Effect of Vinylene Carbonate on Graphite Anode Cycling Efficiency

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Vinylene Carbonate (VC) was added to the electrolyte in graphite-lithium half-cells. We report its effect on the coulombic efficiency (as capacity shift) of graphite electrodes under various formation cycling conditions. Cyclic voltammetry on glassy carbon showed that VC passivates the electrode against electrolyte reduction. The dQ/dV plots of the first lithiation of the graphite suggest that VC alters the SEI layer, and that by varying the cell formation rate, the initial ratio of ethylene carbonate to VC in the SEI layer can be controlled. VC was found to decrease first cycle efficiency and reversible capacity (in ongoing cycling) when used to excess. However, experiments with VC additive used with various formation rates did not show any decrease in capacity shift.

Introduction

Carbonaceous materials, graphite formulations in particular, are the current standard for battery anodes in electric vehicle lithium-ion batteries (1). To attain performance suitable for plug-in hybrid and all-electric vehicles, improvement in longevity of the graphite anode is needed. Electrolyte additives have proven useful for this purpose. For example, vinylene carbonate (VC) added to Propylene Carbonate/$LiPF_6$ electrolyte forms a Solvent-Electrolyte Interphase (SEI) layer on graphite anodes, preventing PC intercolation and reduction (and subsequent graphite exfoliaton) [2]. The addition of VC to EC-based $LiPF_6$ electrolytes is reported to improve performance of graphite anodes by reducing irreversible capacity, suppressing gas formation, and improving cycling behavior [3-7].

An important aspect of anode performance is the effectiveness of the SEI layer in inhibiting the side reactions which form it. The continuation of these side reactions reduces cycling efficiency and consumes electrolyte which reduces the lifetime of the cell. We probe the effect of VC and various rates of formation on these continuing side reactions by measuring the "fractional capacity shift" (8). HydroQuébec's SNG-12 anode graphite was chosen for this study because its relatively high capacity shift is a performance problem in need of a solution.

In the results section, we begin by studying the effect of VC on the electrochemistry of glassy carbon in EC-based LiPF6 electrolyte. Then we determine a basis for choosing the concentration of VC in the cell. This leads to our measurements of the reversible capacity of graphite in lithium half-cells as a function of VC concentration, followed by an examination of the effect of VC on the dQ/dV curves of the first lithiation of graphite.

Finally we show the effect of formation rate and VC concentration on the fractional capacity shift.

Experimental

Electrode laminates with SNG-12 graphite as the active material were provided by Hydro Québec, Inc (HQ). Coin cells were assembled in an argon atmosphere glove box (MBraun Unilab) with oxygen and water held below 5ppm and -80°C dewpoint respectively. Physical characterization of the graphite, the laminate, and coin cell fabrication and cycling instrumentation details have been published previously (8). Vinylene carbonate (Sigma-Aldrich) and our electrolyte (1M$LiPF_6$ in 1:2 EC:DEC) were used as received (9).

Cyclic voltammetry was done in the same argon atmosphere glove box, in a two-compartment glass cell with the working and reference electrode compartments separated by a glass frit, using a EG&G PAR 273A Potentiostat. The reference electrode was Li foil and the working electrode was glassy carbon (10).

Results

Cyclic voltammetry of glassy carbon in our electrolyte, without VC and with 5% VC are shown in Figure1a and 1b respectively. Both plots show two cycles between the initial OCV of the clean electrode, and a negative limit of 0.25 V vs. Li. The first cycle was a slow (0.2 mV/s) formation scan. The second cycle was done at 2mV/s. The reduction current on the second negative scan with 5% VC was less than 25% of the current in the second scan without VC. Thus the presence of VC increased passivation of the glassy carbon to reduction of the solvent mixture. This suggests that VC might decrease coulombic inefficiency due to electrolyte solvent reduction in the cycling of graphite electrodes.

