Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

for

High Performance Silicon Nanoparticle Anode in Fluoroethylene Carbonate-Based Electrolyte for Li-ion Batteries

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Experimental Section

The silicon nanoparticles (average particle size ≤ 50nm, 98%) in this study were purchased from Alfa Aesar and used without any further treatment. The SiNP electrodes were prepared by forming an aqueous slurry of the SiNP (40 wt%), conductive carbon black (Super P-Li, Timcal) (40 wt %) and 90 kDa CMC (Aldrich) (20 wt %) in a stirring tube (ST-20, IKA). The slurry was cast onto a Cu foil using an automatic applicator and a notch bar with 50 µm clearance and then dried in a vacuum oven at 120°C for 12 hrs. The final film thicknesses are around 12 µm. Typically, the mass loading of materials on Cu foil is ~500 µg/cm^2, which contains ~200 µg/cm^2 of Si. After cooling to room temperature, the cast film was punched into disks, which constituted the working electrodes of 2032 type coin cells. The cells, assembled in an argon filled glove-box, had lithium foil counter/reference electrodes, polypropylene (Celgard 2400, Celgard) membrane separators and used for the electrolyte either: i) 1M $LiPF_6$ in EC/DMC (1:1) (LP30, EMD Chemicals), ii) 1M $LiPF_6$ (≥ 99.99%, Aldrich) in FEC (> 99%, Solvay Chemicals)/DMC (≥ 99%, Aldrich) (1:1), or iii) 1M $LiPF_6$ in FEC/EC/DMC (1:1:2). The cells were galvanostatically cycled at room temperature using a multichannel battery test system (BT 2043, Arbin), all the specific capacities are calculated based on the weight of silicon. An electrochemical analyzer (CHI 604D, CH Instruments) was used for EIS, carried out over a wide frequency range from 100 kHz to 0.01 Hz with an ac perturbation voltage of 5 mV.

Supplementary Figures

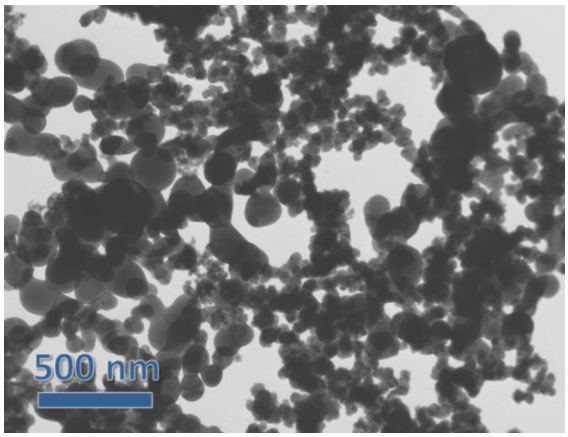

Figure S1. STEM image of Si nanoparticles.

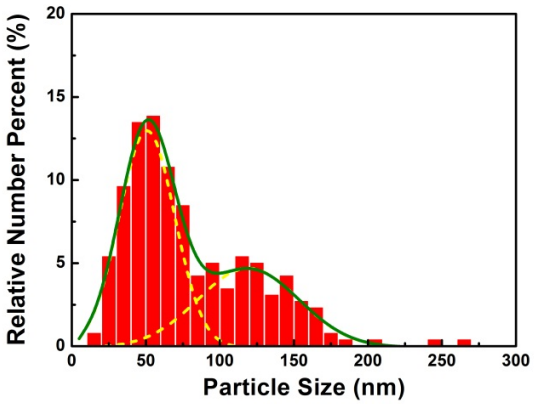

Figure S2. Particle size distribution of Si nanoparticles by measuring the sizes of the 250 particles in the STEM image shown above.

