Effect of electrolyte on cycle performances of the electrodeposited Sn-O-C composite anode of lithium
secondary batteries

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Abstract

The electrodeposited Sn-O-C composite anode cycling with LiClO_4 delivered stable cycle performances showing discharge capacity of $473 \text{ mAh g}_{\text{of Sn}}^{-1}$ with 95 % of coulombic efficiency at 100th cycle. However, the anode showed poor cycle performances with LiPF_6 delivering discharge capacity of $69 \text{ mAh g}_{\text{of Sn}}^{-1}$ at 100th cycle with 70 % of coulombic efficiency. Electrochemical investigation performed by cyclic voltammetry and differential capacity plots revealed that the Sn-O-C composite cycling with LiPF_6 suffered from retarded phase transition reaction between Li and Sn during charge/discharge process. X-ray photoelectron spectroscopy declared the existence of fluorinated-Sn and LiF. Moreover, energy dispersive X-ray spectroscopy found increase in their amount with repeated cycles. The morphologies of the Sn-O-C composite cycled with LiPF_6 showed aggregated particles containing the chemical state of fluorinated-Sn and LiF on its surface. Furthermore, the significant pulverization and aggregation of the active material were observed from the Sn-O-C composite cycled by LiPF_6 rather than that of LiClO_4 , which was probably promoted by the generated HF strongly corroding metallic component.

Key words : Tin, Anode, Sn-O-C composite, Electrodeposition, Electrolyte, Lithium secondary batteries

Introduction

LiPF₆ is one of the most common electrolytes in lithium secondary batteries due to its low toxicity, good ion conductivity and wide electrochemical window [1]. However, The LiPF₆ reacts with the trace amount of water, which generates HF during electrochemical reaction as following mechanisms [2,3],

Although the HF is classified as an acid weaker than sulfuric or hydrochloric acids, it is highly corrosive for most metals [4], which causes to unwilling effects for lithium secondary battery performances. Therefore, its application for lithium secondary batteries should consider about reactivity with water. In general, at least less than 20 ppm of water exist even in battery grade electrolyte. Furthermore, it is inevitable that the anode and cathode active materials absorb quantity of water during cell preparation [2]. Another troublesome derived by using LiPF₆ electrolyte is electrophilical attack of strong Lewis acid of PF₅ and POF₃ against Sn, causing deactivation of the active material [5].

Previously, we achieved electrochemical synthesis of the Sn-O-C composite anode by the galvanostatic electrodeposition technique from an organic carbonate solvent, which delivered a discharge capacity of 465 mAh g_{of Sn}⁻¹ after the 100th cycle showing 80% capacity retention against the first cycle in the electrolyte of 1M of LiClO₄ in ethylene carbonate (EC) : propylene carbonate (PC) (1 : 1 (v/v) [6]. During the electrodeposition process, Sn deposition and decomposition of the organic carbonate solvent were simultaneously carried out. Consequently, the Sn-O-C composite containing polycrystalline Sn phase surrounded by the decomposed products of an organic carbonate solvent with inter-particle void spaces was successfully achieved. The unique structure would act as a buffer effectively enduring volume expansion, resulting in a stable cycle performance with high capacity. Furthermore, its electrodeposition mechanism and convection enhanced Sn ion movement during the deposition process were thoroughly examined as well to figure out effects of deposition condition on battery performance as an anode material [7, 8]. Recently, there have been many reports related to electrodeposition using inaqueous electrolyte such as organic solvent and ionic liquids [9-11]. However, the

specific application of the electrodeposition method from inaqueous electrolyte for synthesis of electrode material of lithium secondary batteries has not been generally discussed yet. The aim at application of the novel electrodeposition process has been attempting in our previous works to synthesis anode materials showing outstanding performances for lithium secondary batteries [6-8, 12-15].

Herein, the effect of LiPF_6 was compared to that of LiClO_4 which attained stable cycle performances. In general, LiClO_4 is widely used as an electrolyte for battery application due to superior solubility, high conductivity, hygroscopicity and anodic stability [16]. However, it also shows critical problems for practical application such as strong oxidizing property of perchlorate under the circumstance of high temperature and current density [16] and corrosive to an Al current collector [17]. We report, for the first time, the effect of LiPF_6 on cycle performances of the electrodeposited Sn-O-C composite anode. The preliminary investigation on suitability of LiClO_4 or LiPF_6 as an electrolyte for the binder free Sn-O-C composite anode was examined by means of electrochemical and morphological investigation.

Experimental

For electrodeposition of the Sn-O-C composite, 2.5 mM SnCl_2 (Sigma-Aldrich) was dissolved in to 1.0 M LiClO_4 in EC : PC (1 : 1 (v/v), Kishida, H_2O content < 20 ppm) to prepare electrodeposition bath. The 1.0 M LiClO_4 was used as a supporting electrolyte.

