Effects of HF on the Lithiation Behavior of the Silicon Anode in LiPF$_6$ Organic Electrolyte Solution

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ABSTRACT: As one of the major impurities in the organic electrolyte, HF can react with the alkali components in the solid electrolyte interphase (SEI), such as lithium alkoxide and lithium carbonate, to form more LiF-rich SEI. Here, the effects of HF on the lithiation behavior of the single crystal Si(111) anode were studied using scanning electron microscopy, soft X-ray emission spectroscopy, and windowless energy-dispersive X-ray spectroscopy. When the Li–Si alloy is formed in 1.0 M LiPF$_6$ in the propylene carbonate solvent, it has a layered structure that contains the first layer of crystalline Li$_{15}$Si$_4$ (c-Li$_{15}$Si$_4$) alloy pyramids, the second layer of amorphous Li$_{13}$Si$_4$ (a-Li$_{13}$Si$_4$) alloy, and a third layer of Li-diffused Li$_x$Si alloy. When the more concentrated HF is in the electrolyte solution, less amount of the c-Li$_{15}$Si$_4$ alloy is formed in the first layer. It suggests that the Si lithiation can form only amorphous Li$_x$Si alloy relative to the components in the electrolytes. The study also explains why only amorphous Li$_x$Si alloy formation was observed in some previous studies.

1. INTRODUCTION

Si is one of the most promising candidates among all the anode materials investigated for Li-based secondary batteries because of its high theoretical capacity of 3600 mAh g$^{-1}$ when a fully alloyed Li$_x$Si$_4$ phase forms at room temperature. However, a large volume expansion of close to 400% prevents the application of Si anodes in Li-based secondary batteries. The solid electrolyte interphase (SEI) between the Si anode and electrolyte can be destroyed because of the expansion and shrinkage of the Si anode during a cycle. The physical and chemical stability of the SEI can affect battery performance in terms of the cycle life and capacity. An unstable SEI is detrimental to the cycle life of secondary batteries because the electrolyte is consumed because of the reaction with the Si anode. Several strategies, such as the use of Si nanoparticles or nanowires, have proven to be effective to reduce the volume expansion to reduce damage to the SEI. In addition, the use of electrolyte additives is also an effective strategy to form a stable SEI to retard the electrolyte decomposition.

In general, there are some impurities such as H$_2$O or HF that cannot be eliminated completely in the organic electrolyte. LiPF$_6$ is commonly used in carbonate-based electrolytes because of its high solubility in the organic solvent. LiPF$_6$ is thermally unstable when there is trace H$_2$O and easily decomposes to generate POF$_3$ and another impurity HF, which will further etch SiO$_x$ in the Si anode. As an impurity, HF has some beneficial effects on SEI stability in the Li-based secondary batteries. It can react with the alkali components in the SEI, such as lithium alkoxide and lithium carbonate, to form a more LiF-rich SEI which can protect the Si anode. However, little effort has been devoted to study the effect of HF on the lithiation behavior of Si anodes, especially on the structures and compositions of Li–Si alloys. Our previous studies had verified the availability of using soft X-ray emission spectroscopy (SXES) and windowless energy-dispersive X-ray spectroscopy (EDS) to determine the structures and compositions of electrochemically formed Li–Si alloys. It is revealed that the Li–Si alloy has a layered structure and composition, which contains c-Li$_{15}$Si$_4$, a-Li$_{13}$Si$_4$, and Li-diffused Li$_x$Si (LPS). The determined composition consists of three different alloys and differs from other studies that only reported the c-Li$_{15}$Si$_4$ alloy or only reported the amorphous Li$_x$Si alloy formation. In this work, we move forward to study how HF, one of the major impurities in the electrolyte, affects the structures and compositions of the Li–Si alloy by using these techniques.

2. RESULTS AND DISCUSSION

Figure 1a,b shows scanning electron microscopy (SEM) images of the surface and the cross section of Li–Si alloys formed in the 1.0 M LiPF$_6$/PC electrolyte. Figure 1a shows that a large number of pyramid structures (inset figure in Figure 1a) covered the Si surface. Figure 1b shows the layered structure of the Li–Si alloy. The first layer consists of triangular pyramid structures with a height of approximately 0.7 μm. Underneath the first layer, there are the second and...
third layers distinguished by the SEM image contrast, respectively.