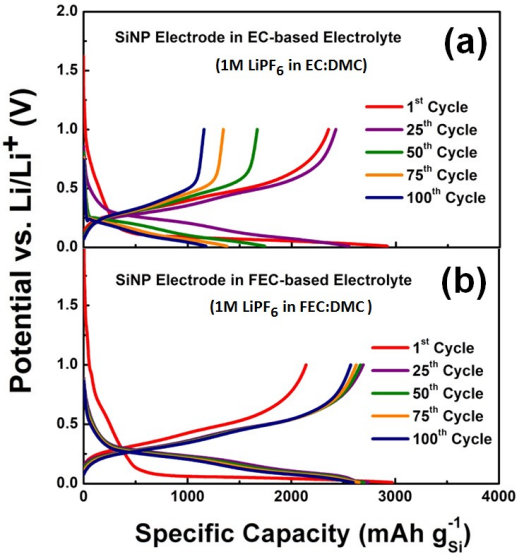

Figure S3. Charge and discharge curves of SiNP electrodes cycled in (a) EC-based electrolyte and (b) FEC-based electrolyte at a 0.2 C rate (716 mA g_{Si}^{-1}).

A supplemental study for four select cycles (1, 2, 33, and 100) of the differential capacity as a function of the potential of the SiNP anodes tested in different electrolytes was done to provide information about the phase transformation of the SiNP during lithiation and delithiation and about the chemistry responsible for the irreversible capacity losses. The profiles were generated from the galvanostatic cycling data by taking the first order derivative of the capacity values with respect to the voltages (Figure S4). The first cycle irreversible capacities for each of the anodes is shown in Table S1. SEI formation is believed to begin forming around 1V for both EC and FEC electrolytes (Figure S4a),[1] but the capacity contributions from reactions at potentials above the onset of silicon lithiation at 150 mV does not fully account for the irreversible capacity losses (Table S1), suggesting that SEI formation may be continue to occur during the lithiation of the crystalline silicon (corresponding to the sharp peaks below 150 mV). This is potentially due to re-formation of SEI as the layer is damaged by the expansion of the silicon active materail during lithiation. The second cycle lithiation profiles (Figure S4b) for each anode shows the persistance of the low voltage feature attributed to the lithiation of crystalline silicon. It has shifted to higher overpotentials near or below 50 mV and has decreased magnitude. This indicates that the particles were not fully lithiated in the first cycle. However, for each anode after their first cycle, the majority of the lithiation of the SiNP occurs during the two amorphous lithiation peaks (Figure S4b-d), as reported in other works.[2] In the second cycle, the Coulombic efficiency for the FEC:EC:DMC is low, 91.0% vs 95.3% for the FEC:DMC. The relatively high irreversible capacity of the electrode in FEC:EC:DMC (which presists throughout the cycling test, climbing only to 94.1% by cycle 100 vs. the 99.1% then observed for the FEC:DMC), yet stable capacity is inconsistent with a model where the irreversible capacity results in a continual thickening of the SEI layer.

Comparison of the electrodes in EC:DMC and FEC:EC:DMC consistently show greater irreversible capacity losses for the electrode in FEC:EC:DMC, despite its relatively stable cycling performance and the significant capacity fade observed for the EC:DMC anode. From cycle 1 to 100, the reversible capacity of the electrode in EC:DMC declines by 51% while that of the electrode in FEC:EC:DMC declines by just under 2%, a result comparable to the performance of the FEC:DMC (which shows an increase in performance when comparing cycles 1 vs 100). The lack of significant capacity fade coupled with consistently low Coulombic efficiencies for the FEC:EC:DMC suggests that the presence of EC in the electrolyte degrades the quality of the SEI layer, but does not negate all of the benefits of including FEC in the electrolyte.