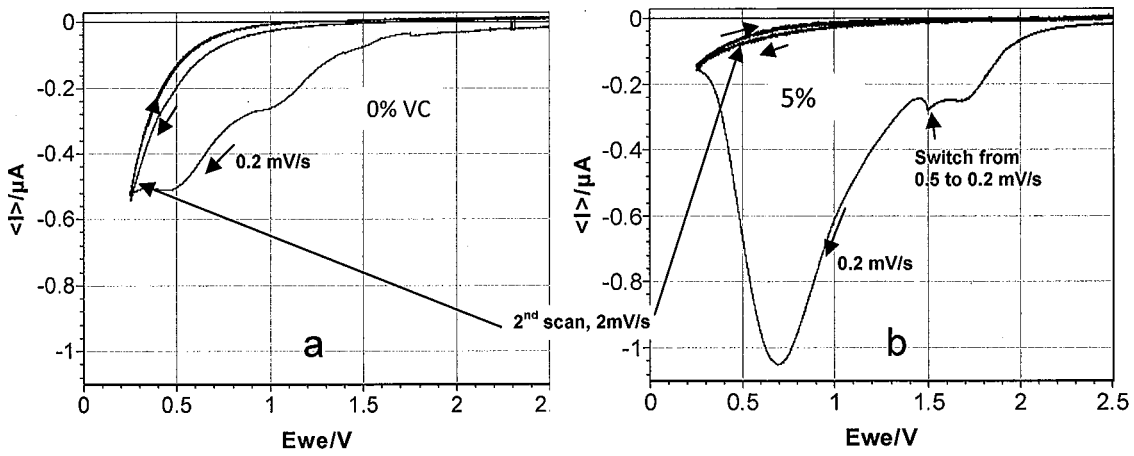

Figure 1. Cyclic voltammetry of glassy carbon in 1:2 EC:DEC, 1M $LiPF_6$ without VC (a) and with 5% VC (b).

Having decided, based on the CV data in Figure 1, to test the effect of VC on graphite anodes in coin cells with lithium counter electrodes, we considered a rationale for choosing the VC concentrations to test. Previous experiments with SNG-12 graphite in coin cells with this electrolyte versus lithium, gave first cycle coulombic efficiencies of ~84% (8). Assuming that capacity loss (~.2mAh) was due to electrolyte reduction at two electrons per molecule, ~4 μmol of solvent was reduced. To add that amount of VC to our coin cells we prepared electrolyte solution with 0.5% VC. To test the effect of additional VC, we also cycled cells with 2.5 and 15% VC, as well as 0%VC. The first cycle irreversible capacity and efficiency tabulated in Table 1 show that 0.5% VC has no effect on these performance measures, but the higher VC concentrations degrade cell performance by these metrics.

cell #	VC wt%	VC initial (umol)	Cyc1 irrev cap(mAh)	Elyte consumed @ 2e-(umol)	Cyc1 eff (%)
0a	0		0.20	3.8	83.6
0b	0		0.20	3.8	83.7
0.5a	0.5	3.5	0.21	3.9	82.1
0.5b	0.5	3.5	0.19	3.6	82.5
2.5a	2.5	17.4	0.25	4.7	79.7
2.5b	2.5	17.4	0.19	3.5	80.6
15a	15	104.6	0.24	4.5	61.6
15b	15	104.6	0.24	4.4	66.1

Table 1. First cycle performance of sng12 graphite-Li coin cells (30°C)

The reversible capacities of the first twelve cycles of these cells, plotted in Figure 2, also show no deleterious effect with 0.5%VC, but performance by this measure decreases at the higher VC concentrations tested.