The compositions of the Li–Si alloys were determined using SXES. Figure 1c shows SXE spectra for the first, second, and third layers, in addition to those for Li metal and c-Si as references in the photon energy region of 50–105 eV, which covers Li Kα and Si L2,3 X-ray emissions. Combined with density of states calculations, the peak energy of 53.3 eV in Li Kα and 91.8 eV in Si L2,3 has been indicated to be relative to the c-Li15Si4 alloy, and a peak energy of 53.6 eV in Li Kα and 91.6 eV in Si L2,3 is relative to the a-Li13Si4 alloy. The peak energies were used to determine the compositions of the Li–Si alloys. The Li Kα and Si L2,3 emission peak energies of the first layer in the Li–Si alloys formed in propylene carbonate (PC) were 53.3 and 91.8 eV, respectively, which determined that the first layer was the c-Li15Si4 alloy. The Li Kα and Si L2,3 emission peak energies of the second layer in the Li–Si alloys formed in PC were 53.6 and 91.6 eV, respectively, which determined that the second layer was the a-Li13Si4 alloy. There was little Li Kα emission intensity for the third layers because the Li concentration in the third layer was very low. Therefore, the determined composition of the Li–Si alloy formed in PC were consistent with that reported by Aoki et al., which determined that the first layer was a c-Li15Si4 alloy and the second layer was a-Li13Si4 alloy, although they used a different solvent [v(ethylene carbonate, EC)/v(dimethyl carbonate, DMC) = 1:1]. The composition of the third layer was difficult to determine from the SXE spectra. It was previously determined to be a Li-diused LixSi alloy layer using windowless EDS, although the solvent is DMC in that work.

As mentioned above, HF and water are two of the major impurities that cannot be eliminated completely in the LiPF6-containing organic electrolyte. The HF concentration in the 1.0 M LiPF6/PC electrolyte was determined to be less than 0.05 mM using IC. The water content in the electrolytes were determined to be approximately 0.2 mM. In the following section, HF aqueous solution was added in the electrolyte of 1.0 M LiPF6/PC to study the effects of HF on the lithiation behavior of the Si anode. Figure 2a−d shows SEM images of the surface of Li–Si alloys formed in different electrolytes with more concentrated HF. The HF concentration are shown.
along with the water concentration. As is observed, the pyramid structures are present in all of the Li−Si alloys, and their size is dependent on the added amount of HF aqueous solution in the electrolytes. Because 46% HF aqueous solution was used, water was also added when we tried to increase the HF concentration. To make sure water had no effect on the pyramid formation, only ultrapure water was added into the electrolyte and the Li−Si alloy formed therein is shown in Figure 2e. Here, the water concentration of 2.2 mM for Figure 2e is the same as that for Figure 2d, but the HF concentration is only 0.05 mM. Comparing Figure 2a,e, it was found that only 2 mM water addition has negligible effect on the structure of the Li−Si alloy and does not change the pyramid size. The sizes of the pyramid structures that are dependent on the HF concentrations in the electrolytes are shown in Figure 2f. When the more concentrated HF is in the electrolyte solution, the pyramid size of the Li−Si alloys decreased. The effect of HF concentration on the lithiation behavior of Si is also reflected in the current−time profiles, as shown in Figure 2g. It is observed that all the samples have a maximum lithiation current. The maximum lithiation current is corresponding to the time when the pyramids grow to overlap each other. The maximum lithiation current and its corresponding time decreased when the HF concentration increased as indicated by the arrow. Because when the HF concentration increased, more pyramids (the number of pyramids increases in the same area as shown in Figure 2) are formed to overlap each other earlier. Therefore, an earlier overlap of the pyramids leads to the decrease of the pyramid size when the HF concentration increases.

The effects of HF can be better determined by observation of its effects on the layered structures of the Li−Si alloys. Figure 3a−d shows SEM images of the cross section of the Li−Si alloys. Layered structures were observed for all of the Li−Si alloys. The Li−Si alloy formed in the 1.0 M LiPF 6/PC electrolyte without aqueous HF addition was determined to consist of the first layer of crystalline Li 15Si 4, the second amorphous Li 13Si 4 layer, and a third Li-di ffused Li xSi layer. The layer thicknesses of the first and second layers in different Li−Si alloys were dependent on the electrolytes with increased HF concentrations.

