The design of a Li-ion full cell battery using a nano silicon and nano multi-layer graphene composite anode

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HIGHLIGHTS

- Nano-Si and nano-graphene composite is used as an anode of Li-ion battery.
- This anode material shows high cyclability in half-cell and full-cell tests.
- The anode has a greater effect on the full-cell performance with NCA cathode.
- A FEC electrolyte additive improves the cyclability of the full cell.

ARTICLE INFO

ABSTRACT

In this study, a Si–graphene composite, which is composed of nano Si particles and nano-sized multi-layer graphene particles, and micro-sized multi-layer graphene plate conductor, was used as the anode for Li-ion battery. The Si–graphene electrode showed the high capacity and stable cyclability at charge/discharge rate of C/2 in half cell tests. Nickel cobalt aluminum material (NCA) was used as a cathode in the full cell to evaluate the practicality of the new Si–graphene material. Although the Si–graphene anode has more capacity than the NCA cathode in this designed full cell, the Si–graphene anode had a greater effect on the full-cell performance due to its large initial irreversible capacity loss and continuous SEI formation during cycling. When fluoro-ethylene carbonate was added to the electrolyte, the cyclability of the full cell was much improved due to less SEI formation, which was confirmed by the decreases in the 1st irreversible capacity loss, overpotential for the 1st lithiation, and the resistance of the SEI.

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1. Introduction

Li-ion batteries (LIBs) have been widely used as an energy storage system for various electrical devices from small consumer electronics to electrical vehicles (EVs) due to their stable long-term performance (cyclability), good rate capability, and thermal stability in practical use [1–3]. However, one of the most critical challenges of present commercial Li-ion batteries is their insufficient capacity leading to a need for frequent charging. Hence, development of new electrode materials with higher energy density is of significant interest [3]. Silicon is a promising anode material due to its high theoretical specific capacitance (4200 mAh g^{-1}) [4–19]. Unfortunately, Si expands up to 300% during lithiation, resulting in a large irreversible capacity loss (ICL). To mitigate this capacity fade, nanowire-shaped Si [4,5] with good flexibility and Si composites with buffer materials, such as pre-treated carbon [6–8] and various shaped (sized) graphenes [9–18] have been used. Graphene has received a lot of attention because it has high electrical conductivity as well as high mechanical strength, resulting in the simultaneous increase in rate capability and cycle life for the Si–graphene electrode. In order to take full advantage of the two positive effects of graphene, the size and composition of Si and graphene must be optimized. In this study, we used a Si–graphene electrode that was fabricated with the active materials (nano-sized Si (<100 nm) and multi-layer graphene plates (<100 nm)) and conducting additive (micro-sized multi-layer graphene plate).

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Although there are many reports on Si–graphene anode materials, most of the data are from half-cell tests [9–18]. In practice, the electrochemical behavior of a half cell is different from that of a full cell. It was reported that the full cells employing nano Si–graphene anodes with cathodes such as LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$ (NCM) [14] and Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ (LNM) [18] showed lower capacity and greater capacity fade than the individual Si–graphene half cells. These full-cell studies did not report the active material ratio for the electrodes. Consequently, it is difficult to ascribe a cause for the greater capacity fade in full cells. The lower performance might be due to the limited supply of cyclable lithium provided by the positive electrode, an increase in resistance of components by additional SEI formation, or dissolution of electrolyte and metals from the cathode. Accordingly, in order to estimate the feasibility for a practical use of a new material, a full cell is necessary.

Herein, we designed the Li-ion full cell employing a new nano Si–graphene composite anode with an NCA cathode and investigated its electrochemical and microstructural behaviors during charge/discharge cycling. To improve further cyclability, fluoroethylene carbonate (FEC) was added to the EC–DEC electrolyte, and its effect was explored electrochemically.

2. Experimental methods

2.1. Material preparation

A commercially available Si–graphene composite (*XG-SiG™*, supplied by *XG Sciences, Inc.*) was used for the anode. The active material was composed of nano Si particles and nano-sized plate-like multi-layer graphene (*xGnP®*). To make the slurry of adhesive and conductive anode material, the nano-sized active material was combined with polyacrylic acid (PAA) binder (*Sigma Aldrich*, M$_v$: 450,000 g mol^{-1}), carbon black conductive agent, and conductive additive of micro-sized multi-layer granular graphene (*xGnP®*) with very high conductivity of 10^7 S m^{-1}, and PGME solvent (Propyleneglycol monomethyl ether, *Sigma Aldrich*). After mixing the slurry by sonication and stirring with magnetic bar in a jar, the slurry was coated on a 10 μm Cu foil using a doctor blade. The slurry coated on Cu foil was dried for 1 h at a room temperature and then in a vacuum oven of 80 °C for overnight. The active loading was between 1.64 and 1.66 mg cm^{-2}. The theoretical capacity was calculated to 2968 mAh g^{-1} based on the individual theoretical capacities of Si and carbon materials (Si: 4200 mAh g^{-1}, Carbon: 372 mAh g^{-1}).

