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The structural and electrochemical study on the blended anode with graphite and silicon carbon nano composite in Li ion battery

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ABSTRACT

The *in-situ* XRD and *ex-situ* solid state NMR analysis are performed as well as electrochemical measurements to understand transfer properties of Li ion. Capacities of blended anode increased with increasing silicon carbon nano composite content and voltage profiles are differentiated with each other. *In-situ* XRD experiments reveal that structural changes of graphite are retarded as silicon carbon nano composite contents increased. ^{7}Li NMR spectra are measured for blended anodes with different state of discharging and as a result, silicon is discharged prior to graphite at the initial stage of discharging. Moreover, asymmetric behaviors of structural changes between discharging and charging process are explained by comparison with ^{7}Li NMR spectra of anodes at 20% of state of discharge during discharging and charging. Capacity fade of blended anode is investigated with NMR measurement on the different state of health and it is found that portions of graphite and silicon's faded capacities are differently evolved during calendar life and degraded.

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1. Introduction

Li ion battery is the most attractive subject in energy technology in recent years. Its applicable fields are spread out various industries such as mobile devices, energy storage systems and electric vehicles due to high energy density. One of obstacles for using Li ion battery as secondary energy storage is that capacity is not enough to use for appropriate duration. Graphite is well known as representative anode material and it has great advantages of stability and cheaper cost as well as low working voltage [1]. As requests for larger capacity increased, silicon compounds were studied as alterative novel anode. Because silicon compound has greater specific capacity ($3600\,\mathrm{mAh\,g^{-1}}$) which is about ten times larger than graphite, it is good candidate for new anode material. However, the biggest problem for using silicon as anode is huge volumetric expansion up to 300% when silicon is maximally lithiated [2,3]. The mechanical stress caused by huge volumetric expansion of silicon anode induced the lost of contact of ionic and electric conductions between anode particles and electrode environments. Thereafter those silicon anodes suffer from large capacity fade [4]

One of the ways to reduce large volumetric expansion effect and make great use of the large specific capacity of silicon is blending graphite and silicon. Specific capacity of blended anode increased with increasing silicon contents and volume of silicon was limitedly expanded within the space between graphite particles. However, each electrochemical behavior of blended anode with graphite and silicon was less understood because it was difficult to observe silicon and graphite separately. Moreover, because silicon was changed into amorphous phase in early cycling, it was difficult to figure out structural changes due to the (de)lithiation from the XRD experiment [5,6]. ^{7}Li NMR experiment is another method to study structural information of both graphite and silicon [7–12] but signals from lithiated graphite and silicon used to be overlapped in according to their states of discharging for graphite and silicon.

In this study, we performed separately to observe each silicon and graphite and to understand how the silicon contributes to discharge and charge in the blended anode and to the capacity decrease over the lifetime. We analyzed electrochemical properties of blended anode with graphite and silicon carbon nano (SCN) composites. The cell performance obtained from samples with different contents of SCN shows different structural changes which were observed by *in-situ* XRD experiment. ^{7}Li NMR measurements were performed to obtain information of intercalated Li ions amount on both graphite and silicon. Combined results of XRD and

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NMR experiments could distinguish lithiated states of graphite and silicon separately. This could explain asymmetric behaviors between beginning of discharging and end of charging, which were shown in *in-situ* XRD experiment result. Total degradation portion of blended anode was measured separately with NMR by using samples with different calendar life, to verify which elements of anode were severely degraded during cycling.

2. Experimental

SCNs are prepared with mixture of graphite and silicon nano-sized particles with 50 to 50 wt%. The morphology of the materials was investigated by the scanning electron microscopy (SEM) with an FEI Magellan 400L. Fig. 1 is the SEM images of morphological and cross-sectional view of SCNs with different brightness. Silicon nano-particles and graphite are white and dark regions, respectively. Silicon nano particles are imbedded into the graphite so that volumes of SCNs are limitedly expanded within initial of SCN even silicon nano particles are expanded during lithiation. Samples are prepared with blending graphite with different amount of SCNs. The weight percents of SCNs, capacities for discharging and charging for three samples used in experiments were shown in Table 1.

Electrochemical performance of samples was characterized with a half cell in CR2032 coin-type which was fabricated with lithium metal, electrolyte (1.15 M $LiPF_6$ solution in a mixture of ethylene carbonate-diethyl carbonate-ethyl methyl carbonate) and separator (porous polypropylene film). Assembled cells measured at a constant current (CC) density of 1/20C, a constant voltage (CV) density of 0.01C for discharge and a CC density of 1/20C for charge with a voltage cutoff of 0.01/1.50 V vs. Li^+/Li. *In-situ* XRD patterns of all samples were obtained on a PANalytical Empyrean diffractometer with Cu $K\alpha_1$ wavelength of 1.54059 Å. The XRD data was analyzed by Rietveld refinement via the *Fullprof* program [13]. Samples were indexed as hexagonal structure of space group *P*6$_3$/*mmc* likewise graphite. *In-situ* XRD measurements with the exact same coin cell configurations in the electrochemical measurements were used to compare crystallographic changes during discharging and charging. And the discharged and charged conditions were equally applied with that of electrochemical measurement.

