

Lithiation and Delithiation Properties of Si-based Electrodes Pre-coated with a Surface Film Derived from an Ionic-liquid Electrolyte

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1 Ionic-liquid electrolytes can enhance battery
2 performance and safety but are expensive. To reduce the use
3 of ionic-liquid electrolytes, we investigated the
4 charge/discharge properties of Si-based electrodes in an
5 organic-liquid electrolyte, where the electrode surface was
6 pre-coated with a film derived from an ionic-liquid
7 electrolyte. No improvement in the electrode performance
8 was observed compared to that of a nonmodified Si
9 electrode. Once the modified film was broken down, a
10 stable surface film could not be reformed in the organic-
11 liquid electrolyte.

12 **Keywords:** Lithium-ion battery, Silicon electrode, Ionic-
13 **liquid electrolyte**

14 Si is a promising active negative electrode material for
15 lithium-ion batteries because of its high theoretical Li
16 storage capacity corresponding to crystalline $\text{Li}_{3.75}\text{Si}$ (3580
17 mA h g^{-1}). However, its huge volume change during
18 lithiation (charge) and delithiation (discharge) leads to poor
19 cycle stability. To maximize the performance of an Si
20 electrode, optimizing the electrode–electrolyte interphase,
21 that is, forming a stable surface film that enables Li^+ to be
22 stored in Si and suppresses further electrolyte
23 decomposition is important. Various film-forming additives,
24 such as vinylene carbonate (VC) and fluoroethylene
25 carbonate, have been used to prepare such surface films,
26 which has resulted in Si electrode with good long-term cycle
27 stability.^{1–5} Alternatively, Si-based electrodes have
28 demonstrated good cycling performance in electrochemical
29 cells containing certain ionic-liquid (IL) electrolytes
30 because of the formation of a superior surface film.^{6–13} The
31 IL electrolytes can also enhance the safety of the battery
32 because of their unique properties.^{14,15} However, IL
33 electrolytes are expensive compared with typical organic-
34 liquid electrolytes (e.g., 1 mol dm^{-3} (M) LiPF_6 dissolved in a
35 mixture of ethylene carbonate and diethyl carbonate (DEC)).

36 To reduce the use of IL electrolytes in cells, we herein
37 studied the lithiation and delithiation behaviors of Si-based
38 electrodes in an organic-liquid electrolyte, where the
39 electrode surface was preliminarily modified by a film
40 derived from an IL electrolyte. We selected 1 M lithium
41 bis(fluorosulfonyl)amide (LiFSA) dissolved in *N*-methyl-*N*-
42 propyl pyrrolidinium bis(fluorosulfonyl)amide (Py13-FSA)
43 as the IL electrolyte because it has been confirmed to be
44 compatible with Si-based electrodes.^{10,13,16,17} We
45 investigated the effects of different surface geometries on
46 the cycle life of cells. We also added a small amount of the
47 IL electrolyte to an organic-liquid electrolyte and
48 investigated its performance as a film-forming additive.

49 Si powder (FUJIFILM Wako Pure Chemical Corp.,
50 99.9%) was used as an active material. An Si electrode was
51 prepared by a gas-deposition method without any binders or
52 conductive additives.^{10,18} The weight of the electrode was
53 38.2 mg cm^{-2} . A 2032-type coin cell was assembled using
54 an Si electrode as the working electrode, a glass-fiber filter
55 (Whatman GF/A) as the separator, and a Li metal sheet
56 (thickness: 1 mm, 99.9%, Rare Metallic Co., Ltd.) as the
57 counter electrode. The IL electrolyte used in this study was
58 1 M LiFSA (Kishida Chemical Co., Ltd.) dissolved in Py13-
59 FSA (DKS Co., Ltd.). We used 1 M lithium
60 bis(trifluoromethanesulfonyl)amide dissolved in propylene
61 carbonate (LiTFSA/PC, Kishida Chemical Co., Ltd.)
62 including less than 20 ppm of water as a conventional
63 organic-liquid electrolyte. We have confirmed that the Li-
64 salt with either LiFSA or LiTFSA in the organic-liquid
65 electrolyte does not affect the cycle life of Si-based
66 electrodes.¹⁶ Figure S1 displays the chemical structures of
67 electrolytes used in this study. The loading amount of
68 electrolyte solution in the coin cell was approximately $30 \mu\text{l}$.

