

# A High Precision Study of the Effect of Vinylene Carbonate (VC) Additive in Li/Graphite Cells

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Li/graphite coin cells containing different amounts of vinylene carbonate (VC) electrolyte additive were examined at different temperatures using the High Precision Charger at Dalhousie University. The charge endpoint capacities as well as the coulombic efficiency (CE) were compared to characterize the effect of the VC additive on the graphite electrode. The experiments show that VC improves the coulombic efficiency and reduces charge and discharge endpoint slippage at 50 and 60°C. However, the addition of VC has little evident effect on the performance of the graphite electrode at 30 and 40°C and also increases the irreversible capacity. By contrast, additions of VC have a marked impact on the coulombic efficiency and slippages of NMC positive electrodes, even at  $30^{\circ}$ C.

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The next generation of lithium ion batteries (LIBs) for electric vehicles and grid energy applications requires longer cycle life and longer calendar life than LIBs for computer and phone applications. Electrolyte additives can be selected and used to improve the lifetime of LIBs.<sup>1,2</sup>

Vinylene carbonate (VC) is one of the most studied electrolyte additives.<sup>3-6</sup> Aurbach et al. studied the effect of VC on the graphite electrode in Li/graphite half cells and found that VC can improve the capacity retention especially at elevated temperatures. This is because VC is reduced at higher potentials than the major solvent components and is thought to form flexible and cohesive polymeric surface products that serve as a better SEI. Aurbach et al. also found that VC did not have a pronounced impact on Li/LiMnO<sub>4</sub> and Li/LiNiO<sub>2</sub> half cells although it can also react with these positive electrode materials to make an SEI.<sup>3</sup> Ota el al. analyzed the impact of VC on the SEI on the graphite electrode and stated that VC has a major impact on the negative electrode and could also have some effect on the positive electrode.4,5 Recently, Ouatuni et al. stated that VC can react with both the negative and positive electrode materials through a radical polymerization mechanism.<sup>6</sup> Our research found that VC had a more significant effect on the positive electrode, by reducing the rate of electrolyte oxidation, than on the negative electrode.<sup>7,8</sup>

Here, the impact of VC on the coulombic efficiency and charge endpoint slippage of Li/graphite half cells is studied using the High Precision Charger at Dalhousie University.<sup>9</sup> Li/graphite cells with different electrode formulations and different amounts of VC additive were tested at temperatures between 30 and 60°C.

## Experimental

All cells were tested using the High Precision Charger at Dalhousie University.<sup>9</sup> This device is able to measure the CE of cells cycled at rates lower than C/10 to a precision of  $\pm 0.02\%$ . The accumulated error in total irreversible capacity is 0.2% after 10 C/10 cycles and 2% after 100 C/10 cycles. The specific capacity of the charge (delithiation) endpoint measures the total accumulated irreversible capacity for Li/graphite cells.

Graphite electrodes made from mesocarbon microbeads (Osaka Gas, heated to  $\sim 2650^{\circ}$ C), Super-S carbon black (MMM Carbon, Belgium) and PVDF binder (Kynar 301F Elf-Atochem). The weight ratio between the three components was either 86:7:7 or 95:3:2, respectively, so that the impact of electrode formulation could be tested. The NMC electrode was made from Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> (3M Co,

St. Paul, MN.), Super-S carbon black and PVDF. The weight ratio between the three components was 96:2:2, respectively. More details about electrode fabrication are described in reference.<sup>10</sup> All electrodes were dried under vacuum at either 100°C or 120°C overnight before cells were fabricated.

The electrolyte used in all of the cells was 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC) [1:2 v/v, Novolyte Technologies, Cleveland, OH.]. Most samples of VC contain small amounts (50 - 200 ppm) of butylated hydroxytoluene (BHT) stabilizer to prevent VC degradation. We examined VC that contained stabilizer (50 - 200 ppm) and VC that has less than 10 ppm stabilizer (called stabilizer-free VC) in this work. The results were similar so we do not believe the presence of the stabilizer is important. For brevity, only the results for the stabilizer-free VC (obtained from Novolyte) are reported here.

2325 coin-type cells with two Celgard 2300 separators and a lithium foil common counter and reference electrode were assembled in an argon-filled glove box with the graphite electrodes or NMC electrodes described above. Li/graphite half cells with different weight percentages of VC were charged and discharged with a constant current between 1.2 and 0.005 V using a rate of C/20 at 30.0  $\pm$  0.1, 40.0  $\pm$  0.1, 50.0  $\pm$  0.1 and 60.0  $\pm$  0.1°C. Li/NMC half cells with different weight percentages of VC were charged and discharged with a constant current between 3.0 and 4.2 V using a rate of C/20 at 30.0  $\pm$  0.5°C.

