



The effect of fluoroethylene carbonate additive content on the formation of the solid-electrolyte interphase and capacity fade of Li-ion full-cell employing nano Si–graphene composite anodes



Arnaud Bordes, KwangSup Eom*, Thomas F. Fuller

School of Chemical & Biomolecular Engineering, Center for Innovative Fuel Cell and Battery Technologies, Georgia Institute of Technology, Atlanta, GA 30332, USA

HIGHLIGHTS

- Li ion full cells employing Si–graphene anodes were used in this study.
- FEC additive improves cyclability of the full-cell by formation of good SEI.
- 5 wt.% FEC is optimum with high capacity and low capacity fade.
- 5 wt.% FEC forms less amount of SEI compounds consuming Li⁺.

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ABSTRACT

When fluoroethylene carbonate (FEC) is added to the ethylene carbonate (EC)–diethyl carbonate (DEC) electrolyte, the capacity and cyclability of full-cells employing Si–graphene anode and lithium nickel cobalt aluminum oxide cathode (NCA) cathode are improved due to formation of a thin (30–50 nm) SEI layer with low ionic resistance ($\sim 2 \text{ ohm cm}^2$) on the surface of Si–graphene anode. These properties are confirmed with electrochemical impedance spectroscopy and a cross-sectional image analysis using Focused Ion Beam (FIB)–SEM. Approximately 5 wt.% FEC in EC:DEC (1:1 wt.%) shows the highest capacity and most stability. This high capacity and low capacity fade is attributed to a more stable SEI layer containing less $\text{CH}_2\text{OCO}_2\text{Li}$, Li_2CO_3 and LiF compounds, which consume cyclable Li. Additionally, a greater amount of polycarbonate (PC), which is known to form a more robust passivation layer, thus reducing further reduction of electrolyte, is confirmed with X-ray photoelectron spectroscopy (XPS).

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1. Introduction

Lithium-ion batteries (LIBs) are the power source of choice for both portable devices and electric vehicles [1,2]. In order for electrical vehicles with LIBs to be embraced more fully, the specific energy of LIBs needs to be improved without sacrificing safety, material availability, and cost. Silicon, as a negative electrode material with various morphologies or nanostructures, is one possible solution because lithiated silicon provides high specific energy (4200 mAh g^{-1}) and is an earth abundant material [3–5]. However, silicon expands up to 300% during lithiation. Repeated non-uniform

dilation and contraction pulverizes the silicon, leading to a loss of electrical contact and rapid capacity fading [6]. One mitigation is to form a silicon–graphene composite. The graphene is used as a buffer material and enhances electrical conductivity of the electrode [7–16]. Even so, loss of electrical conductivity is not the only cause of capacity fading. Indeed, several mechanisms, such as phase change, insertion of solvated lithium, and electrolyte reduction throughout cycling, can also contribute to irreversible loss of capacity [17,18]. The last two phenomena, although not avoided completely, are at least controlled by the formation of a stable solid electrolyte interphase (SEI) on the surface of electrode during formation [19–22].

Thus, the quality of SEI is a major factor that determines capacity and power capability, lithium deposit morphology, and cyclability. A good SEI should be uniform, adhere well to the anode, and have

* Corresponding author. Tel.: +1 404 747 0451.

E-mail addresses: keom@gatech.edu, kwangsup.eom@gmail.com (K. Eom).

high ionic and electrical conductivity [19–22]. The SEI is formed from the reduction and polymerization of the electrolyte solvents. Additives to the electrolyte can improve the quality and composition of the SEI [23–27]. Specifically, fluoro-ethylene carbonate (FEC) has been shown to be effective in reducing irreversible capacity loss and lowering capacity fade for several carbon and silicon based anode materials [23–27]. The effect of FEC additives on Si-graphene anodes has been reported only for half-cells. In contrast to half cells with a lithium foil counter electrode, with full-cells using practical electrodes there is a limited supply of lithium provided by the positive electrode. Therefore, in addition to the increase in internal resistance of the cell attributed to SEI formation [26], lithium consumed in the formation of the SEI is no longer available for cycling. The effect of the FEC additive on the properties of the SEI layer formed on the Si-graphene anode is not yet fully understood, and the optimization of the FEC contents has not yet been investigated, especially in the full-cells.

For these reasons, the optimal content of FEC additive was investigated in order to enhance the performance of a Li-ion full-cell battery using nano Si-graphene composite anode and NCA (Li [Ni_{0.8}Co_{0.15}Al_{0.05}]O₂) cathode. The influence of the FEC on the electrochemical and morphological behavior of the SEI layer formed on Si-graphene anode was specifically studied using the electrochemical impedance spectroscopy (EIS), Focused Ion Beam (FIB)-Scanning Electron Microscopy (SEM), and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental methods

2.1. Electrode preparation

In this study, we used a Si-graphene negative electrode and a Li [Ni_{0.8}Co_{0.15}Al_{0.05}]O₂ (NCA) positive electrode for the full-cells. The Si-graphene electrode is composed of nano-spherical Si particles, nano-sized multi-layered plate-like graphene, and polyacrylic acid (PAA) binder (*Sigma Aldrich*) and conductive additive of micro-sized multi-layered graphene [26]. NCA with a graphitic carbon conductive additive and polyvinylidene fluoride (PVdF) binder formed the positive electrode [26].