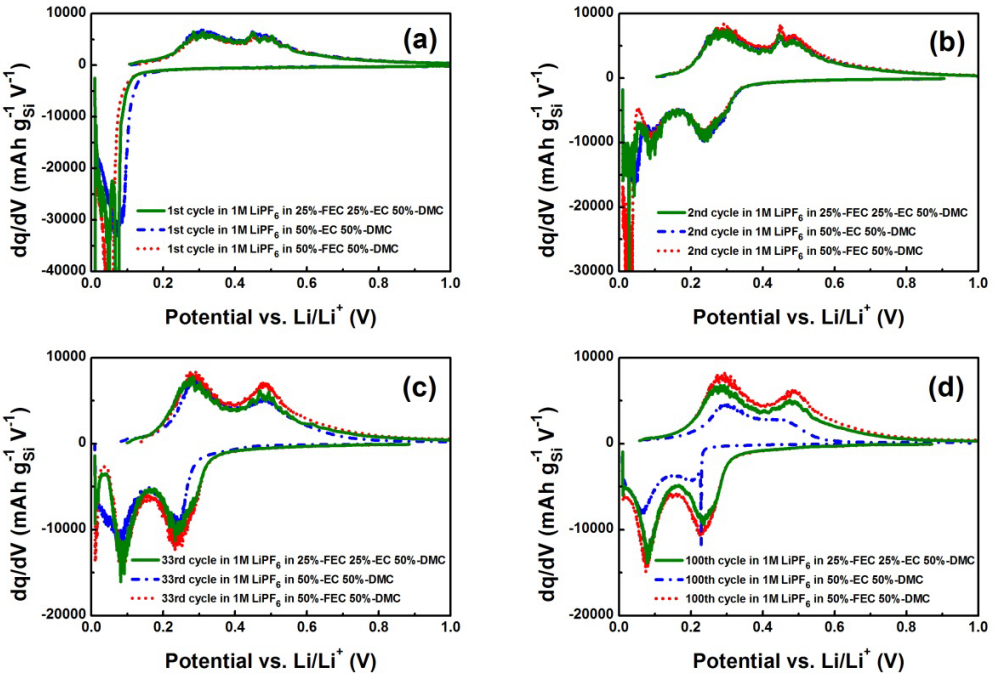

Figure S4. Differential capacity plots of the cycles of SiNP electrodes in the EC-based electrolyte (blue desh-dotted), FEC:EC electrolyte (green line) and in the FEC-based electrolyte (red dotted) for cycles (a) 1, (b) 2, (c) 33 (corresponding to the minimum Coulombic efficiency for the cycling of the EC:DMC anode) and (d) 100.

Table S1. Summary of the reversible capacity, irreversible capacity and Coulombic efficiency of SiNP electrodes cycled in different electrolytes at a 0.2 C rate (cycle 1, 2, 33 and 100).

Cycle 1	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)	Coulombic Efficiency (%)	Contribution to Lithiation Capacity > 150 mV (mAh/g)
EC:DMC	2353	564	80.7	371
FEC:EC:DMC	2201	835	72.5	391
FEC:DMC	2142	830	72.1	480

Cycle 2	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)	Coulombic Efficiency (%)
EC:DMC	2577	89	96.7
FEC:EC:DMC	2385	237	91
FEC:DMC	2715	134	95.3

Cycle 33	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)	Coulombic Efficiency (%)
EC:DMC	2147	119	94.8
FEC:EC:DMC	2368	168	93.4
FEC:DMC	2673	45	98.4

Cycle 100	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)	Coulombic Efficiency (%)
EC:DMC	1157	19	98.3
FEC:EC:DMC	2165	136	94.1
FEC:DMC	2573	23	99.1

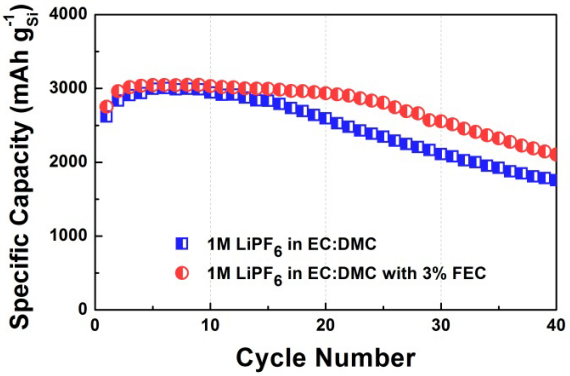

Figure S5. Reversible capacity vs. cycle number of SiNP electrdes cycled in 1M $LiPF_6$ in EC/DMC with and without 3wt% FEC at a rate of C/10 (357.9 mA g_{Si}^{-1}).

References

S1. N. S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim and S. S. Kim, *J. Power Sources*, 2006, **161**, 1254-1259.

S2. (a) M. N. Obrovac and L. J. Krause, *J. Electrochem. Soc.*, 2007, **154**, A103-A108; (b) C. K. Chan, R. Ruffo, S. S. Hong, R. A. Huggins and Y. Cui, *J. Power Sources*, 2009, **189**, 34-39.