^{7}Li MAS NMR measurement were carried out on Bruker Avance III 400 spectrum with 9.4 T superconducting magnet. For magic angle spinning (MAS) NMR experiment, 4.0 mm CP-MAS probe was used with zirconia rotor at 155.51 MHz for ^{7}Li NMR. The samples were rotated with 14 KHz and NMR signal was excited by a single radio frequency (RF) pulse with length of 2.5 μs and recycling time of 2 s. Obtained spectra were deconvoluted and intensity of each deconvoluted spectrum was calculated with *dmfit* software which is a fitting program for solid state NMR spectrum [14].

Table 1
Samples prepared for experiment. The content of SCN and capacities of those in discharging and charging.

SCN (%)	discharge (mAhg^{-1})	charge (mAhg^{-1})
0	360	357
3.5	398	393
9	465	457

3. Result and discussion

Fig. 2 shows electrochemical properties of three-kind graphites blended with different SCNs contents. In Fig. 2(a), voltage profiles of these anodes have different capacities at fully discharging and charging. Since specific capacity of SCN is greater than graphite, capacities at full discharged state become larger as contents of SCN increased. Table 1 shows values of capacities for three different anodes at fully discharged and charged states. During discharging process, voltages of half cells dropped because of inserting Li ions into graphite and/or silicon. At certain voltages including 0.2, 0.12 and 0.08 V, capacities abruptly increased without voltage change. In Fig. 2(b), dQ/dV curves indicate that there were structural changes at these voltages and the voltages of these were almost the same between them. This suggests that structural transitions at three different voltages were caused not by SCN, but graphite. Additionally there were small differences of dQ/dV curves over 0.2 V, which shown in Fig. 2(c). At the beginning of discharging down to 0.2 V, capacities of the cell became larger as contents of SCN increased. This means that SCN is lithiated together with graphite at the beginning of discharging. In the contrastive to the discharging process, capacities for blended anodes were differentiated from each at the end of charging process. However, capacity profiles of three different anodes were not severely different at the end of discharging below 0.2 V and the beginning of charging up to 0.21 V.

With SCNs content increase, these asymmetric behaviors between initial state of discharging and final state of charging are more conspicuous. This result means that SCNs can affect the (de)lithiation on the graphite. Therefore, structural behavior of graphite was examined by *in-situ* XRD experiments. Fig. 3 is *in-situ* XRD patterns for three compounds with SCN contents of 0, 3.5 and

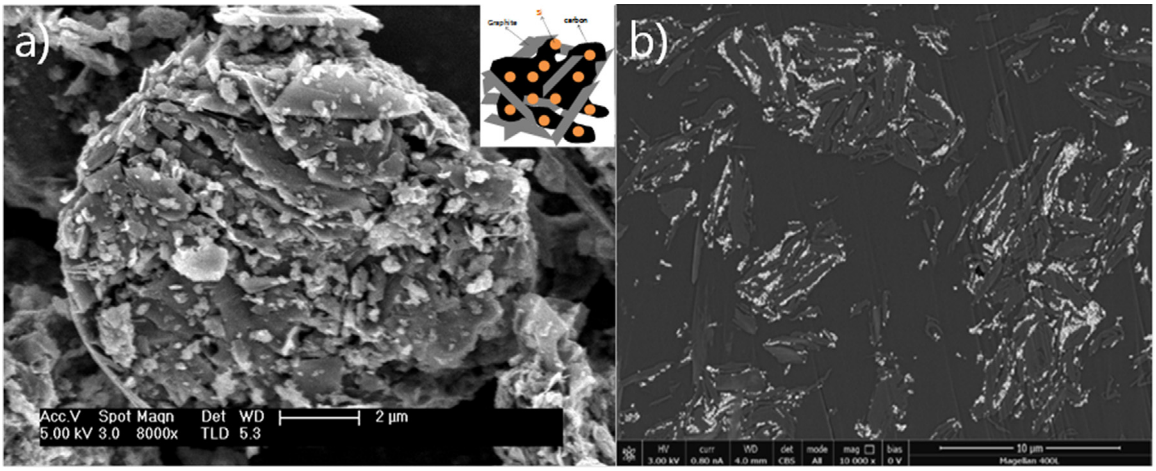

Fig. 1. SEM images of (a) SCN particle and inset is schematic image of SCN. (b) Cross-section view of SCN with white (Si) and dark (Graphite) region.

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