Stabilization of Si Negative Electrode by Li Pre-doping Technique and the Application to a New Energy Storage System

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ABSTRACT

To extend the cyclability of a hybrid capacitor using Li pre-doped Si negative electrodes (NEs) (Si-CAP), we applied a polyimide binder and fluoroethylene carbonate (FEC) as additives in the Li pre-doping step. This binder successfully improved the cyclability by fixing Si nanoparticles as the NE active material on the Cu foil current collector to resist the volume change caused by Li–Si alloying. After Li pre-doping, there were no cracks on the Si NE surfaces, which had been observed in previous work using sodium carboxymethyl cellulose binder. Furthermore, FEC addition into the electrolyte at Li pre-doping improved homogeneity of the Li–Si alloying. As a result, a large amount of Li was pre-doped to the Si NE and a lower open-circuit potential was maintained. A Si-CAP cell of [Li alloyed Si | activated carbon] using polyimide binder exhibited relatively stable charge/discharge behavior and cyclability was maintained up to 800 cycles. Stability of the charge/discharge performance of FEC-containing Si-CAP was improved by formation of a LiF-rich solid-state interphase film on the Si NE. X-ray photoelectron spectroscopy revealed suppression of decomposition of the propylene carbonate solvent by electrochemical reduction.

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1. Introduction

In recent years, electrochemical capacitors have received increasing attention, not only for use in portable electronic devices like smart phones, but also as large-scale power sources for electric vehicles. Electric double-layer capacitors (EDLCs) possess advantages of high rate capability and semi-permanent long cycle life, which are attributed to the fast charge/discharge (adsorption/desorption) reaction at activated carbon (AC) electrodes, regardless of the faradaic reaction; however, the charge/discharge mechanism causes low energy density compared with that of other energy-storage devices, such as Li-ion (LIBs) and nickel–hydrogen batteries.^{1–4} To overcome this weak point, many hybrid capacitor systems with asymmetric electrodes have been studied. Li-ion capacitors (LICs) using a Li pre-doped graphite or hard carbon negative electrode (NE) have recently been developed and released as commercial products.⁴ The cell voltage of LIC systems is much higher than that of EDLCs because the LIC contains a Li pre-doped graphite NE with a low redox potential, around 0.02 V,^{5–7} resulting in an energy density ca. three times higher than that of the EDLC (ca. 10–15 Wh kg^{−1}). To apply LICs to large-scale devices, such as electric vehicles and stationary energy-storage facilities, further improvement of the discharge capacity and energy density is needed. Many researchers have intensively studied titanium oxide materials,⁴ such as Li₄Ti₅O₁₂ (LTO),^{8–10} and TiO₂(B);^{11–13} however, these NEs have relatively high redox potentials of around 1.6 V vs. Li/Li⁺ and lower theoretical capacities (175 and 335 mAh g^{−1} for LTO and TiO₂(B), respectively) than that of graphite (372 mAh g^{−1}), so the discharge capacity and energy density of such LIC cells do not increase as expected.

On the other hand, we have been studying the stabilization of Si NE by using Li pre-doping technique and applied the obtained Si NE to various energy storage systems such as LIBs,¹⁴ hybrid capacitor¹⁵ and also next-generation batteries. As an example, we recently developed an LIC system using Li pre-doped Si NEs (Si-CAP)¹⁵ because the Si NE has a large theoretical capacity,

ca. 4200 mAh g^{−1}, compared with that of graphite (372 mAh g^{−1}) and its redox potential is below 0.5 V vs. Li/Li⁺.^{16,17} This approach enables to increase in the specific capacity and energy density of the LIC system by reducing the amount of NE material. In the previous study, we demonstrated that the Si-CAP cell was improved by using additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), and vacuum pressure impregnation (VPI) treatment during the Li pre-doping step.¹⁵ The treatments effectively promoted preferred solid–electrolyte interface (SEI) film formation on the surface of the Si nanoparticles and homogeneous Li pre-doping into its bulk, which suppressed rapidly fading capacity by electrolyte decomposition^{18,19} and a large volume change of Si.^{20–22} In addition to the Li pre-doping technique, the limitation of Si NE capacity by that of the AC positive electrode (PE) in the hybrid capacitor system was also able to extend the cycle life of the Si-CAP; however, the effects on the charge/discharge properties of Si-CAP were only reported for short cycle periods (up to 50 cycles).

