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High performance silicon nanoparticle anode in fluoroethylene carbonate-based electrolyte for Li-ion batteries†

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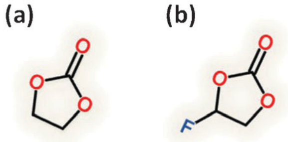
Electrodes composed of silicon nanoparticles (SiNP) were prepared by slurry casting and then electrochemically tested in a fluoroethylene carbonate (FEC)-based electrolyte. The capacity retention after cycling was significantly improved compared to electrodes cycled in a traditional ethylene carbonate (EC)-based electrolyte.

We report excellent performance from a silicon Li-ion battery anode made with commercially-available Si nanoparticles by conventional slurry-casting with a 1 : 1 fluoroethylene carbonate:dimethyl carbonate electrolyte exhibiting reversible capacities of (i) 2.6 Ah g^{-1} when cycled 100 times at 0.2 C and (ii) 2.0 Ah g^{-1} for 250 cycles at 1 C. To the best of our knowledge, this is the first demonstration of stable, high rate capacity results for a slurry cast, silicon particle based anode using an electrolyte with FEC as a co-solvent. For utility, electrodes to be used in lithium ion batteries must simultaneously meet criteria of manufacturability, safety, high capacity, high Coulombic efficiency, high power density and long cycle life.[1] One of the promising alternatives for the conventional graphite anode is silicon because of its high capacity for lithium storage: its maximum theoretical capacity of 3579 mAh g^{-1}, corresponding to the formation of a $Li_{15}Si_4$ alloy upon full lithiation at room temperature,[2] is nearly tenfold higher than that of graphite. However, the lithiation/de-lithiation of Si is associated with a large volume change that typically results in unacceptable rapid capacity fade within a few cycles.[3] It is well known that nanostructured electrode materials not only better accommodate large strains but also provide short diffusion distances in the small grains necessary for rapid Li^+ insertion/de-insertion.[4] Hence, electrode performance has been improved with nanostructured Si for a range of morphologies.[5] Most of this previous research has been conducted employing an ethylene carbonate (EC)-based electrolyte containing lithium salt, with the chemical structure shown in Scheme 1a. Fluoroethylene carbonate (FEC, 4-fluoro-1,3-dioxolan-2-one), with the chemical structure shown in Scheme 1b, was first reported as an alternative solvent for Li-ion batteries with graphite anodes by McMillan and coworkers.[6]



Scheme 1 Chemical structures of (a) ethylene carbonate (EC) and (b) fluoroethylene carbonate (FEC).

Thus far, only Si thin film anodes have been investigated with electrolytes containing FEC. Choi and coworkers were the first to use FEC-added electrolytes with silicon thin film electrodes. They reported that a low concentration of FEC (3%) added to an EC-based electrolyte resulted in a smoother solid electrolyte interface (SEI) layer on the silicon film.[7] Nakai and coworkers further investigated the formation of SEI on Si thin film electrodes in a FEC-based electrolyte (EC was totally replaced by FEC).[8] They concluded that the FEC-derived SEI on the Si thin film was thinner and more stable than the EC-derived SEI, thus improving the capacity retention of the Si anode. Recently, Aurbach and coworkers reported positive effects from FEC as a co-solvent for thin film Si-nanowire anodes which were prepared by a vapour-liquid-solid (VLS) method.[9]

These previous works all showed the attractive merits of using FEC for Si thin film electrodes. However, these anode are not well suited for industrial scale-up. Electrodes for commercial lithium ion batteries are commonly manufactured by casting a slurry comprised of active material, conductive additive, and polymer binder onto a current collector, rather than the thin film electrodes described above. Herein, we report on tests of silicon nanoparticle (SiNP) anodes made by a conventional slurry casting process matched with FEC-based electrolytes. Our results using the FEC : DMC electrolyte have practical importance for the engineering of stable silicon based anodes with improved performance at high charge rates but also have scientific value when combined with consideration of the poor cycling performance we report

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for the nominally identical anodes tested using EC-based electrolytes: an expanded or revised model for understanding capacity fade may be needed to explain how the same nanosized active material either sustains stable cycling performance or rapidly deteriorates during identical testing regimes.

