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Short communication

Improved cycling performance of Si nanoparticle anodes via incorporation of methylene ethylene carbonate

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ABSTRACT

Methylene ethylene carbonate (MEC) has been investigated as an alternative additive to fluoroethylene carbonate (FEC) for Si nanoparticle anodes cycled with 1.2 M $LiPF_6$/ethylene carbonate (EC): diethyl carbonate (DEC) (1:1, w/w) electrolyte. The Si electrodes cycled with 10% MEC-added electrolyte exhibit significantly improved capacity retention after 100 cycles compared to standard electrolyte (73% vs 46%). In addition, the Si electrode cycled with MEC additive has less damage from cracking than the standard electrolyte. Ex situ surface analyses via infrared and X-ray photoelectron spectroscopy reveal a solid electrolyte interphase (SEI) containing a high concentration of a poly(MEC), which is likely responsible for the improved performance of Si anodes.

1. Introduction

Si has been intensively investigated as anode material for lithium ion batteries due to its high theoretical capacity of 3579 mAh/g, which is ten times higher than graphite anodes (372 mAh/g) [1]. However, the large volume change of Si anodes (~280%) upon cycling causes particle pulverization and loss of electrical connection within electrode components [1]. Another problem associated with the large volume change of Si particles is the repeated formation and destruction of the protective solid electrolyte interphase (SEI) which consumes active lithium. One efficient strategy to improve cycling performance of Si anodes is incorporation of electrolyte additives to generate a more stable SEI. Fluorothylene carbonate (FEC) is currently considered as the best additive for enhancing capacity retention of Si anodes [2,3]. FEC is reduced on the Si surface to form an SEI consisting of a combination of poly(FEC) and lithium salts such as lithium alkyl carbonate, lithium carbonate, and lithium fluoride [3,4]. The use of silicon/graphite composite electrodes retains some of the increased capacity of silicon but provides much better capacity retention upon cycling. However, recent investigations suggest that high concentrations of FEC increase the reactivity of the electrolyte with lithiated graphite resulting in large capacity loss [5]. The high concentration of FEC also causes significant gas evolution in graphite/$LiCoO_2$ full cells compared to VC and standard electrolyte [6]. Finally, the cycling performance of Si-graphite/NCM111 full cells with 10% VC was found to be better than 10% FEC [7]. These problems hinder the practical use of Si-graphite composite electrodes in commercial cells since a high concentration of FEC is required to stabilize the added silicon. The use of methylene ethylene carbonate (MEC, Fig. 1a) has been previously reported to significantly improve cycling performance of graphite/NCM111 cells at elevated temperature with no evidence of significant gas evolution [8,9]. The improvement is likely due to the formation of a high concentration of a polycarbonate derived from MEC, poly(MEC), on the electrode surface.

Herein, we report effects of MEC on cycling ability, surface chemistry, and morphology changes of Si electrodes utilizing charge–discharge cycling, field-emission scanning electron microscopy (FE-SEM), attenuated total reflection infrared (ATR-IR), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Silicon (≤50 nm, Alfar Aeasar), super C (Timcal), and sodium carboxymethyl cellulose (CMC, 7000,000, Aldrich) and poly(acrylic acid) (PAA, 450,000, Aldrich) with a ratio of 50: 25: 12.5: 12.5 (in weight) [10] were thoroughly mixed in distilled water. The well mixed slurry was spread on copper foil and dried in air. The electrodes were then punched into 14.0 mm diameter disks and dried at 110 °C in a vacuum oven for 6 h, followed by another 4 h at 150 °C. The electrode loading is ~1 mg of Si/cm^2.

Solvents, salts, and additives were obtained from BASF and used as received. 2032 coin cells consist of a Si working electrode, a lithium foil counter electrode, 100 μl of electrolyte, and two separators (one Celgard 2325 and one Whatman GF/D glass fiber). The standard