A Ni plate with dimension of 10 X 10 mm was used as a substrate for electrodeposition. It was ultrasonicated in trichloroethylene and ethanol followed by acid treatment with 10 % HCl. A three electrode system with a tin metal, as a counter electrode, and a lithium metal dipped in EC : PC solution containing 1 M LiClO_4 sealed in glass tube and glass flit, as a reference electrode, were used for electrodeposition of the Sn-O-C composite.

Electrodeposition of the Sn-O-C composite was carried out via potentiostatic deposition with tree steps at 2.3, 1.5 and 0.3 V vs Li/Li^+ by passing charge quantity of 0.01, 0.04 and 0.21 C cm^{-2} , respectively, using a potentiostat (Hokuto Denko, HZ-5000) with magnetic stirring at a rate of 700 rev. min^{-1} .

Cyclic voltammetry (CV) was performed with a potentiostat (Hokuto Denko, HZ-5000), which was negatively swept from open circuit potential and reversed at 0.01 V and 1.1 V vs Li/Li^+ with scan rate of 0.5 mV

s⁻¹. Electrochemical cycling test was performed with galvanostatic charge/discharge unit (Hokuto Denko, HJ-1010M) by a three-electrode cell using lithium foils used as a counter and a reference electrode between 0.01 and 1.1 V vs Li/Li⁺ with loading current density of C/10. Either 1M LiClO₄ in EC : PC (1 : 1 (v/v), Kishida, H₂O content < 20 ppm) or 1M LiPF₆ in EC : PC (1 : 1 (v/v), Kishida, H₂O content < 20 ppm) was used as electrolyte for charge/discharge test.

Morphology of the Sn-O-C composites after full discharge up to 1.1 V vs Li/Li⁺, i.e., delithiation state, was observed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4500). X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) was employed for investigation of the surface chemistry of the Sn-O-C composites after cycled by two different electrolytes. The binding energies were corrected by setting the C 1s hydrocarbon peak to 284.8 eV. Grazing incidence X-ray diffraction (GIXRD, Rigaku Rint-Ultima III) was examined by Cu K α (λ = 0.1541 nm) radiation operated at 50 kV and 300 mA between scanning range of 2θ = 20°–80°. Scanning electron microscope (SEM, Hitachi TM-3000) equipped with an energy dispersive X-ray spectroscopy (EDS) were performed to observe elemental mappings of the as-prepared Sn-O-C composite and analyze its chemical composition after cycle with different electrolyte.

Results and discussion

Figure 1a indicates FE-SEM image of the as-prepared Sn-O-C composite. It is obviously observed that micro structured clusters with size of ca. 1–1.5 μ m were aggregated by round-shaped particles with several hundred nano meters in size. The aggregation of micro-sized clusters formed inter-particle void spaces. It is supposed that high nucleation rate and slow growth were carried out during electrodeposition process of the Sn-O-C composite, causing the aggregated micro-structures composed of nano particles as discussed in our previous report [8]. The particles were in agreement with tetragonal phase tin showing strong and weak diffraction peaks at 2θ = 30.6, 32.0, 43.8, 44.9, 55.3, 62.5, 63.7, 64.5, 72.4, 73.1 and 79.4 assigned to 200, 101, 220, 211, 301, 112, 400, 321, 420, 411 and 312 crystal planes (JCPDS # 04-0673), which was measured by GIXRD shown in Fig. 1b. Meanwhile, the Sn-O-C composite was prepared by homogeneous distribution of Sn metal with oxygen and carbon elements as indicated in elemental mapping in Fig. 1c. It is considered that the oxygen and carbon elements were reduction products of the organic carbonate electrolyte used as solvent for electrodeposition process as discussed in our previous reports [6-8].

Figure 2 shows discharge capacity and coulombic efficiencies of the Sn-O-C composites cycled with LiClO₄ and LiPF₆. The composite cycled with LiClO₄ achieved stable cycle performance delivering discharge capacity of 467 mAh g_{of Sn}⁻¹ with 51 % of coulombic efficiency at the 1st cycle. The discharge capacity slightly increased up to the 30th cycle showing discharge capacity of 544 mAh g_{of Sn}⁻¹ with 90 % of coulombic efficiency followed by gradual decrease down to 473 mAh g_{of Sn}⁻¹ with 95 % of coulombic efficiency at 100th cycle. While, the Sn-O-C composite cycled with LiPF₆ showed rapid decrease in discharge capacity and low coulombic efficiency. It delivered discharge capacity of 298 mAh g_{of Sn}⁻¹ with 18 % of coulombic efficiency at the 1st cycle followed by increase within few cycles showing 336 mAh g_{of Sn}⁻¹ with 73 % of coulombic efficiency at the 4th cycle. However, the rapid decrease in discharge capacity lasted until the 100th cycle delivering only 69 mAh g_{of Sn}⁻¹ with 70 % of coulombic efficiency.