The effects of HF on the compositions of the Li−Si alloys were determined using SXES. Figure 3e,f shows SXE spectra for the first layers in the Li−Si alloys formed in the electrolytes with increased HF concentrations. When the more concentrated HF is in the electrolyte solution, the Li K α emission peak of the Li−Si alloys changed from 53.3 to 53.6 eV (Figure 3e). The peaks at 53.3 and 53.6 eV were the peak energies of the Li K α emission spectra for c-Li 15Si 4 and a-Li 13Si 4, respectively, according to previous analyses. The change in the peak energy from 53.3 to 53.6 eV indicated that the amount of c-Li 15Si 4 in the first layer was decreased, and instead, the amount of a-Li 13Si 4 increased. The Si L2,3 emission peak of the Li−Si alloys changed from 91.8 to 91.6 eV (Figure 3f). The peak energies of the Si L2,3 emission spectra of c-Li 15Si 4 and a-Li 13Si 4 were 91.8 and 91.6 eV, respectively; therefore, the peak shift from 91.8 to 91.6 eV indicated that the first layer preferred to form a-Li 13Si 4 instead of c-Li 15Si 4. This result is consistent with that from the observed shift of the Li K α emission peak, that is, the amount of c-Li 15Si 4 in the first layer decreased when the...
HF concentration in the electrolyte increased. The compositions of the Li–Si alloys were thus altered by HF addition. Figure 3g,h shows SXE spectra for the second layers in the Li–Si alloys. Although the electrolytes had more concentrated HF, the Li Kα and Si L2,3 emission peaks of the Li–Si alloys had the same energy positions of 53.6 and 91.6 eV, respectively. Both the peak positions correspond to the Li Kα and Si L2,3 emission peaks of a-Li13Si4. The results indicated that the composition in the second layer of all four different Li–Si alloys was a-Li13Si4 and was independent of the HF concentration.

Windowless EDS can be applied to determine the Li distribution and the layer thickness in Li–Si alloys. For the Li–Si alloy formed in the 1.0 M LiPF6/PC electrolyte, the Li distribution profile had been determined by windowless EDS and was consistent with the layered structure determined by SXES.21 The SXE spectral analysis suggested that the compositions of the Li–Si alloys were different when they were electrochemically formed in different HF concentrations. As shown in Figure 4a, the Si L2,3 emission profiles show a distinguishable intensity change along the layered structure. Although there is some contrast difference with the third layer, we determine it as a layer because it has almost no Li Kα emission intensity and its exact composition cannot be accurately determined. Windowless EDS was used here to further reveal the extent of the different compositions, that is, c-Li15Si4, a-Li13Si4, and Li-diffused LiSi alloy. Figure 4b,c shows the changes in the intensities of the Li Kα and Si Kα emissions along the line scan from the pyramid top (the first layer) to the Si substrate for the Li–Si alloys, respectively. The changes in the Li Kα intensities were similar for all four Li–Si alloys in Figure 4b. The Li Kα intensity decreased from the first layer to the Si substrate, which is consistent with the Li–Si alloy-layered structure that consists of the first c-Li15Si4 layer, the second a-Li13Si4 layer, and a third lowly lithiated LiSi layer over the Si substrate. The boundaries between the first and second layers and between the second and third layers can be determined by monitoring the change in the intensity of the Si Kα peak. However, changes in the intensities of the Li Kα and Si Kα peaks could not be used to determine the thickness of each layer in the Li–Si alloys because the boundaries between the third layer and Si substrate were unclear.

As reported previously, the thickness of each layer can be precisely determined by monitoring the change in the Si L2,3 intensity.21 Figure 4d shows the Si L2,3 intensity changes for the four Li–Si alloys. The boundaries between the first, second, and third layers, and the Si substrate can be easily determined by monitoring the change in intensity, as shown by the arrows. The thickness of each layer for all the four Li–Si alloys can then be easily determined, and the results are shown in Figure 4e. When the electrolytes had more concentrated HF from 0 to 2 mM, the first layer’s thickness (the c-Li15Si4 pyramid height) in the Li–Si alloy decreased from approximately 0.7 to 0.1 μm, and the second layer’s thickness increased from approximately 1.0 to 1.3 μm. The Li distribution in the Li–Si alloys was thus changed when the more concentrated HF is in the electrolyte solution. The thicknesses of the third layers were almost the same for all the four Li–Si alloys.

