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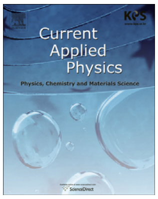

Electrochemical characteristics of amorphous silicon thin film electrode with fluoroethylene carbonate additive

Jung Sub Kim [a,b], Dongjin Byun [b], Joong Kee Lee [a,*]

[a] Center for Energy Convergence, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Department of Material Science & Engineering, Korea University, Seoul 136-713, Republic of Korea

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ABSTRACT

The electrochemical and compositional changes of a solid electrolyte interphase (SEI) layer formed on the surface of silicon thin film are investigated in order to determine the effect of the content of fluoroethylene carbonate (FEC) additive in the electrolyte. Comparisons are made with FEC-free electrolyte, in which the major components are $(CH_2OCO_2Li)_2$ and Li_2CO_3. The $(CH_2OCO_2Li)_2$ and Li_2CO_3 of the SEI layer in the FEC-containing electrolyte decreases, and polycarbonate and LiF increase relatively with the repression of $-OCO_2Li$ groups. The additive affects the composition of the SEI layer, which leads to lower resistance. The electrochemical performance regarding cycle retention, coulombic efficiency, rate capability, and discharge capacity in the FEC-containing cell are significantly enhanced compared to that of the FEC-free electrolyte. The observed optimum FEC concentration in the electrolyte is 1.5%, due to the reduced charge transfer and SEI resistance in our experimental range.

1. Introduction

In order to achieve a negative electrode with high energy density and safety, silicon is a most promising alternative to carbon anode material. Silicon has a high theoretical specific capacity of 4200 mAh g^{-1} in the fully lithiated state ($Li_{22}Si_5$), which is ten times higher than that of graphite anode material [1–3]. In addition, the world's second most abundant element is silicon, which makes it attractive for commercial use. However, silicon anodes have many problems in spite of these advantages. The main obstacle of silicon electrodes is the serious volume change (>300%) during the insertion and extraction of Li^+, which results in the deterioration of electrochemical performance [4–6]. In addition, cracked areas originating from mechanical failure expose fresh electrolyte during the charge and discharge process, resulting in the formation of new solid electrolyte interphase (SEI). The formation of an SEI film can be both beneficial and disadvantageous. The benefit is that it prevents electron transport and consequently limits further electrolyte degradation. In contrast, lithium trapped in passivating films could lead to a significant loss in coulombic efficiency (CE), an increase in the electrical resistance within the cell, and inhibition of the lithium ion transfer kinetics. Therefore, the design of the electrolyte is very important due to its impact on the electrochemical performance [7].

To overcome these problems, many researchers have focused on mitigating the volume change in the silicon electrode. For example, Chan et al. [8] reported silicon nanowires that exhibited stable cycle retention at a rate of C/20, which was a novel attempt in terms of the reduction of physical stress by morphology control of the silicon electrode. Various other morphologies are being studied, such as hollow silicon, core–shell nanowires, and silicon nanotubes [9–11]. In another trial, Chen et al. and Liu et al. showed that the choice of proper binder is very important for the electrochemical performance of anodes. So far, the candidates for various new binders for silicon anodes have included Na-alginate, styrene butadiene rubber–sodium carboxymethyl cellulose (SBR–SCMC), sodium carboxymethyl cellulose (SCMC), polyamide imide (PAI), and polyacrylic acid (PAA) [12–21]. Several studies have been conducted on electrolyte additives such as vinylene carbonate (VC), vinyl ethylene carbonate (VEC), acrylic acid nitrile (AAN), and fluoroethylene carbonate (FEC) [22–29]. Overall, it is most cost-effective when a small amount of additive is added to the electrolyte, which leads to enhanced cell performance. The proper amounts of FEC are still debated between high and low contents. In the present study, the effect of FEC on the physiochemical characteristics of the SEI in silicon electrode is investigated, as well as the

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* Corresponding author.
E-mail addresses: leejk@kist.re.kr, joongkee57@naver.com (J.K. Lee).

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relationship between the content of FEC and the electrochemical performance.

2. Experimental

Silicon thin films were deposited by plasma-enhanced chemical vapor deposition (PECVD). Cu foils cut into circular pieces (2.0096 cm^2) were used as the substrate. The substrates were then cleaned in an ultrasonic bath containing a mixture of acetone and ethanol for 10 min sequentially. The Cu foil was loaded onto the heating block of the PECVD reactor. After the reactor was evacuated to 1.5×10^{-6} Torr and the temperature of the heating block was raised to 300 °C, silane (SiH_4) and argon gas (Ar) were fed into the reactor for the deposition of the Si thin film. The typical conditions for the deposition of the silicon thin film are as follows: working pressure of 7.0×10^{-2} Torr, temperature of substrate of 300 °C, RF plasma power of 200 W, SiH_4 flow rate of 10 sccm, argon flow rate of 30 sccm, and deposition time of 20 min. To observe the morphology and thickness of the silicon thin film, scanning electron microscopy (SEM) was carried out using a field emission scanning electron microscope (FESEM, NOVA NANO SEM200, FEI co.). The secondary electron detector is used for the studies, most of which are performed using an accelerating voltage of 10 kV and a working distance of 5–5.3 mm. Raman spectroscopy (Nicolet Almega XR dispersive Raman, Thermo electron co.) with 632 nm (red) laser excitation was used to obtain the structure of the silicon thin film. Low laser power density with a 50× microscope objective at an exposure time of 4 s was utilized to avoid heating effects of the laser. The spectra were recorded at 4 cm^{-1} resolution between 4000 and 90 cm^{-1}. The laser spot diameter on the sample was about 2 μm.