69 Galvanostatic charge–discharge testing was carried out
70 with an electrochemical measurement system (HJ-1001
71 SM8A, Hokuto Denko Co., Ltd.) in the potential range from
72 0.005 to 2.000 V vs Li^+/Li at 303 K under a constant-current
73 rate of 0.4C (1C: 3600 mA g^{-1}) with a charge-capacity limit
74 of 1000 mA h g^{-1} . We observed the electrode surface by
75 field-emission scanning electron microscopy (FE-SEM,
76 JSM-6701F, JEOL Co., Ltd) with a beam acceleration
77 voltage of 20 kV and a working distance of 10 mm. We
78 estimated the surface roughness of the Si electrode using
79 confocal laser scanning microscopy (VK-9700, Keyence).

80 Figure 1a shows the time dependency of the potential
81 for pre-cycling of an Si electrode in the IL electrolyte. The
82 corresponding charge-discharge profile and the current-time
83 curve were displayed in Figure S2. The pre-cycling was
84 carried out in two modes –constant-current (CC) and
85 constant-voltage (CV), and CC only– to form a stable
86 surface film on the Si electrode. The CCCV mode was
87 conducted under the following conditions; the potential was
88 (1) lowered from the open circuit potential to 0.500 V vs.
89 Li^+/Li at 0.1C, (2) maintained at 0.500 V vs. Li^+/Li for 12 h,
90 and (3) increased to 2.000 V vs. Li^+/Li . To prevent Si from
91 storing Li and expanding or cracking, the potential was set
92 to 0.500 V. In addition, pre-cycling in the CC mode only
93 was carried out at 0.1C for a cycle with a charge-capacity
94 limit of 1000 mA h g^{-1} . In both the CCCV and CC modes,
95 we observed an inflection point at approximately 1.7 V vs.
96 Li^+/Li in the charge curve, which arose from reductive
97 decomposition of FSA anions.¹⁹

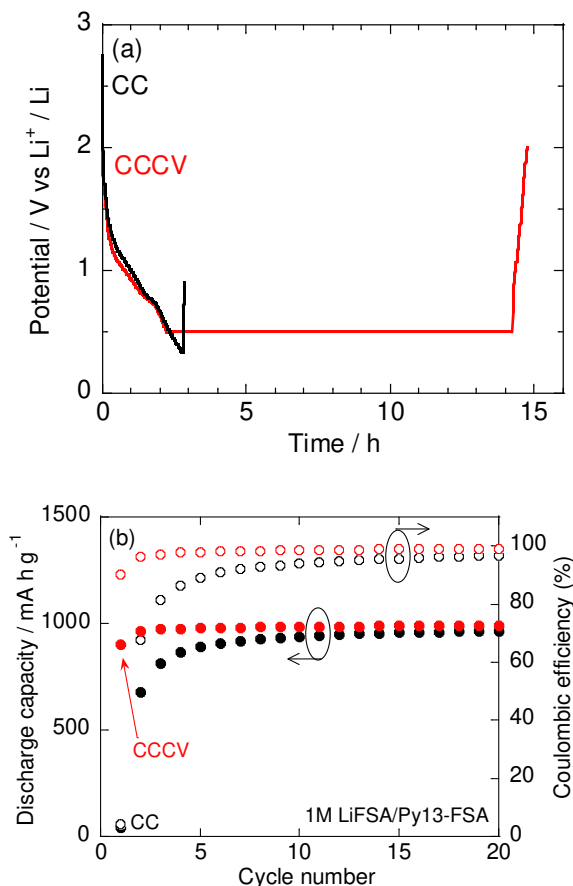


Figure 1. (a) Time dependency of the potential for pre-cycling of an Si electrode in 1 M LiFSA/Py13-FSA. Each pre-cycling condition is described in the main text. (b) Cycle life of an Si electrode after pre-cycling in 1 M LiFSA/Py13-FSA under a constant charge capacity of 1000 mA h g⁻¹.