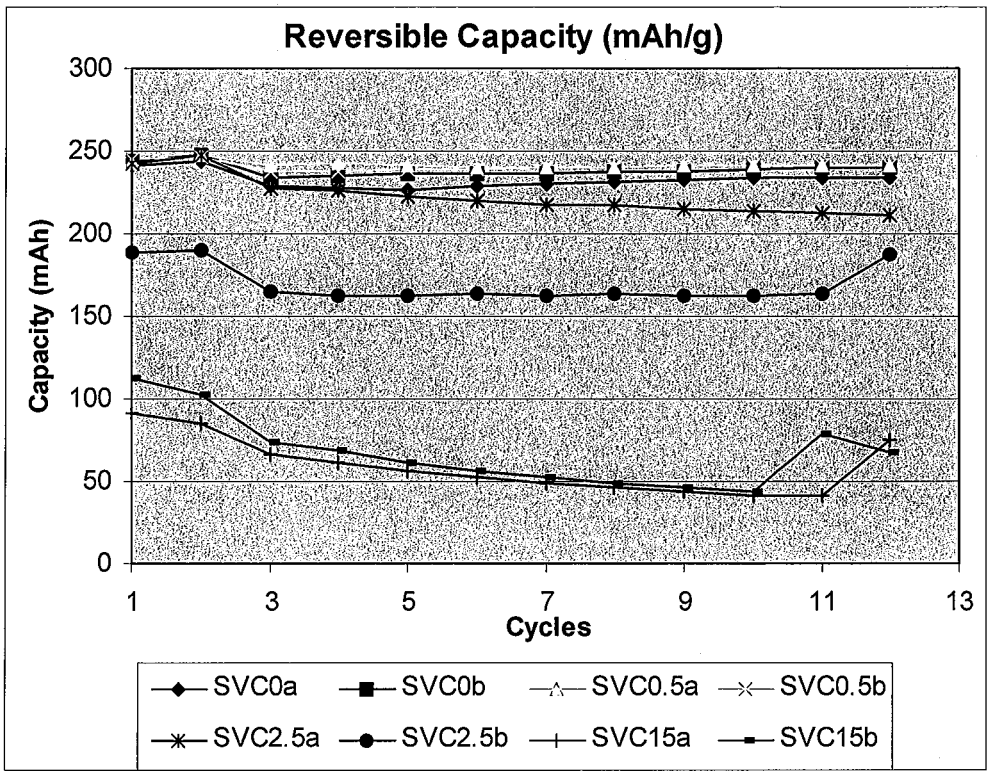

Figure 2. Reversible capacities vs. cycle of cells with 0%VC (blue), 0.5%VC(yellow), 2.5%(red), and 15%VC(green).

The fractional capacity shift (the per-cycle ratio of irreversible to reversible capacity) of these cells is shown in Figure 3. Contrary to our expectation, VC had no effect on the capacity shift in any of the concentrations tested.

