Influence of Li-salts on Cycle Durability of Sn-Ni Alloy Anode for Lithium-ion Capacitor

Yusuke NAKAMURA,a,7 Hiroki NARA,b,† Seongki AHN,b Toshiyuki MOMMA,a,b,∗ Wataru SUGIMOTO,c and Tetsuya OSAKAb

a School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
b Research Organization for Nano & Life Innovation, Waseda University, 513 Waseda-tsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan
c Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

* Corresponding authors: h-nara@aoni.waseda.jp, momma@waseda.jp

ABSTRACT

Tin-nickel (Sn-Ni) alloy is a promising candidate as an anode for the lithium-ion capacitor (LIC) because it is superior in volumetric energy density compared with that of the graphite anode. However, its cycle durability requires improvement, even with a higher utilization ratio of the anode. The effect of lithium salts, LiPF₆ and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is investigated for usage in the LIC in severe conditions (utilization ratio of the anode: 20%). The LIC with LiTFSI delivered its initial capacity up to ~400 cycles, which is 4 times longer than the LIC with LiPF₆. The reason for the capacity decay in the LiPF₆ system is attributed to the narrowing of the potential range of the activated carbon cathode due to a widening potential range of the Sn-Ni alloy anode during operation. This widening is attributed to the loss of the active material due to peeling-off from the substrate. However, when LiTFSI is used, no such decay is observed. It is suggested that a polymer-like solid electrolyte interphase derived from TFSI⁻ may suppress the loss of the active material. This finding can encourage the development of an Sn-based anode for LICs in combination with a mild operating condition and electrolyte additives.

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1. Introduction

Lithium-ion batteries (LIBs) and electric double-layer capacitors (EDLCs), are promising types of energy storage for electric vehicles (EVs).1,2 In comparing LIBs and EDLCs, LIBs are superior in terms of energy density (150–200 Wh·kg⁻¹) and inferior in both power density (<1,000 W·kg⁻¹) and cycle durability (<1,000 cycles),3,4 while EDLCs are superior in both power density (10,000 W·kg⁻¹) and cycle durability (100,000 cycles), and inferior in energy density (5–10 Wh·kg⁻¹).5,6 These performances are in a trade-off relationship; some meet requirements for EV application, and the others do not. Lithium-ion capacitors (LICs) have attracted attention7,8 to meet all the requirements.

LICs are composed of a non-Faradaic cathode, such as activated carbon (AC) as used in EDLCs, and a Faradaic anode, such as graphite (372 mAh·g⁻¹) and Li₄Ti₅O₁₂ (175 mAh·g⁻¹) as used in LIBs.9 To increase the energy density of LICs, we focused on the tin (Sn) anode, which has a theoretical capacity of 994 mAh·g⁻¹ by alloying with lithium. The Sn anode is well known to have a critical drawback of a large volume expansion up to 300% when fully lithiated, resulting in poor cycle durability.10 As a solution to the problem, a tin-nickel (Sn-Ni) alloy anode was reported as an alternative to the Sn anode.11–14 The Sn-Ni alloy anode can buffer the stress derived from the volume change due to the nickel (Ni), which is inactive against lithium, demonstrating improved cycle durability compared to an Sn anode. We recently reported an LIC composed of an Sn-Ni alloy anode (with a utilization ratio of 6.5%), with energy and power densities of 404 Wh·L⁻¹ and 73 W·L⁻¹ (based on the volume of the anode), respectively, and cycle durability of over 3000 cycles with capacity retention of 80%.15 Meanwhile, the choice of lithium salts in organic solvents for electrolytes is an important factor that governs the performance of LICs.16 The anion choice should be important because the anion is physisorbed on the cathode surface. Anion decomposition at the anode should also be taken into consideration. LiPF₆ is commonly used in LIBs because of good ionic conductivity and passivation of an aluminum current collector.16 However, LiPF₆ reacts with a trace amount of residual water in the electrolyte, generating hydrogen fluoride (HF), which attacks the cathode material. Moreover, LiPF₆ forms a solid electrolyte interphase (SEI) at the anode.17–19 As an alternative to LiPF₆, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is known to form a stable SEI film.19–21 The effect has been reported of lithium salts improving the charge-discharge property for an LIC composed of a graphite anode.16 However, the effect of lithium salts on the Sn-Ni anode system has not been reported.

