at constant level in electrolyte. Recycling water at constant temperature was recycled to keep electrolyte at constant temperature. Tin was electrodeposited on substrate (cathode) of 20 micron copper foil, which was treated in corrosive sulfuric acid solution in advance, by pulsed current at 15mA/cm^2 for 1 hour. All plating runs were performed at 25□ with agitation at the pulsed current whose frequency is

1kHz and on/off ratio of waveform is 30%. Finally, the alloy anode was obtained by annealing at 200□ for 24 hours, as described in reference [5].

Lithium hexafluorophosphate ($LiPF_6$), Lithium Tetrafluoroborate ($LiBF_4$), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC), ethylmethyl carbonate (EMC), γ-butyrolactone (γBL) were battery-grade chemicals from Zhangjiagang Guotai-Huarong New Chemical materials Co., Ltd, PR China, and used as received.

The liquid electrolytes of 1M $LiPF_6$ in solvents systems formulated in such ways such as EC+DMC+DEC (1:1:1, volume ratio), EC+PC (1:1, volume ratio), EC+DMC+EMC (1:1:1, volume ratio) and 1M $LiBF_4$ in EC+EMC+γBL (1:1:1, volume ratio) were prepared in a glove box filled with argon gas with less than 10 ppm of water.

The conductivities of electrolytes were measured by conductivity meter (DDS-11A, Shanghai, PR China) at selected temperatures controlled within a chamber of Labconco Shell Freezer (USA).

Experimental test coin type cells were used for measurements of electrochemical performance of as-prepared alloy anode and electrolytes. A lithium metal foil was used as counterpart electrode in this study. The separator of cell was Celguard 2400 microporous polypropylene membranes. The cells were assembled in a glove box filled with argon gas with less than 10 ppm of water. The cell was cycled between 0~2.0V (versus Li/Li^+) at a constant current density of $0.3mA/cm^2$.

Results and discussion

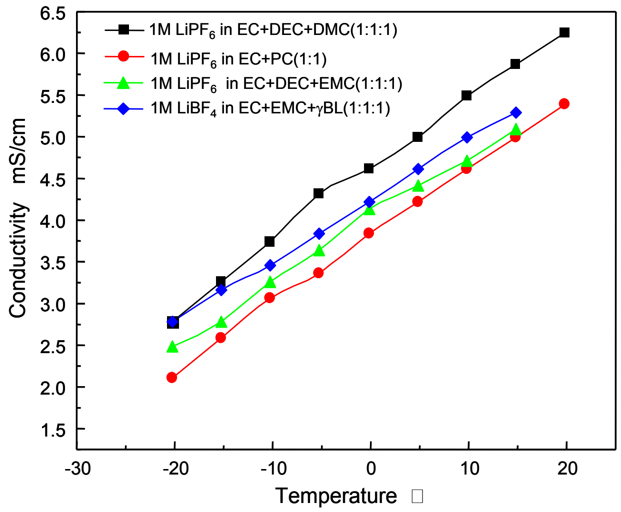

Fig. 1. *Temperature dependence of conductivities of electrolyte solutions of 1M $LiPF_6$ in EC+ DEC+DMC (1:1:1), 1M $LiPF_6$ in EC +PC(1:1), 1M $LiPF_6$ in EC+DMC+EMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1), respectively.*

The conductivities of as-prepared four liquid electrolytes of 1M $LiPF_6$ in EC+ DEC+DMC (1:1:1), 1M $LiPF_6$ in EC +PC(1:1), 1M $LiPF_6$ in EC+DMC+EMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1) were measured at the temperature range of -20~20□, as shown in Fig.

1. The electrolyte of 1M $LiBF_4$ in EC+EMC+γBL solution decreased most slowly when temperature decreasing and it had the highest ionic conductivity at -20□, followed by the electrolyte solution of 1M $LiPF_6$ in EC+DMC+DEC. This result accords to that reported in reference [9]. Thus, these two electrolyte solutions were chosen to test the low temperature performance of anodes.

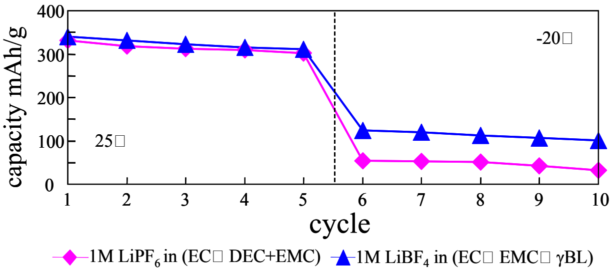

Fig. 2 *The performance of cells with graphite anode in electrolytes of 1M $LiPF_6$ in EC+ DEC+DMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1), respectively.*