Figure 4. (a) Si L2,3 emission profiles in windowless EDS along the cross section of the Li–Si alloy that was formed in the 1.0 M LiPF6/PC electrolyte with 0.05 mM HF. SEM image is part of Figure 3a that is also used for SXE measurement. Windowless EDS (b) Li Kα, (c) Si Kα, and (d) Si L2,3 emission profiles along the cross section from the pyramid top to the Si substrate for the four Li–Si alloys. The HF concentrations in the electrolytes are shown. The boundary between the first, second, and third layers, and the Si substrate can be determined by monitoring the intensity change. In (d), the cyan arrows represent the boundary between the first and second layers, the dark yellow arrows represent the boundary between the second and third layers, and the dark green arrows represent the boundary between the third and fourth layer. (e) Layer thicknesses of the first, second, and third layers for the four Li–Si alloys determined from (d).
Figure 5. (a) XPS F 1s spectra for Si(111) after contact with electrolytes that had increased HF concentrations. Peaks at 688.5 eV are representative of F–Si species, while those at 686.5 eV are representative of LiF species. (b) XPS peak area at 688.5 eV for F–Si on Si(111) after contact with electrolytes that had more concentrated HF. The peak area is normalized to Si 2p intensity.

The thickness \( t \) can be used to estimate the amount of c-Li15Si4, a-Li13Si4, and Li-diffused Li-Si alloy in the Li–Si alloys according to the equation of \( Q = x F V \rho/\left(M A\right) \), where \( Q \), \( x \), \( V \), \( \rho \), and \( M \) are the charge density and the electrode area; \( x \), \( V \), \( \rho \), and \( M \) are the number of Li atoms, the volume, the mass density, and the molar mass of Li-Si alloys, respectively. For c-Li15Si4, the volume \( V \) is equal to \( \frac{2}{3}At \) because it is a pyramid. For a-Li13Si4, the volume \( V \) is \( At \). The lithiation charge density was 1000 mC·cm\(^{-2} \) for each Li–Si alloy. The lithiation charge was due to Li\(^+\) ion reduction to alloy Li; therefore, the amount of Li in c-Li15Si4 and a-Li13Si4 can be evaluated based on their layer thicknesses to reveal how much charge was used to form c-Li15Si4 and a-Li13Si4. The Li–Si alloy formed in the 1.0 M LiPF\(_6\)/PC electrolyte without HF addition had approximately 0.7 \( \mu \)m thick c-Li15Si4 (pyramid) and 1.0 \( \mu \)m thick a-Li13Si4 layers. Therefore, the charges used to form c-Li15Si4 and a-Li13Si4 were approximately 180 and 760 mC·cm\(^{-2} \), respectively, in 1000 mC·cm\(^{-2} \) charge, that is, ca. 18 and 76% of the charge were used to form c-Li15Si4 and a-Li13Si4, respectively. The remaining 6% charge was used for the formation of the third layer and electrolyte decomposition. As a comparison, the Li–Si alloy formed in 1.0 M LiPF\(_6\)/PC with 2 mM HF addition had approximately 0.1 \( \mu \)m thick c-Li15Si4 and 1.3 \( \mu \)m thick a-Li13Si4 layers. The charges used to form c-Li15Si4 and a-Li13Si4 were approximately 30 and 900 mC·cm\(^{-2} \), respectively, that is, ca. 3 and 90% charges were used to form c-Li15Si4 and a-Li13Si4, respectively. The amount of c-Li15Si4 in the Li–Si alloys decreased from 18 to 3% and the amount of a-Li13Si4 in the Li–Si alloys increased from 76 to 90% when the electrolyte used had 2 mM HF addition, as shown in Figure 4e. Formation of the c-Li15Si4 alloy was generally considered to be detrimental to battery performance;\(^{26,27}\) therefore, less formation of c-Li15Si4 in the Li–Si alloy by HF will be expected to be good for battery performance, although HF is generally considered to be harmful in battery and needs to be eliminated. However, a low but suitable amount of HF may be used for the Si-based secondary battery.

