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FOCUS ISSUE OF SELECTED PRESENTATIONS FROM IMLB 2014

## Sodium-Ion Insertion/Extraction Properties of Sn-Co Anodes and Na Pre-Doped Sn-Co Anodes

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The electrochemical properties of Sn-Co were investigated to show the correlation between the cycle performance and the binders of the electrode component materials. Sn-Co electrodes with polyacrylic acid (PAA) exhibited a better cycle property (about 300 mAh/g up to 30 cycles) than those with polyvinylidene difluoride (PVdF). This better cycle property with PAA was due to the slight change in the volume of the electrode that occurred during cycling as revealed by in-situ light microscopy. In addition, Na pre-doping in Sn-Co electrodes improved the average coulombic efficiency from 95.4% to 99.9% at 2-10 cycles. © The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.0141502jes] All rights reserved.

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Lithium-ion batteries (LIBs) are used for power storage in electrical products and electric vehicles, and the demand for them is likely to increase. However, since lithium is not an abundant metal, it is expensive. On the other hand, because sodium is abundant and cheap; and interest in sodium-ion batteries (SIBs) has been growing.

The materials that have been studied for use as SIB anodes include hard carbon<sup>1-4</sup> and tin.<sup>5-7</sup> Hard carbon can be cycled more than 100 times, but the capacity is only about 250 mAh/g.1 In addition, the capacities of sodium cells with hard carbon electrodes are smaller than equivalent lithium cells.<sup>4</sup> On the other hand, the capacity of tin is about 500 mAh/g, but tin electrodes have the drawback of poor cycle performance (only several cycles) due to the large expansion and contraction of the volume of tin electrodes (about 5.3 times larger than hard carbon)<sup>6</sup> that accompanies Na-ion insertion (alloying) and extraction (dealloying). These alloying/dealloying processes of Sn with Na are similar to those of Sn with Li. Therefore, a key factor is that tin-based electrodes inhibit the change in volume during cycling. As reported in Ref. 6, the cycle properties of tin electrodes for SIBs can be improved by adopting a polyacrylic acid (PAA) binder. In that study, the capacity of Sn electrodes remained about 500 mAh/g after 20 cycles. Thus, a binder is one of the most important component materials in an electrode.

LIBs using Sn-Co anodes were first commercialized by Sony Corporation.<sup>8</sup> The Sn-Co anodes exhibit good cycle performance because cobalt does not alloy with lithium and cobalt buffer the change in volume of electrode during cycling.<sup>9–13</sup> This paper evaluates the electrochemical properties of Sn-Co electrodes for SIBs to reveal the correlation between cycle performance and binder.

Sn-Co electrodes were prepared with polyvinylidene difluoride (PVdF) or PAA as binders. The electrochemical properties of Sn-Co electrodes with a PAA binder were examined by performing galvanostatic discharge-charge experiments, and the results were compared with those obtained with PVdF as the binder. Additionally, the change in volume of a Sn-Co electrode with PAA or PVdF during Na-ion insertion (alloying)/extraction (dealloying) was evaluated by in-situ light microscopy for the first time. The crystallographic structural change of Sn-Co during cycling was characterized by X-ray diffraction (XRD), and the morphology change during cycling was analyzed by scanning electron microscopy (SEM) and light microscopy.

Furthermore, tin electrodes and metal oxide electrodes<sup>14</sup> for SIBs tend to reduce the coulombic efficiency, especially in the first cycle.

The first cycle coulombic efficiency of a tin electrode for SIBs is 70%.<sup>7</sup> As reported in Ref. 15 and 16, a Li pre-doping method improves the coulombic efficiency of a Si electrode for LIBs. Therefore, we tried using Na pre-doping to improve the coulombic efficiency.