A scanning transmission electron microscopy analysis (Fig. S1 in the Electronic Supplementary Information, ESI†) of the commercial Si powder shows that it has a bimodal particle size distribution in which the majority of the particles are smaller than 200 nm (Fig. S2 in the ESI†). In order to evaluate the electrochemical performance, electrodes made of SiNPs with sodium carboxymethyl cellulose (CMC) as the binder and carbon black as the conductive additive on Cu-substrates were incorporated into coin cells. Cells were made with: (i) 1 M $LiPF_6$ in EC/DMC (1 : 1), a commercially available EC-based electrolyte for current Li-ion batteries, (ii) 1 M $LiPF_6$ in FEC/DMC (1 : 1), a home made FEC-based electrolyte, or (iii) 1 M $LiPF_6$ in FEC/EC/DMC (1 : 1 : 2). The cells were cycled between 10 mV and 1 V *versus* Li/Li^+ at a 0.2 C rate (716 mA g_{Si}^{-1}), corresponding to a rate of fully charging or discharging the cell within 5 h.

Fig. 1 shows the performance of the cells made with the EC-based (50% EC) and the FEC-based (50% FEC) electrolytes when fully charged/discharged (the detailed voltage profiles can be seen in Fig. S3a and S3b in the ESI†). Reversible capacities for SiNP electrodes in EC and FEC-based electrolytes cycled at 0.2 C rate up to 100 cycles are shown in Fig. 1a. The reversible capacity of the SiNP electrode in the EC-based electrolyte is 2353 mAh g^{-1} for the initial cycle, which gradually increases to a peak value of ~2800 mAh g^{-1} after 10 cycles and then continuously decreases to 1157 mAh g^{-1} by the 100th cycle. The SiNP electrode in the FEC-based electrolyte has an initial capacity of 2142 mAh g^{-1}, slightly lower than that of the same electrode in the EC-based electrolyte. Similarly to the electrode in the EC-based electrolyte, the electrode cycled in the FEC-based electrolyte reaches a maximum capacity of ~2800 mAh g^{-1} after a few cycles. However, unlike the electrode in the EC-based electrolyte, the SiNP electrode in the FEC-based electrolyte demonstrates significantly improved stability during prolonged lithium insertion/de-insertion cycling, with 95% of the reversible capacity being retained from the 10th cycle to the 100th cycle (Fig. 1b). The Coulombic efficiencies in the first cycle are 80% for the electrode in the EC-based electrolyte and 72% for the electrode in the FEC-based electrolyte (Fig. 1c). However, the SiNP electrode in the EC-based electrolyte shows lower efficiencies than with the FEC-based electrolyte after the second cycle. The low Coulombic efficiency (~95%) after ~30 cycles for the electrode in the EC-based electrolyte can be correlated to the pronounced capacity fading between the 20th and the 50th cycles. Although the first cycle efficiency of the SiNP electrode in the FEC-based electrolyte is lower, it quickly increases to 98% within 10 cycles and eventually exceeds 99%. The high Coulombic effiency of the SiNP electrode in the FEC-based electrolyte results in significantly improved electrochemical stability for lithium storage when compared to the same electrode in an EC-based electrolyte.