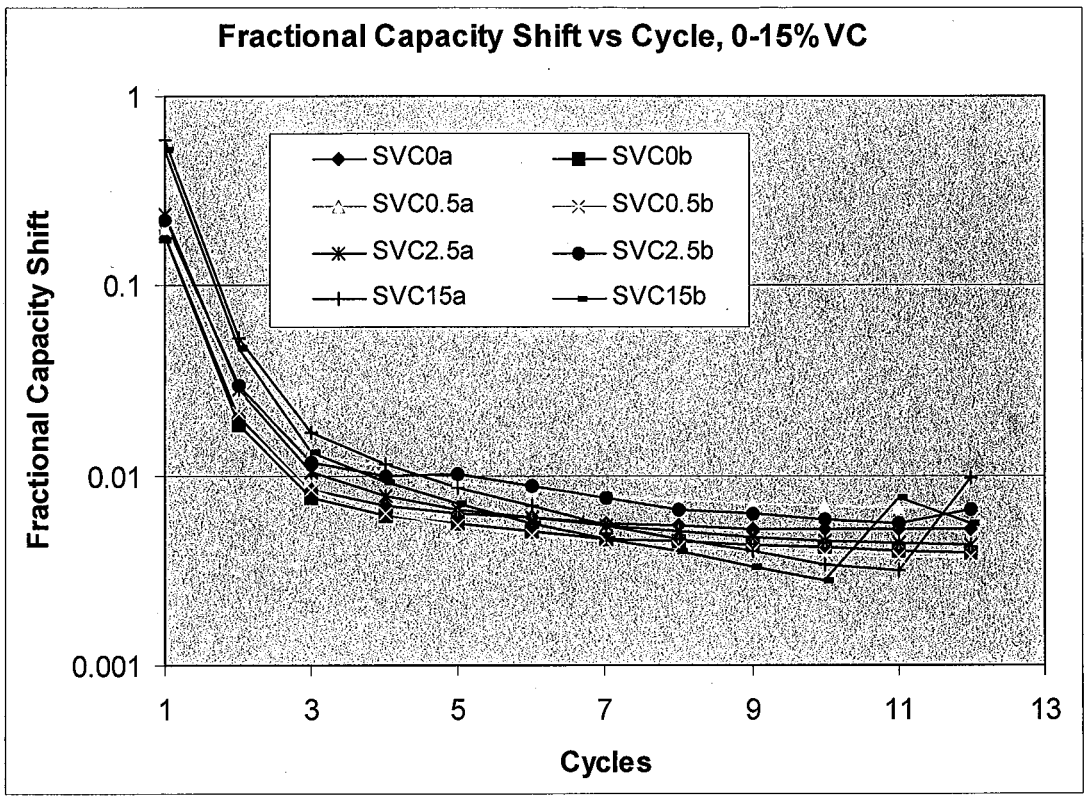

Figure 3. The fractional capacity shift vs. cycle of cells with 0%VC (blue), 0.5%VC (yellow), 2.5%(red), and 15%VC(green).

We then studied the dQ/dV curves of the first formation charge for these cells, which are shown in Figure 4. They indicate that as little as 0.5% VC reduces on the graphite electrode at 0.8V vs Li and suppresses the initial EC reduction which occurs in the absence of VC at 0.7V. This suggests that varying the formation rate, in particular making it very slow, would allow selective reduction of VC during the first cycle formation, which might increase electrode passivation to electrolyte reduction, as it had on glassy carbon as shown in Figure 1.

The capacity shift vs. cycle number for cells with 0, 0.5 and 2% VC at formation rates of C/50, C/100 and C/150 are compared with cells cycled without VC at our standard rate of C/24 are shown in Figure 5. Unfortunately, only one cell (formed at C/150, with 2% VC) showed a lower capacity shift than obtained at C/24 without VC, and it was not repeatable.