2.2. Cell assembly

All full-cells were fabricated as pouch-type cells with an active area of 9 cm². The mass loadings of active material (anode:cathode) were 0.0141 g:0.131 g, indicating that the design capacity of anode is 1.15 times more than that of cathode based on the measured capacity in half cells after the 1st formation cycle [26]. The electrolyte used was EC:DEC = 1:1 (wt.%) with 1 M LiPF₆, and the electrolyte of 2.5 ml was applied for one pouch cell. To investigate the effect of FEC content on the cycling behavior of the cells, 0 to 20 wt.% of FEC was added to the EC-DEC electrolyte. A microporous trilayer membrane (*Celgard 2325*) was used as a separator. The half cell used in this study was composed of the Si-graphene electrode and extra pure Li metal (reference/counter) with active area of 1.584 cm².

2.3. Electrochemical analysis

To characterize the electrochemical properties of the full-cells, capacity–voltage (C–V) tests were performed at C/15 for the 1st charge and discharge cycle and C/2 for subsequent cycles. The C/15 is based on theoretical capacity and C/2 on measured 1st cycle capacity. All cycling tests were conducted at room temperature (~20 °C) using an *Arbin* battery cyler. The full-cells were charged to 4.2 V at constant current (CC) and then held at constant voltage

(CV) until the current was half of applied C-rate. Discharges were done at CC to a cut-off potential of 2.75 V.

Electrochemical Impedance Spectroscopy (EIS) of full-cells was conducted at either a nearly full state of charge (SOC) of 4.09–4.12 V or in the fully discharged state of 3.0–3.1 V using a potentiostat. The frequency was scanned from 1 MHz–0.01 Hz using a 5 mV amplitude perturbation. The values for resistances of individual components were determined with a fitting program. The half cells of Si-graphene electrode were cycled between 0.05 and 1.0 V_{Li+/Li}. The EIS tests of the half cells were performed at fully charged (delithiated electrode) states of 0.75–0.78 V_{Li+/Li}.

2.4. Postmortem analysis

For surface characterization, the cells were opened in an Ar-filled glove box and washed gently for 5 min in extra pure dimethyl carbonate (DMC) solvent (*Sigma Aldrich*) to remove Li salts, and the samples were stored in the packs filled with Ar before analysis.

To observe the morphologies of the surface of the electrodes, the High Resolution (HR)-SEM (*Hitachi SU8000*) was used. To observe the morphologies of SEI layers and measure the thickness, the electrode surfaces were cut with cubic shapes (10 × 10 × 5 μm) by a focused ion beam (FIB), and then the inside cross-section was observed using a SEM (*Nova nanolab FEI 200*).

To examine the compounds of SEI compound, X-ray photoelectron spectroscopy (*Kratos XPS*) analysis was performed. The obtained XPS peaks were separated into several peaks with a fitting program (*XPS Peak*), and then the separated peaks were confirmed as individual chemical components by indexing the binding energy.

3. Results and discussion

3.1. Effect of FEC content on the formation cycle and capacity fade

Fig. 1(a) shows the capacity fade of the full-cells (anode: Si-graphene, cathode: NCA) for 0, 5, 10, and 20 wt.% FEC in EC:DEC (1:1 wt.%) electrolyte with 1 M LiPF₆. The cell was charged and discharged at C/2 except for 1st cycle (C/15). The cell with 5% FEC showed the highest capacity and highest capacity retention through 50 cycles. The values of charge capacity and capacity retention are summarized in Table 1. Whereas the charge capacity of the cell with 5% FEC increased slightly as shown in Fig. 1(b), the charge capacity of the other cells decreased by an average of 25.6% between the 1st and 2nd charges. Although the cell with 5% FEC showed a large decrease in 1st discharge capacity similar to the others, its capacity was almost recovered beginning with the 2nd charge cycle. This behavior is considered likely due to complete formation of more stable SEI layer in the 1st discharge cycle of the cell with 5% FEC. It is evident that the cell with 5% FEC exhibited higher coulombic efficiency than the cell without FEC, especially during the first ten cycles (Fig. 1(c and d)). In particular, the efficiency of the cell with 5% FEC exceeded 99.0% after the 3rd cycle.

The cells with 10% and 20% FEC behaved the same as the cell without FEC on the 1st cycle, but after the 3rd cycle the capacities for cells with FEC recovered slightly and then stabilized. These data indicate that the SEI layer becomes stable after 5 cycles. After 25 cycles, the capacity of the cells with 10 and 20% FEC was about 15% lower than that for the 5% FEC cell, but more than 16% higher than that the cell without FEC (0% FEC). After the initial cycles, the rate of capacity decrease was similar for all cells.

From the above results, it is notable that FEC additive can improve the initial irreversible capacity loss of the full-cell employing Si-graphene anode during initial formation cycling.

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