To compare electrochemical reactions of the Sn-O-C composites during charge/discharge process with LiClO₄ and LiPF₆, CVs were performed as shown in Fig. 3a1 and a2 with 1, 5 and 10th cycles. The anode cycled with LiClO₄ showed small cathodic peak at ca. 0.6 V and strong peak between 0.3–0.01 V followed by broad and sharp anodic peaks between 0.4–0.8 V (Fig. 3a1). These redox peaks defines typical lithiation/delithiation reactions with phase transition of Li_xSn [18] expressed as;

The redox peaks were constantly obtained with the 1, 5, and 10th cycle. On the other hand, the CVs cycled with LiPF₆ showed extremely irreversible reaction with further cycles (Fig. 3b2). The several redox peaks corresponding to phase transition of Li_xSn were obtained at the 1st cycle. While, the peaks disappeared at the 5th cycle. Afterward, strong cathodic peak at ca. 0.07 V was appeared at the 10th cycle and the sharp anodic peaks at the 1st cycle were changed to broad peaks at the 10th cycle.

To investigate electrochemical reactions during cycling in detail, the potential profiles and differential capacity plots (DCPs) of the Sn-O-C composites cycled with LiClO₄ and LiPF₆ were examined and shown in Fig. 3b and c, respectively. Distinctive plateaus at both charge and discharge processes were obtained with the Sn-O-C composite cycled by LiClO₄ (Fig. 3b1). The sharp and broad peaks at ca. 0.4, 0.65 V during charge process and 0.45, 0.6, 0.7, 0.8 V during discharge process were continuously obtained with further cycles of the 2, 10 and 25th (Fig. 3b2-b4), respectively. Those peaks were in agreement with typical potentials corresponding to the multistep phase transition of Li_xSn alloying reaction as discussed with CV results. On the other hand,

unclear plateaus were obtained with the Sn-O-C composite cycled by LiPF_6 (Fig. 3c1). In the DCPs, strong and broad cathodic peak at ca. 0.4 V was shown from the 2nd cycle without any other cathodic peaks. For discharge process, anodic peaks at ca. 0.45, 0.6, 0.7 and 0.8 V (Fig. 3c2) were distinctive at the 2nd cycle. However, the anodic peaks which were changed to two broad peaks at ca. 0.5 and 0.65 V were obtained with 10 and 25th cycle (Fig. 3c3 and c4). The electrochemical investigation suggested that the Sn-O-C composite cycled by LiPF_6 was not able to be performed with complete phase transition reaction between Li and Sn, which was in contrast to cycling with LiClO_4 .

The detailed XPS measurements are shown in Fig. 4a-c for comparison of surface chemical state of the Sn-O-C composite anodes cycled by LiClO_4 (i) and LiPF_6 (ii) after 2nd cycle of delithiation. Sn 3d5 core level peaks of the Sn-O-C composite cycled by LiClO_4 indicated two strong peaks corresponding to Sn (484.8 eV) and SnO_2 (486.6 eV) [19]. However, that of the Sn-O-C composite cycled by LiPF_6 indicated small hump at 484–485 eV and strong peak at 487.8 eV corresponding to Sn and SnF_4 [5], respectively. Li 1s core level peak assigned to 55.8 eV corresponding to LiF was only obtained with the Sn-O-C composite cycled by LiPF_6 , but not in LiClO_4 . F 1s core level peak was also obtained with only the Sn-O-C composite cycled by LiPF_6 with broad peak from 683.8 to 687.8 eV, which was in agreement with the result of Li 1s peak. The broad peak seemed to be deconvoluted into LiF and SnF_4 peaks which were assigned at 684.8 and 685.1 eV [5]. It is considered that, after cycling with LiPF_6 , the Sn reacted with not only Li ion but LiPF_6 -derived Lewis acid as well, causing fluorinated-Sn compounds such as SnF_4 during initial cycles. Moreover, the presence of LiF implies the formation of insulating component which is undesirable for electrical conductivity of the anode. The weight percent concentration of Sn and F elements was examined using EDS spectrum measurements after different number of cycles with LiPF_6 as shown in Fig. 4d. The Sn content was rapidly reduced during a few initial cycles from ca. 48 % to 12 %. While, the F content increased up to ca. 67 %, which was more than twice value compared to after 1st lithiation process. From the XPS and EDS results, it was considered that the fluorinated-Sn and LiF produced in the active material; moreover, their amount rapidly increased within initial cycles, which probably increased in the content of deactivated Sn in the active material resulting in capacity fade as shown in Fig 2.