In this study, we focused on the application of stabilized Si NEs by the Li pre-doping techniques to LIC system. To further extend of the cycle life of this system, we applied a polyimide binder to the Si NE and investigated the effects of FEC addition in more detail using non-exposure scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analysis. Moreover, to elucidate the effects of the capacity limitation of Si NE by the AC PE and the FEC addition (regardless of the AC PE), a Li pre-doped Si half-cell [Li pre-doped Si | Li metal foil] (capacity limitation: 500 mAh g(Si)^{−1}) was fabricated, and its charge/discharge properties and changes in the Si NE morphology and SEI film composition were evaluated including the viewpoint of modeling half-cell for advanced LIBs and next-generation batteries.

2. Experimental

2.1 Preparation of Si negative electrode and Li pre-doping

Si nanoparticles (NPs) (Alfa Aesar®, average particle size: ≤50 nm) were used as the active material for the Si NE. The Si NPs

were relatively sphere-like and their crystallinity was high, despite their nanoscale particle size.¹⁵ A slurry was prepared by mixing 83.3 mass% Si NPs, 5.6 mass% Ketjen Black (Lion, EC600JD) as a conductive agent, and 11.1 mass% polyimide binder (Nippon Kodoshi, SOXR-0/NMP) with N-methyl-2-pyrrolidone (NMP) as a solvent. The slurry was coated on Cu foil (Hohsen, thickness: 18 μm) as a current collector, dried at 80°C for 1 h, and then cured at 200°C for 5 h. The obtained Si NE was cut into circles ($\phi = 16\text{ mm}$; i.e., NE area was ca. 2 cm^2). The thickness of the Si NE coating was ca. 21 μm , which corresponded to a loading mass of around 0.68 $\text{mg}(\text{Si})\text{cm}^{-2}$ for the Si NP active material. Li pre-doping and cell assembly were performed in Ar-filled glove boxes (Miwa, MDB-1BK-NT1). For the Li pre-doping, the Si NE was immersed in 1.0 M LiBF_4 dissolved in propylene carbonate (PC) (Kishida Chemicals, Battery Grade) under vacuum, i.e., VPI treatment, contacted with Li metal foil (Honjo Metal, thickness: 0.05 mm), and then immersed again in the same fresh electrolyte at room temperature for 3 h. The amount of Li pre-doping to the Si NEs was controlled by the treatment time. The morphology change of the Si NE before and after Li pre-doping was observed by a SEM (JEOL, JSM-6510LA or Philips, XL-30). The chemical composition of SEI films formed on the Si NE was characterized by a XPS (ULVAC-PHI, INC., PHI 5000 VersaProbe). In some experiments, FEC was added to the electrolyte at the Li pre-doping stage.

2.2 Electrochemical measurements

Coin-type cells were constructed using a Li pre-doped Si NE, separator (Nippon Kodoshi, TEF4030), and AC PE (Hohsen, thickness: ca. 100 μm) in the same glove boxes used for the Li pre-doping. The average mass of AC in each PE was 11.44 mg, which was ca. 7.0 times larger than the mass of Si NPs required to adjust the capacity balance between the Si NE and AC PE. The electrolyte for the Si-CAP cells was 1.0 M LiBF_4/PC . Charge/discharge tests were carried out in constant-current mode at a current density of 0.10 mA cm^{-2} between 2.0 and 4.2 V using a battery test system (Hokuto Denko, HJ1001SM8). In addition, Li pre-doped Si half-cells [Li alloyed Si | Li metal foil (Honjo Metal, thickness: 0.5 mm)] without and with 10 mass% FEC were examined to understand the effects of capacity limitation ($500\text{ mAh g}(\text{Si})^{-1}$) by the AC PE and FEC on the cell performance. All charge/discharge tests were performed at 30°C.