#### Experimental

Sn-Co powder (element ratio: Sn:Co = 9:1) was obtained from Mitsubishi Materials Corporation. The Sn-Co powder was characterized with an X-ray diffractometer (XRD) (Rigaku, RINT2000) using CuK $\alpha$  radiation, and the morphology of the sample was observed with a scanning electron microscope (SEM) (Hitachi High-Technologies Co., SU1510 or JEOL Ltd., JSM-890) with an accelerating voltage of 15 or 7 kV, respectively.

Working electrodes containing Sn-Co, Sn, or Na-predoped Sn-Co were prepared for the electrochemical measurements. The Sn-Co electrodes were prepared by mixing 80 wt% of Sn-Co powder, 10 wt% of Ketjen Black EC600JD (KB, Lion Co.) and 10 wt% of PVdF (Kureha Battery Materials Japan Co.) or PAA (Sigma Aldrich) in N-methylpyrrolidone (NMP) (Tomiyama Pure Chemicals Industries Ltd.), and then coating the mixture on a Cu sheet as a current collector and drying it at 90°C. For comparison, Sn electrodes were prepared by mixing 80 wt% of Sn powder (particle size: 60-80 nm, IoLiTec), 10 wt% of KB and 10 wt% of PAA in NMP, and coating the mixture on a Cu sheet and drying it at 90°C. Na pre-doped Sn-Co electrodes were prepared by placing a sodium sheet (Kanto Chemical Co.) in direct contact with the Sn-Co electrode and pressing the two together in an Ar-filled glove box (dew point  $< -75^{\circ}$ C). The two samples were immersed in a non-aqueous electrolyte (1 mol/l NaPF<sub>6</sub> EC:DEC 1:1 in volume) (Tomiyama Pure Chemicals Industries Ltd.). After three days, the two samples were taken from the electrolyte solution and excess sodium metal was removed.

The electrochemical performance was evaluated with a 2032 cointype cell using a working electrode (Sn-Co electrode, Sn electrode, or Na pre-doped Sn-Co electrode, 0.02 mm thick and 14 mm in diameter), a non-aqueous electrolyte (1 mol/l NaPF<sub>6</sub> EC:DEC 1:1 in volume), a polypropylene separator (Celgard, 19 mm in diameter), and sodium metal sheets (0.6 mm thick and 15 mm in diameter) as a counter electrode. All cells were assembled in an Ar-filled glove box. Cycling tests were performed with an automatic galvanostatic discharge-charge system (Hokuto HJ1001SD8) at a constant current density of 25 mA/g between 0.01 and 1.5 V at 25°C. After the cell voltage had reached at 0.01 V, the cell was kept at a constant voltage



**Figure 1.** Schematic diagram of the cell for in-situ light microscopy, (a) top view and (b) cross-sectional view. (1) Counter electrode terminal, (2) glass (observation window), (3) sodium metal, (4) separator soaked with electrolyte solution, (5) Sn-Co electrode, (6) Cu sheet, (7) working electrode terminal.

of 0.01 V for 10 h. To analyze the discharged/charged electrodes with the XRD and SEM, the cells were opened after the charge/discharge process in the Ar-filled grove box, and the electrodes were washed with dimethyl carbonate (Tomiyama Pure Chemicals Industries Ltd.) and dried in the glove box overnight.

Changes in electrode volume during cycling were observed by using in-situ light microscopy (Lasertec Corp., ECCS B310). The expansion and contraction of the electrode was estimated in the line analysis mode. The circular cell for in-situ light microscopy examination was a stack consisting of a sodium sheet (0.2 mm thick and 15 mm in diameter) counter electrode, an electrolyte-solution (1 mol/l NaPF<sub>6</sub> EC:DEC 1:1 in volume)-soaked polypropylene separator (19 mm in diameter), and a Sn-Co (0.02 mm thick and 14 mm in diameter) working electrode. The circular cell was cut into semicircles, and the cross-sectional surface of the Na/separator (1 mol/l NaPF<sub>6</sub> EC:DEC 1:1 in volume)/Sn-Co became exposed. Then, the cell was placed in a jig for light microscopy as shown in Fig. 1. Discharge-charge tests were performed in the same condition with a coin type cell, and the cross-sectional surface was observed via an observation window using light microscopy.