1 Figure 1b shows the initial cycle life of the Si
 2 electrodes after pre-cycling, as indicated by their discharge
 3 capacity and Coulombic efficiency (CE). An Si electrode
 4 coated with a surface film exhibited a greater discharge
 5 capacity and greater CE over 20 cycles when cycled in
 6 CCCV mode compared with another Si electrode cycled
 7 only in CC mode. These results reveal that the CCCV mode
 8 could form a stable surface film with high Li⁺ conductivity
 9 and function as an insulator.

10 After the coin cell was pre-cycled in CCCV mode with
 11 its Si electrode in the IL electrolyte, we disassembled the
 12 coin cell and washed the extracted Si electrode with PC and
 13 DEC. We then reconstructed a coin cell using the washed Si
 14 electrode and an organic-liquid electrolyte and investigated
 15 its cycle life, as shown by red symbols in Figure 2. For
 16 comparison, the results for Si electrodes pre-cycled under a
 17 CC and then subjected to charge–discharge tests in ionic-
 18 (green symbols) or organic- (blue symbols) liquid
 19 electrolytes are also shown. Hereafter, we denote the Si
 20 electrode coated with a surface film in CCCV mode in an IL
 21 electrolyte as the “Si electrode with CCCV in IL” and the Si
 22 electrodes pre-cycled in CC mode in ionic- or organic-liquid

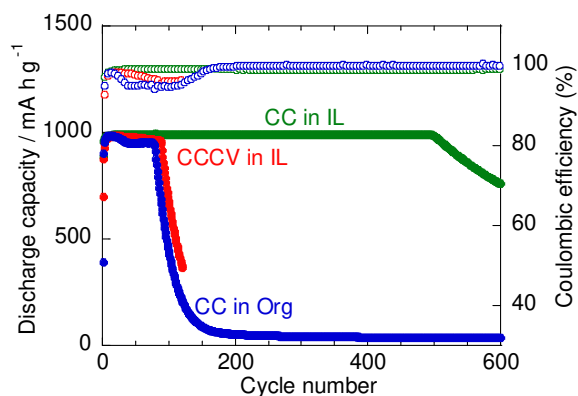


Figure 2. Cycle life of Si electrodes with CCCV, CC in Org, and CC in IL at 0.4C with a constant charge capacity of 1000 mA h g⁻¹. The charge–discharge testing was performed in (CCCV in IL and CC in Org) 1 M LiTFSA/PC and (CC in IL) 1 M LiFSA/Py13-FSA.

23 electrolytes as the “Si electrode with CC in IL” or “Si
 24 electrode with CC in Org,” respectively. The capacity
 25 fading of the Si electrodes, as shown in Figure 2, could be
 26 caused by exfoliation of Si active material from Cu current
 27 collector and/or an increase in internal resistance resulting
 28 from surface film growth during repeated charge–discharge
 29 cycling.

30 We expected the cycle life of the Si electrode with
 31 CCCV in IL to be comparable to that of Si electrodes with
 32 CC in IL. However, contrary to our expectations, the Si
 33 electrode with CCCV in IL exhibited approximately the same
 34 cycle life as the Si electrode with CC in Org. The results
 35 indicate that the surface film that formed from the IL
 36 electrolyte on the Si electrode did not function as a stable
 37 surface film in the organic-liquid electrolyte. Given the
 38 possibility that a stable surface film was not formed under
 39 the aforementioned conditions, we varied the conditions by,
 40 for example, increasing the time the cell was maintained
 41 under the applied potential in CV mode or reassembling the
 42 coin cell with or without washing the electrode (Figures S3–
 43 S6). However, their cycle life did not improve compared
 44 with that of the Si electrode with CC in Org.