For the morphological investigation, FE-SEM images were observed after 2nd and 50th cycle. The Sn-O-C composite cycled with LiClO_4 are shown in Fig. 5a1, a2 and those of LiPF_6 are shown in Fig. 5b1, b2, respectively. The morphologies can be compared with the as-prepared Sn-O-C composite discussed in Fig. 1a.

With low magnification images in Fig. 5a1, the active material particles were moderately coated on the substrate. While, obviously different morphology was obtained from Fig. 5b1 showing roughened and pulverized state of the active material. In their higher magnification images, the different shapes of particles were obviously shown, i.e., round shape at the edge of aggregated particles in Fig. 5a1, but irregular shape of aggregated particles with larger size in Fig. 5b1. It is assumed that there may be two possibilities derived from chemical and morphological, causing this contrastive difference. One is the existence in aggregation with the chemical state of fluorinated-Sn and LiF on the surface of the Sn-O-C composite as revealed from XPS results. As the results, the low discharge capacity and poor columbic efficiency were obtained (as discussed in Fig. 2) since the undesirable particles were produced on the surface of the active material. The other possibility is the effect of HF. On the basis of the assumption that HF has been generated by the electrochemical reaction between LiPF_6 and trace amount of water [2,3], it is supposed that the HF was generated after initial cycle and it corroded the active material. Therefore, these certain morphological distinction after the 2nd cycle implies that the Sn-O-C composite anode was deteriorated by effect of HF and aggregated particles such as SnF_4 and LiF even with a few cycles. Meanwhile, several cracks and aggregated particles with fairly larger size were observed after 50th cycle with LiClO_4 (Fig. 5a2). Some particles were pulverized and aggregated during further cycles, causing cracks on the active material surface. In spite of the state of the active material with many cracks and pulverization, the metastable inner deposit layer still existed after 50th cycle with LiClO_4 (higher magnification image in Fig. 5a2). On the other hand, a number of the active materials were pulverized causing large aggregation particles after 50th cycle with LiPF_6 (see arrows in Fig. 5b2 with low magnification image). The high magnification image showed that even the residual active material suffered from significant disconnection between the particles (see arrows in Fig. 5b2 with high magnification image). The severe degradation of active material such as a pulverization and aggregation was much significant with the Sn-O-C composite cycled by LiPF_6 rather than that of LiClO_4 , which may be due to the existence of the generated HF exacerbating corrosion of metallic component.

To summary, it is demonstrated that the existence of fluorinated-Sn, LiF strongly affected the anomalous phase transition reactions during charge/discharge cycle. Furthermore, the severe morphology of the Sn-O-C composite cycled with LiPF_6 was exacerbated probably by the generated HF, causing poor cycle performances with repeated cycle.

Conclusion

The electrodeposited Sn-O-C composite anodes were cycle with either LiClO₄, delivering discharge capacity of 473 mAh g_{of Sn}⁻¹ with 95 % of coulombic efficiency at 100th cycle, or LiPF₆, delivering discharge capacity of 69 mAh g_{of Sn}⁻¹ with 70 % of coulombic efficiency at 100th cycle. The electrochemical investigation implied that the retarded phase transition reactions were obtained from the Sn-O-C composite cycled with LiPF₆ even after a few initial cycles, which was contrasting results against LiClO₄, showing fairly stable phase transition reactions with repeated cycles. The result of XPS declared the presence of fluorinated-Sn and LiF with the Sn-O-C composite cycled by LiPF₆ even after initial cycles. Furthermore, EDS revealed that the amount of composition of fluorinated-Sn and LiF increased with repeated cycling in LiPF₆. Morphological observations validated that the fluorinated-Sn and LiF were aggregated on the Sn-O-C composite cycled by LiPF₆. The degradation of active material significantly occurred from the Sn-O-C composite cycled by LiPF₆ rather than that of LiClO₄, which was validated from the acutely pulverized and agglomerated active material particles. It was assumed that the HF, which was probably generated from the reaction between LiPF₆ and trace amount of water, promoted deterioration of the morphology of the active material.

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Fig. 1. FE-SEM image (a), GIXRD pattern (b) and elemental mappings (c) of the as-prepared Sn-O-C composite.

Fig. 2. Discharge capacity and coulombic efficiencies of the Sn-O-C composites cycled by LiClO_4 and LiPF_6 .

Fig. 3. CVs (a), potential profiles and DCPs of the Sn-O-C composites cycled by LiClO_4 (b1–4) and LiPF_6 (c1–4).

Fig. 4. The results of XPS measurement (a–c) of the Sn-O-C composites cycled by LiClO_4 (i) and LiPF_6 (ii) after 2nd delithiation cycle, w.t.% concentration of Sn and F on the surface of the electrode at different number of cycles (d).

Fig. 5. FE-SEM images of the Sn-O-C composite anode cycled by LiClO_4 (a1, 2) and LiPF_6 (b1, 2).

Figure1

Figure 2

Figure3

Figure 4

Figure5