3. Results and Discussion

3.1 Morphology change in Si negative electrodes by Li pre-doping

Figure 1 shows SEM images of the Si NEs (a, b) before and after Li pre-doping (c, d) without and (e, f) with FEC. Before Li pre-doping, the Si NE surface was relatively flat and exhibited a dark gray color due to its semi-conductor properties. After Li pre-doping, the surface became rough, both without and with FEC addition, and the color changed to bright gray, indicating an expansion of the Si NPs and improvement in electronic conductivity owing to formation of impurity levels in the electronic orbitals of Si; however, Li–Si alloying was not homogeneous and two separate phases (dark and bright gray parts) formed in the Si NE. In contrast, when 10 mass% FEC was added, the Si NE exhibited a homogeneous surface after Li pre-doping and the entire surface was bright gray. Although no difference could be confirmed in the magnified SEM images, the chemical composition of the SEI film was probably altered by the FEC addition.

3.2 Effects of fluoroethylene carbonate addition on Si-CAP cell performance

Figures 2(a) and (b) present the 2nd and 800th charge/discharge curves of the Si-CAP cell using Li pre-doped Si NEs without and

Figure 1. Scanning electron microscopy images of Si negative electrode surfaces (a, b) before and (c–f) after Li pre-doping (c, d) without and (e, f) with 10 mass% fluoroethylene carbonate additive. (b), (d), and (f) are the magnified images of (a), (c), and (e), respectively.

with FEC, respectively. Both cells enabled charging up to 4.2 V and the discharge curves were convex upward (not linear). Although the specific cell capacity was limited by the AC PE, an increase in the specific capacity was confirmed by FEC addition at the Li pre-doping step. This implies that homogeneous Li pre-doping improved electronic conductivity and reduced the charge-transfer resistance, enabling the operating region to be extended above 2.0 V. In fact, the IR drop from charging to discharging became larger, especially after 800 cycles, and a large difference was confirmed for the Si-CAP cell without the addition of FEC. Utilization of the Si NE was therefore found to increase when using FEC, and the charge/discharge curves also became more stable up to the 800th cycle. Figure 2(c) shows that the Si-CAP cell using Li pre-doped Si NEs with FEC exhibited much more stable cyclability compared with that without FEC addition. As a result, the efficiency of energy density was also relatively high, ca. 90%, even at the 800th cycle.

3.3 Investigation of solid–electrolyte interface films on Li pre-doped Si negative electrode

To elucidate the origin of effects induced by FEC addition, the chemical compositions of SEI films on the Si NEs after Li pre-doping were investigated by XPS analysis. Si 1s peaks derived from pure Si and SiO_2 on the Si NE surface were initially diminished after Li pre-doping (not shown), indicating the formation of an SEI film on the surface. From the F 1s peaks, it was observed that both Si NEs exhibited a large amount of LiF at 685 eV.^{23,24} In the case of FEC addition, the peak for LiF was enhanced and a relatively large peak at $\sim 687\text{ eV}$ due to C–F bonding was confirmed, indicating the presence of $-\text{CHF}-\text{OCO}_2$ -type compounds derived from FEC on the Si NE. In contrast, when FEC was not added, the Si NE exhibited a large number of various types of C 1s peaks derived from decomposition of the PC solvent by electrochemical reduction and an O 1s peak from a byproduct of Li_2CO_3 at $\sim 532\text{ eV}$.^{23,24} From research in the field of LIBs,²⁵ it is well known that the PC solvent is decomposed on the Si NE surface and mainly forms a polymer-like SEI component with Li_2CO_3 as a byproduct, which increases the charge-transfer resistance at the Si NE and deteriorates the cell