45 To clarify why the cycle life of the Si electrode with
 46 CCCV in IL was not improved, we characterized the change
 47 in surface geometry of each Si electrode. Figure 3 shows
 48 FE-SEM images of (a) a pristine Si electrode, (b) an Si
 49 electrode with CC in Org, (c) an Si electrode with CC in IL,
 50 and (d) an Si electrode with CCCV in IL. The Si electrodes,
 51 except for the pristine electrode, were observed after 50
 52 cycles in the (b and d) organic-liquid and (c) IL electrolytes.
 53 The surface roughness of each sample is reported in the
 54 lower-left corner of each image in Figure 3. Although the
 55 electrode surface appears to be relatively flat and the
 56 roughness value was the lowest before charge–discharge
 57 testing (Figure 3a), large cracks formed on the Si electrode
 58 with CC in Org and the corresponding roughness increased
 59 approximately fourfold compared with that of the pristine
 60 electrode (Figure 3b). In addition, the geometry of the Si
 61 electrode with CC in IL was approximately the same as that

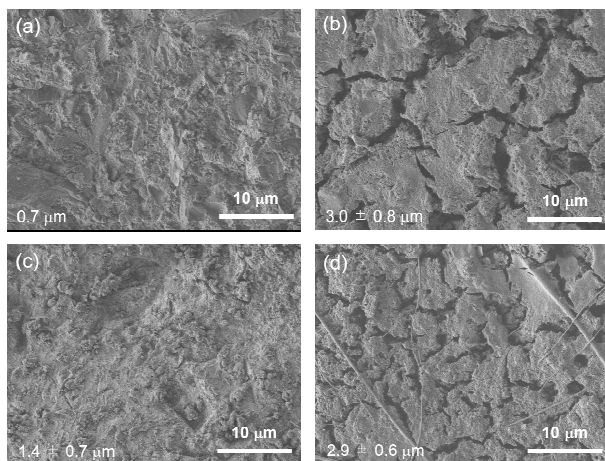


Figure 3. FE-SEM image of (a) a pristine Si electrode, (b) an Si electrode with CC in Org, (c) an Si electrode with CC in IL, and (d) an Si electrode with CCCV in IL. The Si electrodes except for the pristine electrode were observed after 50 cycles in (b and d) 1 M LiTfSA/PC and (c) 1 M LiFSA/Py13-FSA. The surface roughness of each sample is indicated in the lower-left corner of each image.

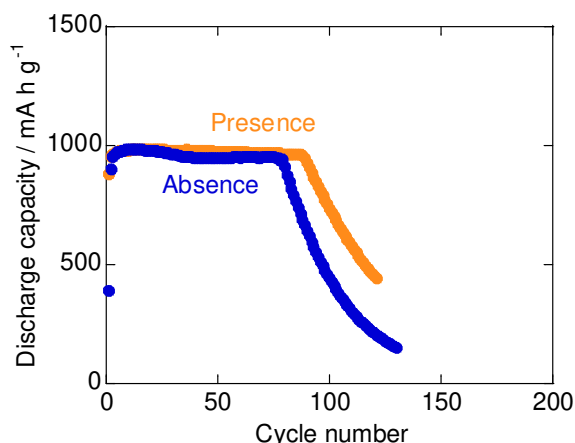


Figure 4. Cycle life of the Si electrode in 1 M LiTfSA/PC in the presence or absence of 1 M LiFSA/Py13-FSA at 0.4C with a charge-capacity limitation of 1000 mA h g⁻¹. The additive amount of IL electrolyte was 20 vol.% with respect to the organic-liquid electrolyte.

12 surface film. Thus, the film reformed on the newly exposed
 13 Si surface. In the IL electrolyte (green symbols in Figure 2
 14 and Figure 3c), the FSA anion undergoes rapid reductive
 15 decomposition,²⁰ leading to re-formation of a homogeneous
 16 and thin surface film after subsequent charge-discharge
 17 cycling. We speculated that the generation of local stress
 18 caused by Si expansion was suppressed; hence, the Si
 19 electrode with CC in IL exhibited a long cycle life in the IL
 20 electrolyte. By contrast, in the organic-liquid electrolyte
 21 (blue and red symbols in Figure 2 and Figure 3b and 3d),
 22 relatively late decomposition of PC occurred,²¹ producing a
 23 thick and inhomogeneous film on the electrode surface. We
 24 have previously reported that PC mainly decomposes on an
 25 Si electrode rather than TfSA anions.¹⁹ Preferential
 26 lithiation of the Si electrode occurred at thinner spots of the
 27 film because of the greater resistance of thicker regions.
 28 Consequently, strain accumulated in the local area, which
 29 caused rapid capacity decay.^{10,19}