Fig. 2 shows the performance of two cells with graphite anode in electrolytes of 1M $LiPF_6$ in EC+DEC+DMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL (1:1:1), respectively, at 25□ and -20□. The two cells get almost the same capacity and cycleability at 25□. The two electrolytes present equivalent effect on the performance of cells with graphite anode at 25□. But the difference between capacities of the two cells is obvious at -20□. At -20□, the capacities of the cells in the electrolyte of 1M $LiPF_6$ in EC+DEC+DMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL (1:1:1) drop to 55 and 126 mAh/g of 6th cycle from 300 and 308 mAh/g of the 5th cycle at 25□, respectively, indicating that the electrolyte of 1M $LiBF_4$ in EC+EMC+γBL (1:1:1) presents better performance at low temperature. The result is consistent with recent reports [9, 13] on the superior performance of cells with graphite anode using $LiBF_4$ based electrolytes.

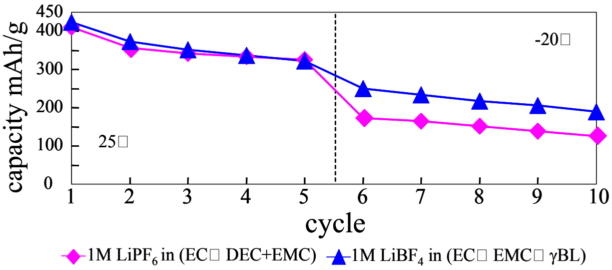

Fig. 3 *The performance of cells with Sn-Cu alloy anode in electrolytes of 1M $LiPF_6$ in EC+ DEC+DMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1), respectively.*

Fig. 3 shows the performance of two cells with Sn-Cu alloy anode in electrolytes of 1M $LiPF_6$ in EC+DEC+DMC (1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL (1:1:1), respectively, at 25□and -20□. The result shows that the Sn-Cu alloy anode has an irreversible capacity at first cycle; this is a common phenomenon for the alloy anode. Similar to the graphite anode, the two electrolytes also present equivalent effect on the performance of cells with Sn-Cu alloy anode at 25□; and the difference between capacities of the two cells is also obvious at -20□.

At -20℃, the capacities of the cells in the electrolyte of 1M LiPF$_6$ in EC+DEC+DMC (1:1:1) and 1M LiBF$_4$ in EC+EMC+γBL (1:1:1) drop to 165 and 241 mAh/g of 6th cycle from 321 and 315 mAh/g of the 5th cycle, respectively, at 25℃, indicating that the electrolyte of 1M LiBF$_4$ in EC+EMC+γBL (1:1:1) also presents better performance at low temperature for alloy anode. Nevertheless, the extent of capacity decreasing for alloy anode is obviously less than that for graphite anode in both of the two electrolytes.

In order to clearly observe the impact of electrolyte on graphite and Sn-Cu alloy anode at -20 ℃, the capacity retentions of the cells with Sn-Cu alloy anode and graphite anode in the electrolytes of 1M LiPF$_6$ in EC+DEC+DMC (1:1:1) and 1M LiBF$_4$ in EC+EMC+γBL (1:1:1), respectively, at -20℃ are shown in Fig. 4. The percentage is based on the corresponding capacity of 5th cycle at 25℃.

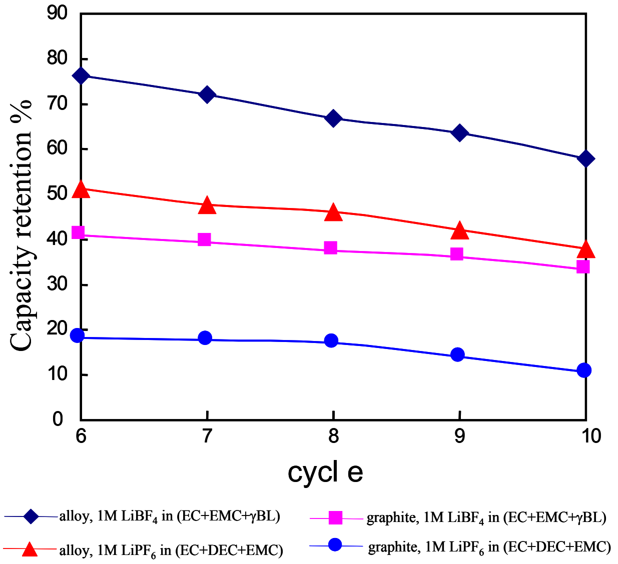

Fig. 4 *The capacity retentions of cells with graphite and alloy anode in electrolytes of 1M LiPF$_6$ in EC+ DEC+DMC (1:1:1) and 1M LiBF$_4$ in EC+EMC+γBL(1:1:1), respectively, at -20℃.*