It is now known that HF can reduce the size of the c-Li15Si4 pyramid structures, that is, increase the number density of the pyramid nuclei. The number density of the pyramid nuclei can be affected by surface electrochemical conditions, such as the surface electrochemical potential or surface ion concentration. Here, HF addition may change the surface electrochemical conditions, which then changes the number density of the pyramid nuclei. It has been reported that HF can be adsorbed on a Si surface to form F–Si bonds.\(^{28–30}\) The adsorption of F species on Si(111) was confirmed by X-ray photoelectron spectroscopy (XPS) measurements, as shown in Figure 5a. The photoelectron emission intensities from F 1s increased when the more concentrated HF is in the electrolyte solution, which indicated that the amount of F on the Si(111) surface increased. The increase in the amount of the F element was due to both enhanced LiF (686.5 eV) deposition through Li\(^+\) and F\(^-\) ions, and to F atom adsorption on the Si(111) surface to generate F–Si bonds (688.5 eV) as shown in Figure 5b. An intensity reverse of LiF and F–Si in the 0.5 mM HF sample might be due to the difference in the formation of the two species. LiF forms in the solution and deposits onto the Si surface within an uncontrolled amount, but F–Si forms on the Si surface and its amount is expected to be relative to HF concentration. Therefore, there is a possibility that LiF deposit more under uncontrolled amount and the intensity reverse appear. The adsorption of the F atom on H-terminated Si(111) can be through the reaction of HF (aq) + SiH (a) = SiF (a) + H\(_2\) (g) or HF (aq) + Si–Si (a) = SiF (a) + SiH (a) in which HF attacks the Si–Si bond as shown in Figure 6. These reactions suggest adsorption of the F atom to replace H and a strong SiF chemical bond formation on Si(111).

Fluorine adsorption can increase the formation of the Li–Si alloy nuclei because it increases the concentration of surface Li\(^+\) ions, which is a function of surface potential according to the equation.\(^{31}\)

Figure 6. Schematic to illustrate that the Li–Si alloys have smaller pyramid structures (lesser amount of c-Li15Si4) when the electrolyte is 1.0 M LiPF\(_6\)/PC with more concentrated HF.
\[ C_s = C_0 \exp(-\frac{FO}{RT}) \]

where \( C_s \) is the concentration of surface Li\(^+\) ions, \( C_0 \) is the bulk Li\(^+\) ion concentration, \( O \) is the surface potential, and \( F \), \( R \), and \( T \) are the Faraday constant, gas constant, and room temperature, respectively. The surface potential \( O \) becomes more negative by \( F \) adsorption, as schematically shown in Figure 6; therefore, the concentration of surface Li\(^+\) ions increases. As a result, the number density of the Li–Si alloy nuclei on the Si surface increases, which results in the formation of smaller pyramid structures. This explains why the Li–Si alloys have smaller pyramid structures (lesser amount of c-Li\(_{15}\)Si\(_4\)) when the electrolyte is 1.0 M LiPF\(_6\)/PC with a higher HF concentration. In addition to \( F \) adsorption to increase the nuclei number density, the deposition of LiF on the Si surface might play a role that retards the growth of the c-Li\(_{15}\)Si\(_4\) pyramid, although some further verification will be conducted.

3. CONCLUSIONS

The Li–Si alloy prefers to form the a-Li\(_{15}\)Si\(_4\) alloy instead of c-Li\(_{15}\)Si\(_4\) when the more concentrated HF is in the electrolyte solution. Through using a suitable electrolyte such as using the fluoroethylene carbonate as the co-solvent which can decompose to generate HF, the Si lithiation can form only amorphous Li\(_x\)Si alloy. The study explains why only amorphous Li\(_x\)Si alloy formation was observed in some previous studies. On the other hand, less c-Li\(_{15}\)Si\(_4\) formation in Li–Si alloys by HF is possible for better battery performance because the crystalline alloy phase is generally considered to be detrimental to battery performance.