In the present study, to improve cycle durability of an LIC composed of an Sn-Ni alloy anode with a higher utilization ratio (20%) and an activated carbon cathode, the effect of lithium salts on the LIC is studied in severe conditions.

2. Experimental

An activated carbon (AC) cathode was prepared by a conventional coating method on aluminum foil with a mass ratio of YP-50F (Kuraray), acetylene black (Denka), and polyvinylidene fluoride (Wako pure chemical) = 90:5:5. The AC cathode was punched into Ø9 mm. The mass loading was 1.92 ± 0.1 mg (~3 mg cm⁻²).
The Sn-Ni alloy anode was electrodeposited according to previous reports. The aqueous electrodeposition bath was composed of 0.500 mol·L⁻¹ of K₂O₇P₂ (Kanto chemical), 0.125 mol·L⁻¹ of C₂H₅NO₂ (Kanto chemical), 0.175 mol·L⁻¹ of SnCl₂·2H₂O (Kanto chemical), 0.075 mol·L⁻¹ of NiCl₂·6H₂O (Kanto chemical), and 5 mL·L⁻¹ of aqueous NH₃ (Kanto chemical).

The electrodeposition cell was composed of a Cu substrate with an area of 1 cm² as the working electrode and a Pt wire as a counter electrode. Electrodeposition was carried out at 5 mA·cm⁻² under 50°C. The Sn-Ni alloy was pre-doped with the following condition. A 2032 coin-type cell was assembled, composed of the Sn-Ni alloy as anode and Li metal as counter electrode. The Sn-Ni alloy anode was electrochemically lithiated and delithiated for 5 cycles in the voltage range of 0.01–1.2 V, and then lithiated to 0.01 V, followed by delithiation to match the capacity of the AC cathode of AC/Sn-Ni LIC. The pre-doped Sn-Ni alloy anode was taken out by disassembling the coin-type cell.

The LIC, composed of the AC cathode and the pre-doped Sn-Ni alloy anode with mass balanced to AC:Sn = 4:1 (equal to the capacity balance of 1:5), was evaluated by using a three-electrode cell with Li metal reference electrode or a 2032 coin-type cell. The severe anode utilization ratio of 20% was selected to emphasize the effect of the lithium salts. The electrolyte was 1 mol·L⁻¹ LiPF₆ or LiTFSI in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 vol.) (Tomiyama Pure Chemical Industries) with a glass fiber separator (15 mm). The LIC was charged and discharged in the voltage range of 2.0–3.8 V with a current density of 0.2 A (g-AC)⁻¹. The Sn-Ni alloy anodes pre-doped in the electrolyte of LiPF₆ or LiTFSI were evaluated by electrochemical impedance spectroscopy (EIS). The EIS conditions are an amplitude of 10 mV and a frequency range of 10 kHz to 10 mHz at open-circuit voltage (OCV) after full lithiation (0.01 V).

The morphology of the Sn-Ni alloy anode was observed using a field emission scanning electron microscope (FE-SEM, SU8240, Hitachi). Elemental analysis of the SEI was investigated by energy dispersive X-ray (EDX) equipped on the FE-SEM. The samples were transferred under ambient air conditions.

3. Results and Discussion

Figure 1 shows the capacity retention of the LICs with LiPF₆ and LiTFSI evaluated with a three-electrode cell. The capacity of the LICs with LiPF₆ and LiTFSI at the first cycle was 30.5 ± 1.4 mAh (g-AC)⁻¹ (average of 7 experiments, N = 7), and 29.6 ± 1.2 mAh (g-AC)⁻¹ (N = 5), respectively. Evident capacity decays for the LICs with LiPF₆ and LiTFSI were observed after around the 100th and 400th cycle, respectively. The insufficient cycle durability as LICs was derived from the severe condition of the high utilization ratio of the anode. The results clearly show that the cycle durability of the LIC with LiTFSI was superior to that with LiPF₆.