The capacity retentions of 6th cycle for graphite and alloy anode in electrolytes of 1M LiPF$_6$ in EC+ DEC+DMC (1:1:1) and 1M LiBF$_4$ in EC+EMC+γBL (1:1:1) are 18%, 41%, 51% and 76%, respectively, at 6th cycle at -20℃, as shown in Fig. 4. The best performance results from the cell with alloy anode in the electrolytes of 1M LiBF$_4$ in EC+EMC+γBL (1:1:1), followed by alloy anode in the electrolytes of 1M LiPF$_6$ in EC+DEC+DMC (1:1:1), indicating that the better performance of graphite anode resulting from the use of LiBF$_4$ instead of LiPF$_6$ at low temperature [9] is further demonstrated by that of the Sn-Cu alloy anode. The performance of Sn-Cu alloy anode using LiBF$_4$ salt further verifies that the salt plays a key role in controlling the electrochemical reactivity between the anode and the electrolyte notably at low temperature as it does for graphite anode [9]. The results also suggest it is promising to formulate better low temperature electrolytes through the use of LiBF$_4$ salt in place of LiPF$_6$. Considering the performance of different anode at low temperature, the Sn-Cu alloy anode presents much better performance that graphite anode at -20℃ in both of the two electrolytes, as shown in Fig. 4. The low performance at low temperature is because the increasing total resistance, which is predominated by the charge-transfer resistance relating to kinetics of the electrochemical reaction between the anode and the electrolyte [8], produces high polarization. Owing to the high polarization, the charge/discharge voltage is quickly jumped up/down to the cut-off limit so that the charge/discharge process ends, resulting in low capacity. It is suggest that the electrochemical reactivity between the Sn-Cu alloy anode and the electrolyte is notably quicker than that between the graphite anode and the electrolyte at low temperature, resulting in that the Sn-Cu alloy anode shows better performance at -20□.

This is a start of study on the performance of Sn-Cu alloy anode at low temperature. It is needed to further investigate the performance of alloy anode to understand more.

Summaries

Sn-Cu alloy anode was prepared by pulsed electrodeposition for lithium ion batteries, and its electrochemical performance was tested at low temperature. Four liquid electrolytes of 1M $LiPF_6$ in EC+DMC+DEC(1:1:1), 1M $LiPF_6$ in EC +PC(1:1), 1M $LiPF_6$ in EC+DMC+EMC(1:1:1) and 1M $LiBF_4$ in EC+EMC+γBL(1:1:1) were prepared and their ionic conductivities were measured at the temperature range of -20~20□. It was found that the liquid electrolyte of 1M $LiBF_4$ in EC+EMC+γBL solution decreased most slowly when temperature decreasing and it had the highest ionic conductivity below -20□, followed by the electrolyte solution of 1M $LiPF_6$ in EC+DMC+DEC; the alloy anode with electrolyte of 1M $LiBF_4$ in EC+EMC+γBL presented better performance than it did with electrolyte of 1M $LiPF_6$ in EC+DMC+DEC at -20□, as graphite anode did; and the alloy anode presented much higher capacity retention than that of graphite at -20□. The Cu-Sn alloy anode in the electrolyte of 1M $LiBF_4$ in EC+EMC+γBL is promising for low temperature application of lithium batteries.

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Reference

1. Thackeray M.M.; Vaughey J.T.; Fransson, L.M.L *JOM*, 54 (2002) 20-23
2. Wachtler, Mario; Besenhard, Jürgen O.; Winter, Martin J. Power Sources, 94 (2001) 189
3. Winter, Martin; Besenhard, Jürgen O. Electrochimica Acta, 45(1999) 31
4. Yongyao Xia, Tetsuo Sakai, Takuya Fujieda, Masashi Wada, Hiroshi Yoshinaga, J. Electrochemical Society, 148(2001) A471
5. Tamura, Noriyuki; Ohshita, Ryuji; Fujimoto, Masahisa; Fujitani, Shin; Kamino, Maruo; Yonezu, Ikuo J. Power Sources, 107 (2002) 48
6. Kepler, K.D.; Vaughey, J.T.; Thackeray, M.M. J.Power Sources, 81-82(1999) 383

7. Wolfenstine, J.; Campos, S.; Foster, D.; Read, J.; Behl, W.K., J. Power Sources, 109(2002) 230
8. S.S. Zhang, K. Xu, T.R. Jow, Electrochem. Electrochimica Acta 49(2004) 1057
9. T.R. Jowa, M.S. Dinga, K. Xua, S.S. Zhanga, J.L. Allena, K. Amineb, G.L. Henriksen, J Power Sources 119–121 (2003) 343
10. Kim, D.G.; Kim, H.; Sohn, H.-J.; Kang, T., J Power Sources, 104(2002) 221.
11. Nee, C. C.; Kim, W.; Weil, R., J. Electrochem. Soc., 135(1988) A1100.
12. Beattie S.D., Dahn J.R., J. Electrochem. Soc., 150(2003) A894
13. N. Takami, T. Ohsaki, H. Hasebe, M. Yamamoto, J. Electrochem. Soc. 149 (1) (2002) A9.