4. EXPERIMENTAL SECTION

4.1. Materials. H\(_2\)SO\(_4\) (96–98%), H\(_2\)O\(_2\) (30–35%), HCl (35%), and HF (46%) aqueous solutions and anhydrous PC solvent (>98%, battery grade) were purchased from Wako Pure Chemicals. The PC solvent was dried at least 3 days by a molecular sieve which was pre-dried in a vacuum at 200 °C for 12 h. Every time before the PC solvent was used to prepare the fresh electrolyte, PC will be filtered using a 100 nm nylon filter. NH\(_4\)F aqueous solution (40%) (semiconductor grade) was purchased from Morita Chemical Industry. LiPF\(_6\) salt (99.9%) and Li wire (99%) were purchased from Kishida Chemical. LiPF\(_6\) was dried under a vacuum at room temperature for 6 h at first and then increase the temperature to 105 °C and kept for 6 h. The water vapor was trapped by a cold trap using liquid nitrogen. Si(111) single-crystal wafers (thickness: 500 μm, resistivity: 1–10 Ω·cm\(^{-1}\), n-type: phosphorous-doped) were purchased from a Shin-Etsu Semiconductor. Ultrapure water from a Milli-Q purification system and 99.999% Ar gas were used throughout the experiments.

4.2. Electrochemically Formed Li–Si Alloys under Potentiostatic Lithiation. The Si(111) wafer was cut into 1.0 × 1.0 cm\(^2\) pieces. Hydrogen-terminated Si(111) was prepared through chemical etching, as reported previously.\(^{32}\) Li wire was used as reference and counter electrodes. The electrolyte used was 1.0 M LiPF\(_6\) dissolved in the PC solvent. To study the effect of HF, electrolytes of 1.0 M LiPF\(_6\) in PC were prepared with the addition of 0, 0.5, 1.0, and 2.0 mM HF aqueous solution. For example, for the addition of 1 mM HF aqueous solution, 1.5 μL of 46% HF aqueous solution was added to 40 mL of 1.0 M LiPF\(_6\) in PC. Because HF aqueous solution was used, water was also added simultaneously. For example, 2.2 mM H\(_2\)O was included when 2 mM HF aqueous solution was added. Here, the effect of H\(_2\)O on the structures and compositions of the Li–Si alloy was examined separately by the addition of 2.2 mM pure H\(_2\)O to the 1.0 M LiPF\(_6\)/PC electrolyte. Li–Si alloys were formed under potentiostatic lithiation at 10 mV versus Li/Li\(^+\) in these electrolytes to determine the effects of HF. For each Li–Si alloy, the lithiation charge density was 1000 mC·cm\(^{-2}\). After electrochemical formation, the Li–Si alloys were washed with the DMC solvent and broken in half along the Si (110) direction with a diamond pen to expose the cross section. The samples were then transferred using a Ar-filled transfer vessel without air exposure for SXES and windowless EDS measurements.

4.3. SXES and Windowless EDS Measurements. SXES and windowless EDS measurements were conducted using a SXES system (JEOL, SS-9400SXES) and a windowless silicon drift detector (SDD) system (Oxford Instruments, X-Max Extreme), respectively. Both systems are installed in a scanning electron microscope (JEOL, JSM-7800F) under an ambient pressure of less than 10\(^{-4}\) Pa and using an accelerating voltage of 5.0 kV.

The incident electron spot size for SXES was approximately 1.0 μm and a varied line-space grating (JEOL, JSS0XL) was applied with a resolution of approximately 0.15 eV. The probe current and acquisition time were 50 nA and 200 s, respectively. The EDS line scan method was applied by performing point detection at intervals of 100 nm along the Li–Si alloy layer. Each point accumulation time was set to 15 s because the accumulated intensity with this time was appropriate for deconvolution analysis, and the specimen was not destroyed by the electron beam within 15 s.

4.4. HF Concentration Measurements. The HF concentration in the electrolytes was measured using an ion chromatography (IC) system ( Dionex, ICS-2100). The electrolytes were diluted 100 times for the purpose of accurate determination.

4.5. X-ray Photoelectron Spectroscopy. The surface species on the Si(111) wafers were investigated using a 1 × 10\(^{-9}\) Torr base pressure XPS spectrometer (ULVAC-PHI, VersaProbe II) equipped with an Al K\(_\alpha\) source operated at 150 W. High-resolution scans were observed in constant energy mode with a pass energy of 46.95 eV. The size of the analysis area on all specimens was set at 220 μm × 220 μm. The Si wafer specimens for XPS measurements were prepared by immersion in the electrolytes with increased HF concentration and then washing with DMC to remove the electrolyte.