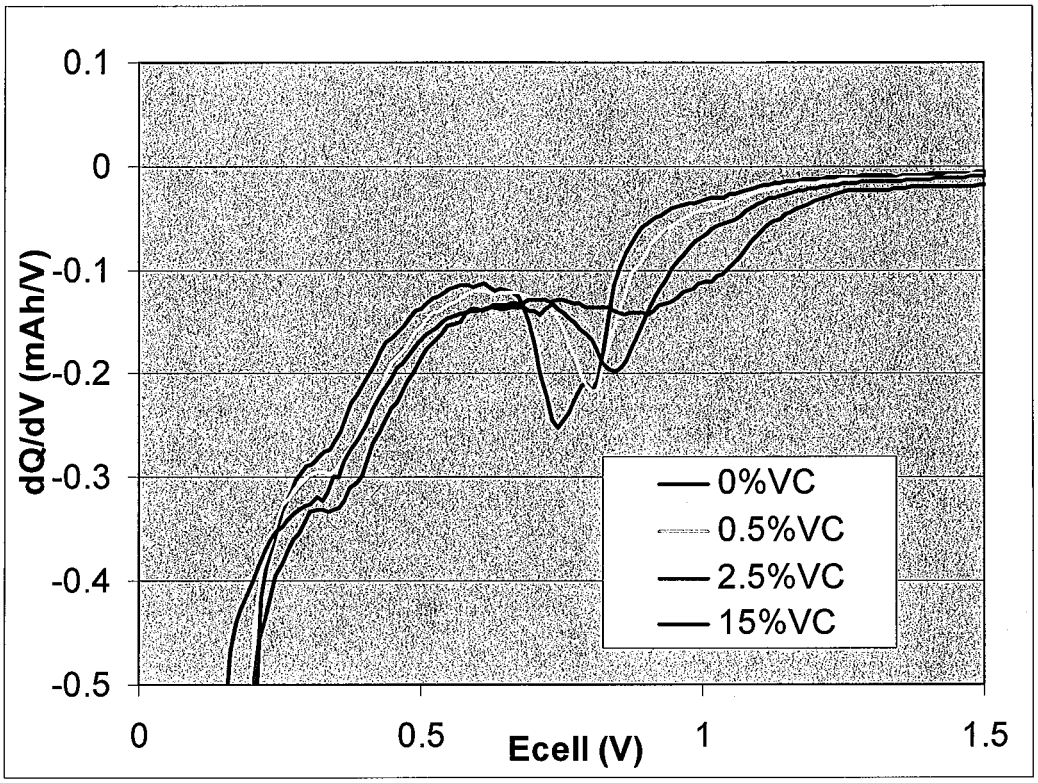

Figure 4. dQ/dV: SNG graphite vs. Li foil, 1:2 EC:DEC, 1MLiPF6, 0-15% VC, 1rst Charge, 2325 Coin cells, I=C/24

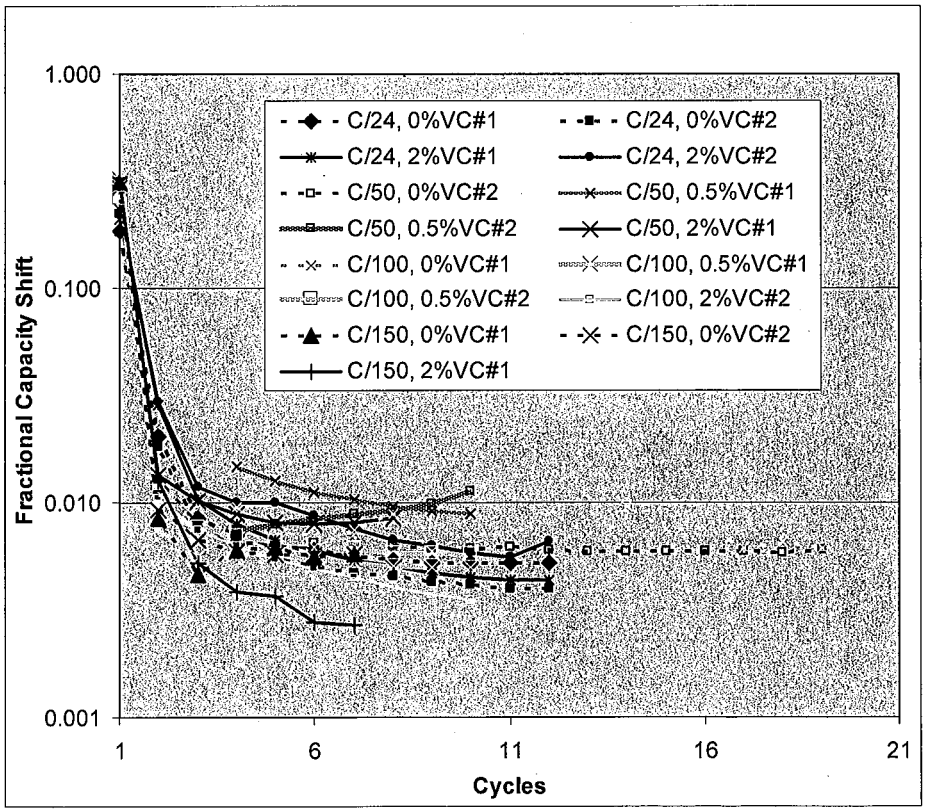

Figure 5. Capacity shift for cells formed at C/24, C/50, C/100 and C/150 with, 0, 0.5 and 2%VC.

Summary

Though cyclic voltammetry experiments showed that VC increases passivation of glassy carbon with respect to EC/DEC electrolyte solvent reduction, and dQ/dV curves of first cycle lithiation of graphite indicate that it is possible to preferentially reduce of VC on graphite by using low first-lithiation electrode formation rates, no reproducible effect of VC and/or formation rate on capacity shift was found.

Acknowledgments

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9. $LIPF_6$ and solvent purchased premixed from Ferro Corporation, 7500 East Pleasant Valley Rd, Independence OH 44131, USA. Vinylene carbonate from Aldrich was stabilized with <2% BHT
10. Working Electrode: 3mm dia glassy carbon, Bio-Analytical Systems