The density of material was between 0.63 and 0.70 g cm^{-3} without calendaring. An active material of NCA was used for a cathode with a graphitic carbon conductive additive and polyvinylidenefluoride (PVdF) binder.

2.2. Cell assembly and electrochemical properties

All half cells were assembled as 2032 coin cells, and all full cells were fabricated as pouch-type cells with an active area of 9 cm^2. The composition of electrolyte was EC: DEC = 1:1 (w/w) with 1 M LiPF$_6$ with/without 10 wt.% FEC. The loadings of active material (anode:cathode) were 0.00263 g:0.0230 g and 0.0141 g:0.131 g in a coin and pouch cell, respectively. Hence, the design capacity of anode and cathode based on the theoretical capacity (Si–graphene anode of 2968 mAh g^{-1} and NCA cathode of 274 mAh g^{-1}) was 7.80 and 6.38 mAh for coin cells, respectively; that is, the theoretical capacity of the anode was 1.22 times more than that of cathode. Using the measured capacity after the 1st formation cycle for the half cells, the lithiation capacity of Si–graphene anode is 4.46 mAh (1696 mAh g^{-1}) and the delithiation capacity of NCA cathode is 3.83 mAh (169 mAh g^{-1}) for coin cells, indicating that the design

capacity of anode is 1.16 times more than that of cathode. To see both effects of anode and cathode on the capacity fade of the full cell during cycling, the capacity ratio of anode: cathode was designed to be close to 1:1.

To characterize the electrochemical properties of the full cells, capacity–voltage (*C–V*) tests were performed at various C-rates (C/15 for 1st 5 cycles, C/5 for 2nd 5 cycles, and C/2 for subsequent cycle), which were determined from the capacity of cathode on the 1st cycle. All cycling tests were conducted at room temperature (20 °C) using an *Arbin* battery cycler. The full cells were charged to 4.2 V at constant current (CC), and then held at a constant voltage (CV) until the current was half of applied C-rate (C/30, C/10, and C/4). Discharges were done at CC to a cut-off potential of 2.75 V. The capacities of full cells were normalized by the weight of NCA cathode. The half cells were cycled between 0.05 and 1.0 V$_{Li+/Li}$ (Si/graphene) and 2.75–4.20 V$_{Li+/Li}$ (NCA). Electrochemical Impedance Spectroscopy (EIS) of full cells was conducted using a potentiostat in a frequency range of 1 MHz ∼ 0.01 Hz with an amplitude of 5 mV at full state of charge (SOC) of 4.09–4.12 V. The values for resistances of individual components were determined with a fitting program.

2.3. Surface and microstructural analysis of electrode

The surface morphologies and compositions of electrode materials were analyzed by a high resolution scanning electron microscopy (SEM, *Hitachi SU8000*). The atomic composition was analyzed by energy dispersive spectroscopy (EDS). The microstructure of nano-sized Si and graphene composite was analyzed by a transmission electron microscopy (TEM) and X-ray diffraction (XRD).

3. Results and discussion

3.1. Nano-Si and nano-graphene composite for Li-ion battery anode

Fig. 1a shows the HR–SEM surface morphology, TEM bright field images, and XRD patterns of the as-prepared electrode of nano Si–graphene composite coated on a Cu foil. As shown in Fig. 1a–b, the electrode is composed of micro-sized graphene plates (diameter: 0.4–1 μm) and many spherical agglomerates of nano-sized particles composed of Si and graphene. Specifically, it is confirmed that the sizes of graphene plate particles are between 40 and 70 nm from the high magnification images (below) of Fig. 1a and the diameter of spherical Si is between 10 and 80 nm from TEM images (black dots and their agglomerates) of Fig. 1b. The TEM diffraction pattern of the Si–graphene electrode coated on Cu film shows the poly-crystalline ring and halo indicating an amorphous structure, which is probably due to activated carbon black. In particular, it was found from the XRD pattern of Fig. 1c that in the as-prepared electrode, the Si has poly-crystalline structure with sharp Si (111), Si (220), and Si (311) peaks, and the carbon materials show features of both an amorphous phase and a crystalline phase with graphitic C (002) and small C (004) peaks due to activated carbon black and multi-layer graphene plates in nano- and micro-scale.

Fig. 2a–b displays voltage–capacity curves and the corresponding differential curves showing the lithiation and delithiation behavior of half cells of Si–graphene, respectively. For the first cycle (C/15), the half cell of the Si–graphene composite showed the initial irreversible capacity loss (ICL) of 19.9% (CE of 80.1%) from 2782 to 2227 mAh g^{-1}, which is considerably improved value when compared with those from previous reports (27% [9], 30% [11], 37% [12], 23.1% [16], 22.6% [18], and 20–30% [10,13,15,17]). Recently, one Si–carbon composite material reported a very high 1st coulombic efficiency of 86% [19], however, the values of most Si–carbon/