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Notes

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REFERENCES

(1) Kasavajula, U.; Wang, C.; Appleby, A. J. Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells. J. Power Sources 2007, 163, 1003–1039.
(2) Su, X.; Wu, Q. L.; Li, J. C.; Xiao, X. C.; Lott, A.; Lu, W. Q.; Sheldon, B. W.; Wu, J. Silicon-Based Nanomaterials for Lithium-Ion Batteries: A Review. Adv. Energy Mater. 2014, 4, 1300882.
(3) Chan, C. K.; Peng, H.; Liu, G.; McWhorter, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y. High-performance lithium battery anodes using silicon nanowires. Nat. Nanotechnol. 2008, 3, 31–35.
(4) Lee, Y. M.; Lee, J. Y.; Shim, H.-T.; Lee, J. K.; Park, J.-K. SEI layer formation on amorphous Si thin electrode during precycling. J. Electrochem. Soc. 2007, 154, A515–A519.
(5) Ogata, K.; Salager, E.; Kerr, C. J.; Fraser, A. E.; Ducati, C.; Morris, A. J.; Hofmann, S.; Grey, C. P. Revealing lithium–silicide phase transformations in nano-structured silicon-based lithium ion batteries via in situ NMR spectroscopy. Nat. Commun. 2014, 5, 3217.
(6) Gregorczyk, K. E.; Liu, Y.; Sullivan, J. P.; Rubloff, G. W. In Situ Transmission Electron Microscopy Study of Electrochemical Lithiation and Delithiation Cycling of the Conversion Anode RuO2. ACS Nano 2013, 7, 6354–6360.
(7) Pharr, M.; Zhao, K.; Wang, X.; Xue, Z.; Vlassak, J. J. Kinetics of Initial Lithiation of Crystalline Silicon Electrodes of Lithium-Ion Batteries. Nano Lett. 2012, 12, 5039–5047.
(8) McDowell, M. T.; Ryu, I.; Lee, S. W.; Wang, C.; Nix, W. D.; Cui, Y. Studying the Kinetics of Crystalline Silicon Nanoparticle Lithiation with In Situ Transmission Electron Microscopy. Adv. Mater. 2012, 24, 6034–6041.
(9) Szczep, J. R.; Jin, S. Nanostructured silicon for high capacity lithium battery anodes. Energy Environ. Sci. 2011, 4, 56–72.
(10) Liu, X. H.; Zhong, L.; Huang, S.; Mao, S. X.; Zhu, T.; Huang, J. Y. Size-Dependent Fracture of Silicon Nanoparticles During Lithiation. ACS Nano 2012, 6, 1522–1531.
(11) Teki, R.; Datta, M. K.; Krishnan, R.; Parker, T. C.; Lu, T.-M.; Kumta, P. N.; Koratkar, N. Nanostructured Silicon Anodes for Lithium-Ion Rechargeable Batteries. Small 2009, 5, 2236–2242.
(12) Lin, Y.-M.; Klavetter, K. C.; Abel, P. R.; Davy, N. C.; Snider, J. L.; Heller, A.; Mullins, C. B. High performance silicon nanoparticle anode in fluoroethylene carbonate–based electrolyte for Li-ion batteries. Chem. Commun. 2012, 48, 7268–7270.
(13) Etacheri, V.; Haik, O.; Goffer, Y.; Roberts, G. A.; Stefan, I. C.; Fasching, R.; Aurbach, D. Effect of Fluoroethylene Carbonate (FEC) on the Performance and Surface Chemistry of Si-Nanowire Li-Ion Battery Anodes. Langmuir 2012, 28, 965–976.
(14) Yang, H.; Zhuang, G. V.; Ross, P. N. Thermal stability of LiPF6 salt and Li-ion battery electrolytes containing LiPF6. J. Power Sources 2006, 161, 573–579.
(15) Lux, S. F.; Lucas, I. T.; Pollak, E.; Passerini, S.; Winter, M.; Kosteczki, R. The mechanism of HF formation in LiPF6 based organic carbonate electrolytes. Electrochem. Commun. 2012, 14, 47–50.