#### **Results and Discussion**

Characterization of Sn-Co powder.— The XRD pattern of the Sn-Co powder is shown in Fig. 2. It was identified as a mixture of tin (ICDD#01-071-4638), CoSn (#01-073-8000), and Co<sub>3</sub>Sn<sub>2</sub> (#01-071-7459). The main peak at 32.7 deg. was identified as the tin phase. The XRD pattern and element ratio (Sn: Co = 9: 1) showed that the main component phase of the Sn-Co powder was tin unreacted with cobalt. Figure 3 shows SEM images of the Sn-Co powder and a cross-section of a Sn-Co particle. The particles are 0.7–2.0  $\mu$ m in size, and the Sn-Co powder particles are cubes. It is conceivable that there are three phases (tin, CoSn and Co<sub>3</sub>Sn<sub>2</sub>) in a cubic particle. The inner structure of the Sn-Co particle includes a large void, and this structure might have some advantages in terms of buffering the change in electrode volume during Na-ion insertion (alloying)/extraction (dealloying).

Discharge-charge performance, crystallographic and morphological changes of Sn-Co electrodes.— Figure 4 shows the discharge-



Figure 2. XRD pattern of Sn-Co powder.

charge curves of Na/Sn-Co cells with PAA or PVdF as the binder and those of a Na/Sn cell with PAA as the binder for comparison in the 0.01 to 1.5 V range. The cells were kept at a constant voltage of 0.01 V for 10 h after the discharging voltage had reached 0.01 V. The first discharge capacities of the Sn-Co electrode with PAA and PVdF were 505 and 569 mAh/g-Sn-Co (corresponding to 2.5 and 2.8 mol of Na-ion insertion), respectively. In addition, the first discharge capacity of the Sn electrode with PAA was 687 mAh/g-Sn (corresponding to 3.0 mol of Na-ion insertion). Since the tin content in the Sn-Co powder is 90 wt% and the first capacity of the tin was 687 mAh/g-Sn, the capacities per tin weight for Sn-Co with PAA should be 505/0.9 = 561 mAh/g-Sn. This suggests that the capacity of the Sn-Co electrode with PAA was about 100 mAh/g less than that of the Sn electrode. Some of the Sn-Co particles might not have formed an electrical connection due to the large internal void and would therefore be deactivated. Na/Sn-Co cells using both binders showed two distinct plateaus (at about -0.3 and 0.3-0.01 V for the first discharge process), and the plateau regions are similar to that of Na/Sn as shown in Fig. 4c. The electrochemical reaction between sodium and Sn-Co is similar to the one between sodium and tin. Assuming that during Na-ion insertion into the tin phase of Sn-Co, the -0.3 and 0.3-0.01 V regions correspond to the NaSn phase and Na<sub>9</sub>Sn<sub>4</sub>, respectively. Figure 5 shows the cycle properties of Na/Sn-Co cells with PAA or PVdF as the binder together with those of a Na/Sn cell with PAA. The Sn-Co electrode with PAA showed a better cycle property than that with PVdF, and the discharge capacity of the former reached about 300 mAh/g after 30 cycles. The fact that PAA has larger adhesion strength than the PVdF binder (respectively, 2.3 N cm<sup>-1</sup> and 0.3 N cm<sup>-1</sup>, in Ref. 17) might contribute to improving the cycle performance. In addition, properties of the Sn-Co electrode with PAA were superior to those of the Sn electrode with PAA. This is because the cobalt phase and void structure of the Sn-Co powder might buffer the change in electrode volume during Na-ion insertion (alloying)/extraction (dealloying). In the tin-based electrode, the buffer phase and structure and PAA as the binder are effective for providing better cycle performance.