To investigate this difference electrochemically, the potential of both cathode and anode was evaluated by using a three-electrode cell with a lithium metal reference electrode. Figure 2 indicates the potential of AC cathodes and Sn-Ni alloy anodes during charge–discharge cycles. The upper and lower limits of the anode potential represent the potential of the discharged state (2.0 V in full cell) and the charged state (3.8 V in full cell), respectively. Conversely, the

![Figure 1](image1.png)

**Figure 1.** Capacity retention of LICs composed of AC cathode and Sn-Ni alloy anode in a three-electrode cell with different lithium salts, LiPF₆ and LiTFSI, evaluated with a three-electrode cell. The capacity of the LICs with LiPF₆ and LiTFSI at the first cycle was 30.5 ± 1.4 mAh (g-AC)⁻¹ (N = 7) and 29.6 ± 1.2 mAh (g-AC)⁻¹ (N = 5), respectively.

![Figure 2](image2.png)

**Figure 2.** Potentials of AC cathode (red line) and Sn-Ni alloy anode (blue line) in a three-electrode cell with different lithium salts, LiPF₆ and LiTFSI, which were charged and discharged in the voltage range of 2.0–3.8 V. Potential profiles of the LICs with LiPF₆ and LiTFSI around 80 h.
upper and lower limits of the cathode potential represent the potential of the charged state (3.8 V in full cell) and the discharged state (2.0 V in full cell), respectively. For the LIC with LiTFSI shown in Fig. 2(b), the upper limit of the anode potential was constant at $\sim 0.5$ V vs. Li/Li$^+$ up to 80 h (equals to $\sim 260$ charge–discharge cycles). Conversely, for that with LiPF$_6$ shown in Fig. 2(a), the upper limit of the anode potential obviously increased from 0.5 V to 1.6 V vs. Li/Li$^+$ from 25 h to 80 h (equals to $\sim 650$ charge–discharge cycles). The potential profiles of the LICs with LiPF$_6$ and LiTFSI around 80 h are shown in Fig. 2(c) and (d), respectively. During discharge, the increase of the upper limit of the anode potential means there was an increase of the lower limit of the cathode potential because the lower cut-off voltage of the LICs was fixed to 2.0 V. For the LIC with LiPF$_6$, the lower limit of the cathode increased because the upper limit of the anode potential increased, narrowing the cathode potential range. However, for the LIC with LiTFSI, the upper limit of the cathode was relatively stable because the lower limit of the anode was constant at $\sim 0.1$ V vs. Li/Li$^+$. Therefore, the capacity decay is attributed to a narrowing of the cathode potential range due to the widening of the anode potential range. The reason for the widening of the anode potential range was investigated from the standpoint of its morphology change.

Figure 3 shows FE-SEM images of as-deposited Sn-Ni alloy and delithiated Sn-Ni alloy after pre-doping treatment for 5 cycles with LiPF$_6$ and LiTFSI, and discharged Sn-Ni alloy after 300-cycle LIC operation with LiPF$_6$ and LiTFSI. The as-deposited Sn-Ni alloy had no cracks, as shown in Fig. 3(a). After the pre-doping treatment with LiPF$_6$ and LiTFSI, the surface was observed to bear similar cracks, which is caused by volume expansion followed by contraction (Fig. 3(b) and (d)). After the 300-cycle LIC operation, a clear difference between the Sn-Ni alloy anodes with LiPF$_6$ and LiTFSI was observed. The peeling-off of Sn-Ni alloy from the Cu substrate was confirmed in the anode cycled with LiPF$_6$ (Fig. 3(c)). In contrast, such a phenomenon was not observed with LiTFSI (Fig. 3(e)). Thus, deactivation of active material due to the peeling-off is considered to accelerate the capacity decay. Because the increase of inactive material concentrates the charge–discharge current into the remaining active material, this is predicted to widen the potential range of the anode. The widening of the potential range of the anode will, in turn, enhance stress due to the increase in the volume expansion and contraction, thereby accelerating the peeling-off.