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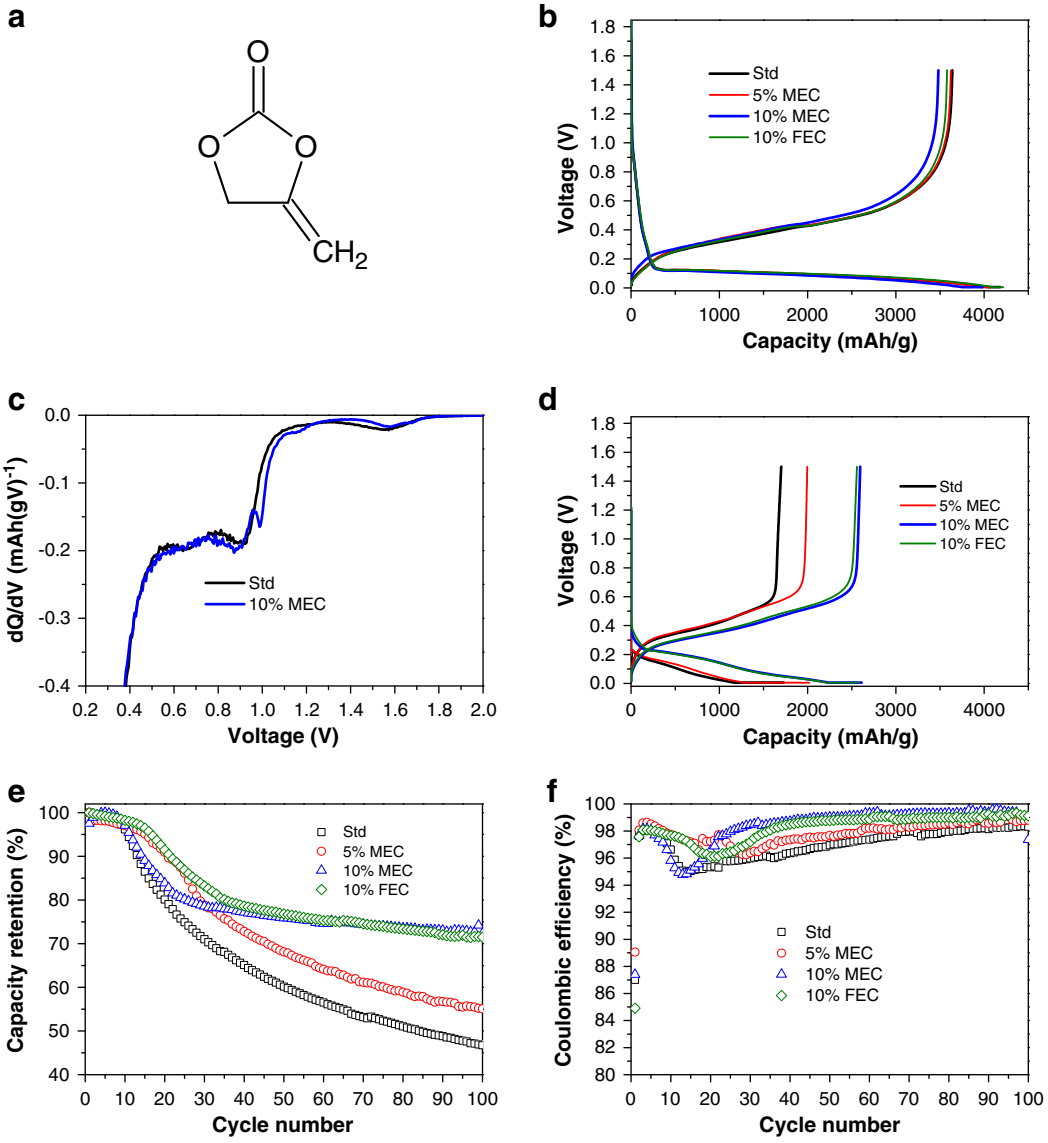

Fig. 1. Structure of methylene ethylene carbonate (MEC) (a), voltage profiles (b), and their differential capacity plots (c) for first cycle, voltage profiles after 100 cycles (d), capacity retention (e) and coulombic efficiency (f) as a function of cycle number of Si electrodes in different electrolytes.

electrolyte was 1.2 M $LiPF_6$/EC: DEC (1:1, w/w). MEC and FEC were added into standard electrolyte with 5–10 wt.%. The cells were charged (lithiation) and discharged (delithiation) between 0.005 and 1.5 V with constant-current and constant voltage (CC-CV) at a rate of C/20 for first cycle and C/3 for an additional 99 cycles using an Arbin BT2000 battery cycler at 25 °C. At the end of lithiation, the voltage of the cells was held at 0.005 V until the current decreases to C/40 for first cycle and C/20 for the subsequent cycles. The rate was calculated based on the theoretical capacity of Si at 3579 mAh/g.

Prior to ex situ analysis, cycled electrodes (100th delithiation) were carefully rinsed with DMC four times (1 mL in total) to remove residual electrolyte and then dried in a glove box. Infrared spectra with attenuated total reflectance (IR-ATR) were measured with 512 scans and a spectral resolution of 4 cm^{-1} using a Bruker Tensor 27 equipped with LaDTG detector inside a nitrogen-filled glovebox. Surface compositional analysis was conducted using ex situ XPS (K-alpha, Thermo) with Al K_α X-ray source and measured spot size of 400 μm. The electrodes were transferred from the glove box to the XPS analysis chamber using a special vacuum-sealed module (Thermo) without exposure to air at any time. The binding energy was corrected based on the C 1 s of hydrocarbon at 285 eV. The change in surface morphology before and after cycling was examined by ex situ SEM (Sigma VP, Zeiss Carl).

3. Results and discussions

The electrochemical cycling data of Si/Li cells cycled with standard electrolyte with and without added MEC are presented in Fig. 1b–f. The cycling data of Si with 10% FEC are also included for comparison. All cells show similar initial voltage profiles with initial delithiation capacity of about 3600 mAh/g, based on weight of silicon (Fig. 2.b). The dQ/dV plots for the first charge (Fig. 1c) for cells cycled with standard electrolyte exhibit peaks at ~0.9 and 0.65 V due to the reduction of EC and DEC [11]. An additional peak observed at ~1.6 V is likely from the reduction of the hydroxyl groups of the PAA and CMC binders. The cell cycled with 10% of added MEC contains an additional new peak at ~1 V, which is likely due to the reduction of MEC, forming poly(MEC) as previously reported [8]. The electrode cycled with standard electrolyte has rapid capacity fade to 1500 mAh/g, corresponding to 46% capacity retention (Fig. 2d and e), over the first 100 cycles. Addition of MEC into the standard electrolyte dramatically improves both capacity