Test cells were fabricated using silicon thin films on Cu foil as the anode material with and without FEC additive. CR2032 coin-type half cells were assembled and sealed in a dry room. The test cells consisted of a working electrode, lithium foil as the counter electrode, and polypropylene (PP) membrane as a separator. The liquid electrolytes with and without FEC (Foosung co., Republic of Korea) were 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) (1:1:1 in vol %). The FEC contents were adjusted to 0.5, 1, 1.5 and 2% (vol %). After 80th cycling, the electrodes were washed in DMC solution for the elimination of salts in an Ar filled glove box to avoid their reactivity with other components. The samples were moved for compositional analysis using the transfer vessel. For chemical bond and compositional analysis of SEI film on the silicon electrodes, X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) with a background pressure of 6.7×10^{-8} Pa was carried out in argon. Galvanostatic charge–discharge cycling tests for the testing of the electrical and chemical properties were carried out on a Maccor automated battery tester (MACCOR series-4000) in the potential range of 0–2 V at a constant current density of 200 μA cm^{-2}. Cyclic voltammetry (CV) was also conducted in the potential range of 0–2 V at a scan rate of 0.01 mV s^{-1}. To examine the rate capability of silicon electrode with and without FEC, current densities of 100, 200, and 300 μA cm^{-2} were also applied. For the calculation of specific capacities, the mass of the silicon electrodes is derived from their density (2.33 g cm^{-3}) and electrode thickness (450 nm). All measurements were performed at room temperature. Electrochemical impedance spectroscopy (EIS) experiments with the fully discharged (up to 2 V) cells on three electrodes were performed using an impedance/gain-phase analyzer (Solartron SI 1260) equipped with an electrochemical interface (Solartron SI 1286). The AC amplitude was 5 mV, with a frequency range of 1 Hz–10^6 Hz.

3. Results and discussion

The silicon thin film of surface, cross section morphologies and Raman spectra is investigated and the data are illustrated in Fig. 1. As shown in Fig. 1(a, b), the silicon thin film prepared by PECVD has rough surface and thickness of 450 nm. Raman spectroscopy with red laser of 632 nm is used to obtain structural information from the as deposited silicon electrode. It is known that for crystalline silicon, a sharp peak, attributed to the transverse optical vibrational modes, is reported to appear at 520 cm^{-1}. Since the long range order is lost, the transverse optical peak becomes broad and shifts to lower wavenumbers about 35 cm^{-1}. It is clear that for the deposited films, no sharp peak at 520 cm^{-1} is observed, whereas a broad peak with the peak position at 485 cm^{-1} is found suggesting that the deposited film is predominantly amorphous, as shown in Fig. 1(c).

The Li^+ insertion (reduction) and extraction (oxidation) reactions of the amorphous silicon electrodes are studied by CV, which measures the potential over the region where the main reaction of an electrode occurs. The CVs of the 450 nm silicon electrodes are measured from 0 to 2 V at relatively slow scan rate of 0.01 mV s^{-1}, as shown in Fig. 2. The peaks observed in the 1st cycle (solid line in Fig. 2) have a different shape pattern from those in the 2nd cycle (dotted lines in Fig. 2). The intensity at 0.07 V was sharper and larger, because it reflects the irreversible capacity in the first charge cycle. In the 2nd cycle, the appearance of three peaks at 0.31, 0.21, and 0.07 V indicates that three different Si–Li alloy states exist during the lithiation process. In the oxidation peaks (delithiation), the two peaks at 0.29 and 0.49 V correspond to the delithiation process of lithium. More interestingly, the CV plots of the inset in Fig. 2 indicate different behavior between the FEC-free and FEC-containing electrolytes. The silicon electrode with FEC additive shows increased reduction current between 1.1 and 1.16 V, corresponding to the decomposition of the FEC additive [30]. It is clear that the decomposition of FEC takes place at a higher potential than the EC reduction peak of 0.8 V, as shown in the inset of Fig. 2. Since decomposition of the reductive additive takes place at higher potentials than the solvent reduction, the improvement by such additives is mainly in the initial stage of SEI formation, which results in a reduction of gas generation, a decrease of columbic efficiency, and stabilization of the SEI against prolonged cycling.

Since the composition of the SEI layer is an important role in the electrochemical performance, it is necessary to understand the control of the surface chemistry. XPS is well known as a useful tool to study the surface chemistry of the SEI layer [31]. Fig. 3 shows high-resolution XPS spectra (Si2p, F1s, C1s, and O1s) of silicon electrodes in FEC-free and FEC-containing electrolytes. The peaks are obtained by Gaussian–Lorentzian fitting from the spectra. The spectra of Si2p peaks at 103.3, 102.1, 100.8, and 99.6 eV are characteristics of SiO_2, C–O–Si, Si–C, and Si–Si bonds, respectively, as shown in Fig. 3(a) [32–34]. A greater amount of silicon oxide is observed in the case of the FEC-free electrolyte than in the FEC-containing electrolyte. In particular, a new peak with a Si–F bond is observed at 107 eV in the silicon electrode of the FEC-containing electrolyte. With or without FEC additives, in the F1s spectrum, two major peaks matching LiF and LiP_xF_y are observed [35–39]. The intensity of LiP_xF_y in the FEC-free electrolyte (unstable salts) is higher than that of the FEC-containing electrolyte. On the other hand, the portion of LiF in the FEC-containing electrolyte is relatively increased with the FEC-free electrolyte. Choi et al. [40] proved that the surface layer at the interface between silicon and the electrolyte without FEC contains EC derivatives such as metastable linear alkyl carbonates, which are less dense. The electrolyte can penetrate into the active silicon phase through the less dense surface layer and break the Si–Si network bonds by