30 After the surface film that formed from the IL
 31 electrolyte on the Si electrode with CCCV in IL was broken
 32 down, a stable surface film could not be formed again in the
 33 organic-liquid electrolyte. The Si electrode with CCCV in
 34 IL therefore exhibited poor cycle life. We subsequently used
 35 the IL electrolyte as a film-forming additive. Figure 4 shows
 36 the cycle life of the Si electrode in 1 M LiTfSA/PC with or
 37 without 1 M LiFSA/Py13-FSA. The amount of IL
 38 electrolyte added was 20 vol.% with respect to the organic-
 39 liquid electrolyte. The cycle life of the Si electrode was
 40 approximately the same in both electrolytes.

41 We considered that a stable surface film was not
 42 formed in a mixed electrolyte with a low ratio of IL, i.e., 1
 43 M LiTfSA/PC with 1 M LiFSA/Py13-FSA (20 vol.%),
 44 because the solvated Li⁺ (Li⁺-PC) was more likely to
 45 approach the negatively charged Si electrode than the FSA
 46 anions. By contrast, we have reported that the cycle life of
 47 an Si electrode in 1 M LiFSA/1-ethyl-3-methylimidazolium
 48 (EMD)-FSA with 20 vol.% VC and a Li_{1.00}Si electrode in 1
 49 M LiFSA/Py13-FSA with 2 vol.% VC was improved
 50 compared with that in electrolytes without VC.^{13,22} The
 51 enhanced performance was confirmed in the mixed
 52 electrolyte with a high ratio of IL and few organic
 53 molecules (VC), which we attributed to the formation of
 54 VC- and/or FSA-derived surface films. Therefore, we
 55 concluded that the LiFSA/Py13-FSA IL electrolyte cannot
 56 be used as a film-forming additive.

57 In summary, we investigated the cycle life of an Si
 58 electrode pre-coated with a surface film derived from FSA
 59 anion in 1 M LiTfSA/PC and another Si electrode in 1 M
 60 LiTfSA with 1 M LiFSA/Py13-FSA (20 vol.%) to lower the
 61 cost of cells produced using an IL electrolyte. Unfortunately,
 62 we confirmed no improvement in the electrode performance.
 63 SEM images revealed that large cracks formed on the
 64 modified electrode after cycling and that a stable surface
 65 film could not be reformed in the organic-liquid electrolyte.
 66 Hence, we concluded LiFSA/Py13-FSA did not function as
 67 a film-forming additive and is preferably used as a pure
 68 electrolyte.
 69

1 of the pristine electrode even though the roughness
 2 increased slightly (Figure 3c). By contrast, we observed
 3 numerous cracks on the surface of the Si electrode with
 4 CCCV in IL, and the corresponding roughness was fourfold
 5 higher than that before charge-discharge cycling (Figure 3d).
 6 Although the CE of the Si electrode with CCCV in IL
 7 and that of the electrode with CC in Org began to decrease
 8 at approximately the 30th cycle (Figure 2), the Si electrode
 9 with CC in IL did not exhibit a decrease in CE. The large
 10 volume change in Si during charge and discharge caused
 11 cracking and/or pulverization of Si as well as collapse of the

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5 http://dx.doi.org/10.1246/cl.*****.

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Textual Information	
A brief abstract (required)	To reduce the use of ionic-liquid electrolytes (IL) in batteries, we investigated the lithiation/delithiation properties of Si-based electrodes in an organic-liquid electrolyte (Org), where the electrode surface was preliminarily coated with an IL-derived film. The electrode cycle life was not improved compared with that of a nonmodified electrode because a stable surface film could not be reformed in the Org.
Title(required)	Lithiation and Delithiation Properties of Si-based Electrodes Pre-coated with a Surface Film Derived from an Ionic-liquid Electrolyte
Authors' Names(required)	Yasuhiro Domi, Hiroyuki Usui, Yoshiko Shindo, Akihiro Ando, Hiroki Sakaguchi
Graphical Information	