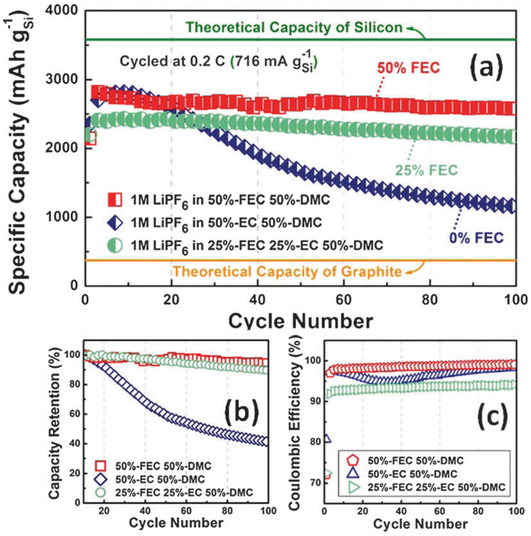

Fig. 1 (a) Reversible capacity (b) capacity retention and (c) Coulombic efficiency of SiNP electrode cycled in various electrolytes at a 0.2 C rate (716 mA g_{Si}^{-1}). (The mass loading of Si is ~200 μg cm^{-2}).

SiNP electrodes were tested in 1 M $LiPF_6$ in FEC/EC/DMC (25%/25%/50%), as the results in Fig. 1 show. The reversible capacities are lower in 25% FEC compared to the results in 50% FEC, but still show much better stability than in the 50% EC. Interestingly, the Coulombic efficiency of SiNP electrodes in 25% FEC was the lowest among these three electrolytes. A supplemental study of the differential capacity plot (Fig. S4) along with additional discussion can be found in the ESI.† Besides being used as a primary cosolvent, FEC was also tested as an additive in the EC-based electrolyte. Fig. S5 in the ESI† shows the result of the SiNP electrode cycled in 1 M $LiPF_6$ in EC/DMC with and without 3% FEC at a charge/discharge rate of C/10. Although adding a small amount of FEC (3%) into the EC-based electrolyte can slightly improve the cycling stability, the capacities still dropped rapidly after 20 cycles. Combined with the cycling test data shown above, these results suggest that the more FEC present (up to 50%) in the electrolyte, the better the cycling performance.

Electrochemical impedance spectroscopy (EIS) of the SiNP electrode tested in the EC-based electrolyte after 100 cycles at a 0.2 C rate are presented in a Nyquist plot (Fig. 2a). The plot consists of two semicircles in the high frequency region which can be attributed to charge transfer processes, and a sloped line in the low frequency region that is related to the mass transfer of lithium ions. The first small semicircle represents the contribution of the charge transfer between the electrolyte and the SEI (as indicated by the green arrow in the inset of Fig. 3a), and the second semicircle represents the charge transfer between the SEI and the silicon. The electrochemical system can be modeled by an equivalent circuit as shown in Fig. 2b,[10] where R_Ω is the ohmic resistance, R_{SEI} is the charge resistance between the SEI layer and the electrolyte, R_{CT} is the charge transfer resistance between the SEI and Si, C_{SEI} is the capacitance of the SEI, C_{dl} is the double layer capacitance on Si, and Z_W is the Warburg impedance describing the solid state diffusion of Li^+ in the electrode. The charge transfer resistances are determined to be 8 Ω (R_{SEI}) and 57 Ω (R_{CT}) for

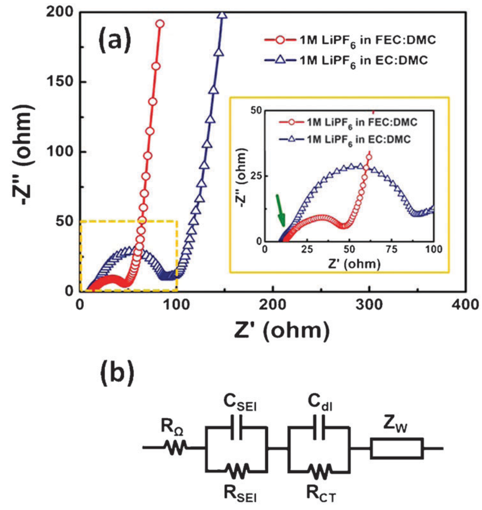

Fig. 2 (a) Electrochemical impedance spectroscopy of SiNP electrodes cycled in EC and FEC-based electrolyte after 100 cycles with an inset that shows a zoom view of Z′ between 0 and 100 ohms. (The green arrow indicates a small semicircle contributed by the SEI derived from the EC-based electrolyte.) (b) Equivalent circuit.