(16) Zhang, S. S. A review on electrolyte additives for lithium-ion batteries. J. Power Sources 2006, 162, 1379–1394.
(17) Kanamura, K.; Shiraishi, S.; Takehara, Z. Electrochemical deposition of very smooth lithium using nonaqueous electrolytes containing HF. J. Electrochem. Soc. 1994, 141, L108–L110.
(18) Kanamura, K.; Shiraishi, S.; Takehara, Z. i. Electrochemical Deposition of Uniform Lithium on an Ni Substrate in a Nonaqueous Electrolyte. J. Electrochem. Soc. 1994, 141, L108–L110.
(19) Tomita, K.; Noguchi, H.; Uosaki, K. Effect of Water and HF on the Distribution of Discharge Products at Li-O2 Battery Cathode. ACS Appl. Energy Mater. 2018, 1, 3434–3442.
(20) Aoki, N.; Omachi, A.; Uosaki, K.; Kondo, T. Structural Study of Electrochemically Lithiated Si(111) by using Soft X-ray Emission Spectroscopy Combined with Scanning Electron Microscopy and through X-ray Diffraction Measurements. ChemElectroChem 2016, 3, 959–965.
(21) Lin, H.; Noguchi, H.; Uosaki, K. Application of windowless energy dispersive spectroscopy to determine Li distribution in Li-Si alloys. Appl. Phys. Lett. 2018, 112, 073903.
(22) Obrovac, M. N.; Christensen, L. Structural Changes in Silicon Anodes during Lithium Insertion/Extraction. Electrochem. Solid-State Lett. 2004, 7, A93–A96.
(23) Liu, X. H.; Wang, J. W.; Huang, S.; Fan, F.; Huang, X.; Liu, Y.; Krylyuk, S.; Yoo, J.; Dayeh, S. A.; Davydov, A. V.; Mao, S. X.; Picraux, S. T.; Zhang, S.; Li, J.; Zhu, T.; Huang, J. Y. In situ atomic-scale imaging of electrochemical lithiation in silicon. Nat. Nanotechnol. 2012, 7, 749–756.
(24) Chan, C. K.; Rufio, R.; Hong, S. S.; Huggins, R. A.; Cui, Y. Structural and electrochemical study of the reaction of lithium with silicon nanowires. J. Power Sources 2009, 189, 34–39.
(25) Lyalin, A.; Kuznetsov, V. G.; Nakayama, A.; Abarenkov, I. V.; Tuptyn, I. I.; Gabis, I. E.; Uosaki, K.; Taketsumu, T. Lithiation Products of a Silicon Anode Based on Soft X-ray Emission Spectroscopy: A Theoretical Study. J. Phys. Chem. C 2018, 122, 11096–11108.
(26) Beaulieu, L. Y.; Hatchard, T. D.; Bonakdarpour, A.; Fleischauer, M. D.; Dahn, J. R. Reaction of Li with Alloy Thin Films Studied by In Situ AFM. J. Electrochem. Soc. 2003, 150, A1457–A1464.
(27) Misra, S.; Liu, N.; Nelson, J.; Hong, S. S.; Cui, Y.; Toney, M. F. In Situ X-ray Diffraction Studies of (De)lithiation Mechanism in Silicon Nanowire Anodes. ACS Nano 2012, 6, 5465–5473.
(28) Craig, B. I.; Smith, P. V. The chemisorption of HF and F2 on the Si(100) surface. Surf. Sci. 1990, 239, 36–41.
(29) Michalak, D. J.; Amy, S. R.; Aureau, D.; Dai, M.; Estève, A.; Chabal, Y. J. Nanopatterning Si(111) surfaces as a selective surface-chemistry route. Nat. Mater. 2010, 9, 266–271.
(30) Saito, Y. Adsorption of Anhydrous Hydrogen Fluoride onto Silicon and Native Oxide by XPS. Surface Science Spectra 1999, 6, 228–236.
(31) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley, 2000.
(32) Ye, S.; Ichihara, T.; Uosaki, K. Attenuated total reflection Fourier transform infrared spectroscopy study of the adsorption of organic contaminants on a hydrogen-terminated Si(111) surface in air. Appl. Phys. Lett. 1999, 75, 1562–1564.