The difference of the peeling-off between LICs with LiPF$_6$ and LiTFSI was further evaluated, taking into consideration SEI formation. Figure 4 shows EDX results of carbon, nitrogen, oxygen, and fluorine in SEI of Sn-Ni alloys formed during pre-doping process in the electrolyte of LiPF$_6$ and LiTFSI. Comparing the elemental content from the SEI, the intensity of nitrogen in the LiTFSI system was slightly higher compared with that of LiPF$_6$. Because nitrogen was detected even in the SEI formed during pre-doping treatment with LiPF$_6$, nitrogen was mainly introduced during sample transfer in ambient air. However, such a difference may possibly be due to the TFSI-derived product; note that fluorine in the SEI formed in LiTFSI system is compact. Additionally, oxygen and carbon content in the case of LiPF$_6$ was 30% and 55% higher than that of LiTFSI, respectively. The SEI formed by LiPF$_6$ is reported to be thick and porous, while the SEI formed from LiTFSI is compact. Thus, the higher oxygen and carbon content in the LiPF$_6$ system may be due to a thicker SEI. Furthermore, the SEIs formed under the conditions studied in this study seem to be in accordance with those in lithium ion battery conditions. In addition, the SEI formed in LiTFSI system is

![Figure 3. FE-SEM images of Sn-Ni alloys (a) as-deposited, delithiated after pre-doping treatment for 5 cycles with (b) LiPF$_6$ and (d) LiTFSI and discharged after 300-cycle LIC operation with (c) LiPF$_6$ and (e) LiTFSI.](image)

![Figure 4. EDX results of carbon, nitrogen, oxygen, and fluorine in SEI of Sn-Ni alloys formed during pre-doping process in the electrolyte of LiPF$_6$ and LiTFSI.](image)
Nyquist plots were measured at 0.7 V where Sn-Ni alloy anode is less reactive with lithium (not shown). The Nyquist plots of Sn-Ni alloy/Li half-cell after pre-doping process in the electrolyte of LiPF₆ and LiTFSI at 0.01 V. Circles are filled at each decade.

The difference in the SEIs of Sn-Ni alloy formed during the pre-doping process in the electrolyte of LiPF₆ and LiTFSI was evaluated by electrochemical impedance spectroscopy. Figure 5(b) shows Nyquist plots of Sn-Ni alloy/Li half-cell after the pre-doping process in the electrolyte of LiPF₆ and LiTFSI at OCV after full lithiation. The Nyquist plots represent two semicircles in the high- and middle-frequency regions. Their top frequencies in the high- and middle-frequency regions were ~630 Hz and ~4 Hz, respectively. Their loci were related to diffusion at low frequencies. The Nyquist plots were fitted by using the equivalent circuit in Fig. 5(a). The equivalent circuit counted an SEI resistance, a charge transfer resistance, and diffusion resistance of lithium in Sn-Ni alloy. Although the SEI resistance and the charge transfer resistance of Sn-Ni alloy and Li electrodes cannot be separable clearly due to the fusion resistance of lithium in Sn-Ni alloy. Although the cracking degree observed in Fig. 3(b) and (d) looks almost the same, the Rₚ suggests that the Sn-Ni alloy pre-doped in the electrolyte of LiPF₆ has cracks inside of the Sn-Ni alloy. These cracks may possibly accelerate peeling-off from the substrate in the case of LiPF₆.

Therefore, longer cycle durability was achieved in the LiTFSI system compared with that in the LiPF₆ system.

4. Conclusion

The effect of LiPF₆ and LiTFSI lithium salts on the cycle durability of the Sn-Ni alloy under severe cycling conditions was evaluated for the LIC with a capacity ratio balanced to AC:Sn = 1:5 (i.e., 20% utilization of the anode). The LIC with LiTFSI delivered a stable capacity up to ~400 cycles, which was 4 times longer than the LIC with LiPF₆. The reason for the capacity fading was attributed to a narrowing of the potential range of the AC cathode, which in turn originates from a widening in the potential range of Sn-Ni alloy anode during operation. This widening in the anode potential was attributed to the loss of active material due to peeling-off from the substrate. Moreover, the loss of active material should accelerate the widening of the anode potential range due to concentration of current to the remaining active material. SEM, EDX, and EIS analysis have suggested that the suppression of peeling-off for LiTFSI was caused by a polymer-like structure in an SEI derived from LiTFSI. Although the results indicated that the Sn-Ni alloy anode in LIC could degrade even with the anode utilization ratio of 20%, the degradation of Sn-Ni alloy anode could be suppressed by choosing lithium salts. This finding can encourage the development of an Sn-based anode for LICs: The cycle durability of the LIC can be expected to further improve by maintaining mild operating conditions as reported and applying electrolyte additive to improve the SEI, while realizing volume energy and power densities exceeding the LIC with a conventional graphite anode.