Figure 6 shows XRD patterns of Sn-Co electrodes with PAA during cycling. After the first discharge, new peaks appeared at around



Figure 3. SEM image of (a) Sn-Co powder and (b) cross-section of Sn-Co particle (courtesy of Mitsubishi Materials Corporation).



**Figure 4.** Discharge-charge curves of (a) Na/Sn-Co cell with PAA as binder, (b) Na/Sn-Co cell with PVdF as binder and (c) Na/Sn cell with PAA as binder in the 0.01 to 1.5 V range at a current density of 25 mAh/g.

36.0, 36.4 and 36.8 deg., and they disappeared completely after the first charging, but the original peaks remained unchanged. Similar behavior was confirmed in the second cycle. This electrode reaction for Sn-Co might be reversible. These peaks are not indexed to crystalline phases such as Sn, Co,  $Sn_xCo$  or  $Na_xSn$ . This electrochemical reaction is similar to the one of Li-ion with  $Co_3Sn_2^8$  and amorphous Sn-Co.<sup>10</sup> In the XRD patterns of  $Co_3Sn_2$  electrodes and amorphous Sn-Co electrodes, new peaks also appeared/disappeared during Li-ion insertion/extraction, and the original peaks remained unchanged. Additionally, the new peak is not indexed to crystalline phases such as Sn, Co,  $Sn_xCo$  or Li<sub>x</sub>Sn. The mechanisms of the electrochemical



Figure 5. Cycle properties of Na/Sn-Co cells with (a) PAA or (b) PVdF as binder and (c) Na/Sn cell with PAA.



Figure 6. XRD patterns of Sn-Co electrodes with PAA: (a) Pristine, (b) after first discharge, (c) after first charge, (d) after second discharge, and (e) after second charge.

reaction of both Na ions and Li ions with Sn-Co might be the same. Two possibilities remain: one is that the  $Na_xSn$  peaks were shifted due to the existence of cobalt; the other is that the peaks of the Na-Sn-Co alloy phase. Clarifying the origin of this mechanism requires further investigation. In either case, these peaks might indicate some electrochemical reaction between sodium and Sn-Co during cycling.

Figure 7 shows SEM images of Sn-Co electrodes with PAA or PVdF as-prepared and after the fifth cycle. Before cycling, the surface morphologies were almost the same as for electrodes with PAA and PVdF binders. But after the fifth cycle, the electrode with PAA remained unchanged and the Sn-Co particle remained a cube, whereas the electrode with PVdF had a large crack. This indicates that the electrode with PAA expanded less than that with PVdF during discharge (Na-ions insertion process (alloying)). According to Y. Park et al.,<sup>18</sup> PAA has a porous structure (13% greater porosity than PVdF). Moreover, the adhesion strength of PAA binder (2.3 N cm<sup>-1</sup>) is higher than that of PVdF binder (0.3 N cm<sup>-1</sup>), as reported by Komaba et al.<sup>17</sup> This porous structure and higher adhesion strength are attributed to buffering of the volume change during the insertion and extraction of Na ions to and from Sn-Co electrodes.



Figure 7. SEM images of Sn-Co electrodes with PAA or PVdF before testing and after fifth cycle.



Figure 8. Cross-sectional images of Sn-Co electrodes with PAA or PVdF (a) before testing and (b) after second discharge. (1) Sodium metal, (2) separator, (3) Sn-Co electrode, (4) Cu sheet.