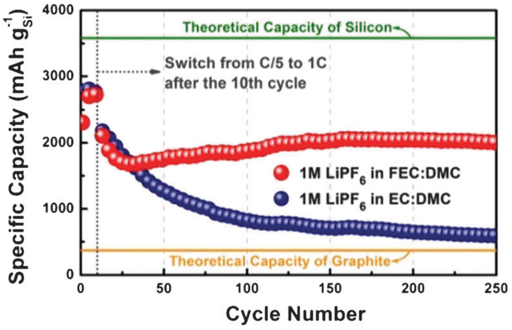

Fig. 3 Reversible capacity *vs.* cycle number of SiNP electrodes cycled in EC and FEC-based electrolyte at C/5 (716 mA $g_{Si}{}^{-1}$) for the initial 10 cycles and switched to 1C (3.6 A $g_{Si}{}^{-1}$) for subsequent cycles.

the electrode cycled in the EC-based electrolyte. The Nyquist plot of the SiNP electrode cycled in the FEC-based electrolyte at the same rate and cycle numbers is also shown in Fig. 2a. Unlike the electrode cycled in the EC-based electrolyte, only a single semicircle can be observed for the SiNP electrode cycled in the FEC-based electrolyte. The absence of the first semicircle implies that the resistance through the FEC-derived SEI is negligible, consistent with the thin SEI formation on thin film Si in a FEC-based electrolyte reported by Nakai and coworkers.[8] The SiNP electrode cycled in the FEC-based electrolyte has a charge transfer resistance (R_{CT}) of $\sim$34 Ω, smaller than the electrode cycled in the EC-based electrolyte, indicative of the ease of interfacial charge transfer between Si and the FEC-derived SEI.

In order to further investigate the high rate performance of the SiNP electrodes, galvanostatic tests were carried out by applying a higher current density onto electrodes within the same voltage window (10 mV to 1 V) in the EC and the FEC-based electrolyte, separately. Cells were initially tested for 10 cycles at 0.2 C (716 mA g^{-1}) followed by continuous charging/discharging at 1 C (3.6 A g^{-1}) up to 250 cycles, and their reversible capacity for lithium storage as a function of cycle number is shown in Fig. 3. The SiNP electrodes in both electrolytes show capacities of $\sim$2800 mAh g^{-1} at their 10th cycle tested at 0.2 C, consistent with the previous results in this communication. After switching to a 1 C rate, the capacity of the electrode in the EC-based electrolyte monotonically decays to $\sim$600 mAh g^{-1} after 250 cycles. However, the capacity of the SiNP electrode in the FEC-based electrolyte continued increasing from the 30th cycle to the 160th cycle before attaining stable reversible capacity. A linear fit from cycle 160 to cycle 250 shows that the rate of capacity fade is only $\sim$0.57 mAh g^{-1} per cycle, or $\sim$0.03% per cycle. The Coulombic efficiencies for these cycles are in a range from 99.4% to 99.6%. At the end of the cycling test, a reversible capacity of more than 2000 mAh g^{-1} is achieved for the SiNP electrode cycled at 1 C within the FEC-based electrolyte.

In conclusion, slurry cast silicon nanoparticle-based electrodes matched with an electrolyte containing fluorinated ethylene carbonate were electrochemically tested in coin cells *vs.* Li/Li$^+$. The SiNP electrode in the FEC-based electrolyte outperforms the electrode in the conventional EC-based electrolyte in terms of capacity retention and Coulombic efficiency. The improved performance of the SiNP electrode in the FEC-based electrolyte is attributed to the better properties of the FEC-derived solid electrolyte interface on the surface of the silicon. Future work will further characterize and investigate the properties of these alternative electrolytes and their effect upon the silicon anode system.

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