Figure 2. (Color online) (a, b) Charge/discharge curves and (c) changes in discharge energy density and efficiency during cycling of Si-CAP cells with Li pre-doped Si negative electrodes using 1.0 M LiBF₄/PC (a) without and (b) with 10 mass% fluoroethylene carbonate.

performance, especially with respect to cyclability. Similar SEI components were confirmed for Li pre-doping without FEC; however, the chemical composition of the SEI film was changed by the FEC addition. A LiF-rich film was formed and the amounts of polymer-like species and Li₂CO₃ were significantly reduced by this protective film. This result is in good agreement with observations reported for Si NEs in LIBs.^{23,25} These similar effects were therefore successfully confirmed for Li pre-doping.

To confirm the effects of FEC, we also conducted a Si half-cell test using a Li metal counter-electrode to avoid the influence of the AC PE. In this test, the capacity limitation was suggested from Si-CAP cells (Fig. 2), which was $\leq 500 \text{ mAh g(Si)}^{-1}$. Maximum utilization of the Si NE was estimated from the balance of the AC PE and Si NE: a specific capacity of $450\text{--}590 \text{ mAh g(Si)}^{-1}$ was obtained. The Si half-cell was therefore tested at a capacity limitation of $500 \text{ mAh g(Si)}^{-1}$ and a morphology change was observed after 50 charge/discharge cycles. The charge/discharge reaction was found to be stabilized below 0.6 V by Li pre-doping with 10 mass% FEC, while the Si NE without the addition of FEC exhibited a gradually increasing potential for the charge/discharge (Li–Si alloying/de-alloying) reactions (not shown). After 50 cycles (Fig. 3), the Si NE without FEC was covered by a thicker SEI film (the surface could not be observed) than that with the addition of FEC. In contrast, the surface of Si NE with FEC addition could still be observed by SEM and maintained a similar surface morphology after Li pre-doping. This fact also suggests that the SEI film, which contained a large amount of LiF, suppressed subsequent PC reductive decomposition during the charge/discharge cycles. This is in good agreement with the results of IR drops for the Si-CAP cells (Fig. 2). Further investigations, using a three-electrode-type cell and alternating-current impedance analysis, are now in progress to understand the operation and degradation mechanism of the Si-CAP cell in more detail.

4. Conclusions

To extend cyclability of the Si-CAP cell, we applied a polyimide binder and FEC additive. This binder successfully fixed the Si

Figure 3. (Color online) X-ray photoelectron spectra of the surface of Si negative electrodes after Li pre-doping (a, c, e) without and (b, d, f) with 10 mass% fluoroethylene carbonate, and (g, h) their scanning electron micrographs after 50 cycles in the Li pre-doped Si half-cell [Li pre-doped Si | Li metal foil] test.

nanoparticles on the Cu foil current collector and improved cyclability of the cell. Moreover, FEC addition into the PC-based electrolyte at the Li pre-doping stage enhanced homogeneity of the pre-doping. This improved electronic conductivity; performance was stabilized by the formation of a LiF-rich SEI film on the Si NE surface. The improved SEI film prevented reductive decomposition of the PC solvent. This was important in suppressing the increase in charge-transfer resistance by growth of the SEI film due to charge/discharge cycling and resulted in lower cell resistance. The Si-CAP cell with both polyimide and FEC exhibited a high energy density of over 120 Wh kg⁻¹ and stable cyclability up to 800 cycles. The cycleability was clearly extended compared with that of the Si-CAP using sodium carboxymethyl cellulose binder reported previously,¹⁵ where a relatively high energy density around 140 Wh kg⁻¹ was obtained in the initial cycles; however deterioration of the cell performance was confirmed after 160 cycles. These results suggest that other improvements to the Si NE adapted from the LIB field may also be useful for Li pre-doping and offer the possibility of further stabilization of the Si NE in the Si-CAP. Further analysis and improvement of the Li pre-doped Si NE is expected to open new opportunities, not only for hybrid capacitors, but also for other advanced energy-storage systems.

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