The expansion and contraction of Sn-Co electrodes have a strong correlation with cycle performance, and analyzing the correlation is very important. We therefore evaluated the change in volume of a Sn-Co electrode with PAA or PVdF during Na-ion insertion (alloying)/extraction (dealloying) by in-situ light microscopy, and this is the first observation of the change in volume of an electrode for SIBs. Figure 8 shows cross-sectional images of Nax(Sn-Co) electrodes with PAA or PVdF before testing and after the second discharge. Compared with the as-prepared electrode, the electrode with PAA expanded a little and the electrode with PVdF expanded a lot after the second discharge. To give the electrodes a quantitative expansion rating, the thickness of the Sn-Co electrode measured by line analysis during cycling can be seen in the image in Fig. 8. Figure 9a shows the voltage versus the state of charge (SOC) of the Na/Sn-Co cells for in-situ light microscopy, and Fig. 9b shows the expansion rate (the thickness of the as-prepared electrode is defined as expansion rate = 100%) versus the SOC during cycling. SOC values of 100% and 0% mean full charge and full discharge, respectively. After the second discharge, the electrode with PAA was 1.4 times larger, and that with PVdF was 5.5 times larger. Moreover, the electrode with PAA shrank during charging, but the one with PVdF did not. The porous structure and higher adhesion strength of PAA enabled the buffering of the change in electrode volume during cycling. As a result, the electrode with PAA showed good cycle performance.

*Pre-doping effect of Sn-Co electrodes.*— Figure 10 shows discharge-charge curves of Sn-Co electrodes with/without Na pre-doping. The Sn-Co electrode without Na pre-doping exhibited a large irreversible capacity of about 272 mAh/g in the first cycle. Some of the irreversible capacity in the first cycle might be caused by the formation of a solid electrolyte interphase (SEI) layer.<sup>14</sup> The first charge capacity of the Sn-Co electrode with Na pre-doping was 307 mAh/g (corresponding to 1.0 mol of Na-ion insertion). This result indicates 1.0 mol or more of Na-ion insertion into the Sn-Co electrode with the pre-doping technique. In addition, there was seldom any irreversible capacity in the first cycle.

Figure 11a shows the cycle properties of Sn-Co electrodes with/without Na pre-doping and Fig. 11b shows the coulombic efficiency. The coulombic efficiency is defined as the ratio of the charge capacity to the discharge capacity. The average coulombic efficiencies of Sn-Co electrodes with and without Na pre-doping after the second cycle were 99.9 and 95.4%, respectively. These data indicate that Na pre-doping improves the coulombic efficiency. In the Na pre-doped Sn-Co electrode, the molar number of Na ions inserted into the Sn-Co with the pre-doping technique is about equal to the molar number of Na ions responsible for the irreversible capacity. On the other hand, in the Sn-Co electrode without Na pre-doping, the molar number of Na ions that are gradually inserted is about equal to the number responsible for the irreversible capacity during each cycle. These are the reasons for the low capacity of the Na pre-doped Sn-Co electrode increasing the electrode weight (equivalent to Na ion insertion) and the electrode deteriorating due to rapid Na ion insertion. Accordingly, the



Figure 9. (a) Voltage versus state of charge (SOC) of Na/Sn-Co cells for insitu light microscopy and (b) expansion rate of Sn-Co electrode versus SOC during cycling.



**Figure 10.** Discharge-charge curves of Sn-Co electrodes (binder: PAA) (a) with/(b) without Na pre-doping.



**Figure 11.** (a) Cycle properties and (b) coulombic efficiency of Sn-Co electrodes with/without Na pre-doping.

Na pre-doping technique can greatly reduce the irreversible capacity in the first cycle and improve the coulombic efficiency.

#### Conclusions

The first discharge capacities of the Sn-Co electrodes with PAA or PVdF as the binder were 505 and 569 mAh/g, respectively. A Sn-Co electrode with both binders exhibited two distinct plateaus at about -0.3 and 0.3-0.01 V. The cycle property of the Sn-Co electrode

with PVdF was poor (38 mAh/g at 30 cycles); in contrast, the one with PAA showed good cycle stability (300 mAh/g up to 30 cycles). This is attributed to the buffering of the volume change during the insertion and extraction of Na ions because of the porous structure and larger adhesion strength of PAA. In addition, Na pre-doping reduced the irreversible capacity in the first cycle, and improved the average coulombic efficiency from 95.4% to 99.9% after the second cycle.

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