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Table 1. Resistances of electrolyte solution (Rₛ), SEI (R₁), charge transfer (R₂), and diffusion in Sn-Ni alloy (Rₚ), measured Sn-Ni alloy/Li half-cell at 0.01 V.

| Electrolyte | Rₛ (Ω) | R₁ (Ω) | R₂ (Ω) | Rₚ (Ω) |
|-------------|-------|-------|-------|-------|
| LiPF₆       | 10.8  | 48.1  | 33.8  | 1.3   |
| LiTFSI      | 9.3   | 60.9  | 37.6  | 7.2   |

References

1. M. Ruska and I. Kiviluoma, VTT Tied. - Vtt. Tek. Tutkimus, 1 (2011).
2. C. Liu, F. Li, L. P. Ma, and H. M. Cheng, Adv. Mater., 22, E28 (2010).
3. L. Ramatha and J. Andrew, Asian Biotechnol. Dev. Rev., 14, 19 (2012).
4. F. Zhang, Y. Tang, H. Liu, H. Ji, C. Jiang, J. Zhang, X. Zhang, and C. S. Lee, ACS Appl. Mater. Interfaces, 8, 4691 (2016).
5. F. Zhang, Y. Tang, H. Liu, H. Ji, C. Jiang, J. Zhang, X. Zhang, and C. S. Lee, ACS Appl. Mater. Interfaces, 8, 4691 (2016).
5. L. L. Zhang and X. S. Zhao, *Chem. Soc. Rev.*, **38**, 2520 (2009).
6. M. Winter and R. J. Brodd, *Chem. Rev.*, **104**, 4245 (2004).
7. K. Naoi, S. Ishimoto, J. I. Miyamoto, and W. Naoi, *Energy Environ. Sci.*, **5**, 9363 (2012).
8. W. H. Qu, F. Han, A. H. Lu, C. Xing, M. Qiao, and W. C. Li, *J. Mater. Chem. A.*, **2**, 6549 (2014).
9. K. Naoi, S. Ishimoto, Y. Isobe, and S. Aoyagi, *J. Power Sources*, **195**, 6250 (2010).
10. N. Nitta, F. Wu, J. T. Lee, and G. Yushin, *Mater. Today*, **18**, 252 (2015).
11. L. Y. Beaulieu, S. D. Beattie, T. D. Hatchard, and J. R. Dahn, *J. Electrochem. Soc.*, **150**, A419 (2003).
12. H. Mukaibo, T. Sumi, T. Yokoshima, T. Momma, and T. Osaka, *Electrochem. Solid-State Lett.*, **6**, A218 (2003).
13. H. Mukaibo, T. Momma, and T. Osaka, *J. Power Sources*, **146**, 457 (2005).
14. H. Mukaibo, T. Momma, M. Mohamedi, and T. Osaka, *J. Electrochem. Soc.*, **152**, A560 (2005).
15. S. Ahn, Y. Nakamura, H. Nara, T. Momma, W. Sugimoto, and T. Osaka, *J. Electrochem. Soc.*, **166**, A3615 (2019).
16. M. Dahbi, F. Gharrouss, F. Tran-Van, D. Lemordant, and M. Anouti, *J. Power Sources*, **196**, 9743 (2011).
17. Z. Chen, W. Q. Lu, J. Liu, and K. Amine, *Electrochim. Acta*, **51**, 3322 (2006).
18. H. Nara, K. Morita, T. Yokoshima, D. Mukoyama, T. Momma, and T. Osaka, *AIMS Mater. Sci.*, **3**, 448 (2016).
19. A. M. Andersson, M. Herstedt, A. G. Bishop, and K. Edström, *Electrochim. Acta*, **47**, 1885 (2002).
20. M. Nie and B. L. Lucht, *J. Electrochem. Soc.*, **161**, A1001 (2014).
21. T. Yoon, N. Chapman, D. M. Seo, and B. L. Lucht, *J. Electrochem. Soc.*, **164**, A2082 (2017).
22. S. Leroy, H. Martinez, R. Dedryvère, D. Lemordant, and D. Gontbeau, *Appl. Surf. Sci.*, **253**, 4895 (2007).
23. V. Eshkenazi, E. Peled, L. Burstein, and D. Golodnitsky, *Solid State Ionics*, **170**, 83 (2004).