#### **Results and Discussion**

Coulombic efficiencies (CE) of Li/graphite cells are measured as the ratio of the capacity of the charge (delithiation capacity),  $Q_c$ immediately following the previous discharge  $Q_d$ , as CE(graphite) =  $Q_c/Q_d$ . CEs for Li/NMC cells are measured as the ratio of the capacity of the discharge  $Q_d$  to the previous charge  $Q_c$ , CE(NMC) =  $Q_d/Q_c$ . Given these definitions, the CEs are less than 1 for these two types of half cells. Additionally, these definitions correspond to the charge associated with  $Q_d/Q_c$  for a full Li-ion cell, since the discharge of a Li-ion cell (graphite is delithiating) corresponds to the charge of a Li/graphite cell (graphite is also delithiating).

Figure 1 shows the cell potential vs specific capacity of Li/graphite (86:7:7) cells with  $0\% \ 1\%, \ 2\%, \ 3\%$  or 4 wt % VC cycled at  $60^{\circ}$ C. The insets in Figure 1 show that the cells containing VC show more capacity during the first discharge at potentials greater than 0.9 V, consistent with literature reports.<sup>3</sup> The first-cycle irreversible capacity, given by the endpoint capacity of the first charge, generally increases as amount of VC increases. However, the charge endpoint slippage, the rate at which the total irreversible capacity increases with cycle

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**Figure 1.** The potential vs specific capacity (mAh/g) for Li/graphite (86:7:7) cells with 0, 1, 2, 3, and 4 wt % VC at  $60^{\circ}$ C. The insets show the impact of VC on the first lithiation above 0.9 V and the impact of VC on the first cycle irreversible capacity.

number, is reduced as the amount of VC is increased. This will be more evident in the discussion below.

Figure 2 shows the specific capacity (bottom panels), CE (middle panels) and charge capacity endpoint (top panels) vs cycle number for Li/graphite (86:7:7) cells with 0, 1, 2, 3 and 4 wt % VC at different temperatures. Figures 2c, 2f, 2i and 2l show that the reversible capacity increases slightly with temperature due to improved diffusion. Figures 2b and 2e show that the CE for VC-containing cells is not better than the control cell at 30 and 40°C. However, Figure 2k shows that the CE for the VC-containing cells is better at 60°C. Figure 3h shows that cells with 1 and 2% VC are preferred at 50°C. Figures 2a, 2d, 2g and 2j show the total irreversible capacity for all the cells plotted versus cycle number. The preferred situation is to maintain the lowest total irreversible capacity and the highest CE. Combining the results in the top two rows of panels in Figure 2, one can determine the optimum amount of VC for each temperature as is displayed in Table I. In some instances, two VC contents are more or less equivalent, or one is slightly preferred in maximizing CE while

Table I. Showing the optimum VC content for Li/graphite cells selected based on the experiments described in Figures 2–4. A table entry of "2", "3" or "4" means the best (or equivalent) VC content based on the results in Figures 2 and 3 or 4, respectively, at the given temperature.

Percent VC	30°C	40°C	50°C	60°C
0 0.25 0.5	2, 3, 4 4 4	2, 3		
1 2 3 4	2, 3	3	2, 3 3	2 3

the other is slightly preferred in minimizing total irreversible capacity. In such instances, two compositions are listed in Table I.

Figure 3 shows specific capacity (bottom panels), CE (middle panels) and charge capacity endpoint (top panels) vs cycle number for Li/graphite (95:3:2) cells with 0, 1, 2 and 4 wt% VC at different temperatures. There is some problem, probably slight dendrite penetration of the separator after cycle 8, with the cell having 0% VC cycled at 50°C (panels 3h and 3g) and we will neglect the results for that cell. Figure 3 shows similar trends as Figure 2, however all CE's are higher and all accumulated irreversible capacities are smaller due to the smaller carbon black content (only 3%) in these electrodes compared to the 7% carbon black used in the cells reported in Figure 2. This is because the carbon black has a specific surface area of 70 m<sup>2</sup>/g so it is important to minimize carbon black content in order to improve CE and minimize total irreversible capacity.<sup>11</sup> The trends from Figure 3 have been incorporated into the summary of Table I.

Figure 4 shows the specific capacity (bottom panels), CE (middle panels) and charge capacity endpoint (top panels) vs cycle number for Li/graphite (95:3:2) cells with low weight percentages of VC (0, 0.25, 0.5 and 1 wt %) at 30°C. These experiments were performed to see if there was an optimum amount of VC in the range between 0 and 1% for cells cycled at 30°C. The CE for the cell with 0.5% VC was the highest, but the small differences between the cells may be less than our experimental error. However, this cell clearly has more total irreversible capacity than the cells with 0 and 0.25% VC. Therefore, we have ranked cells with 0 to 0.5% VC as equivalent at 30°C based on the data in Figure 4.

Figure 5 summarizes the data in Figures 2–4 and Table I in an attempt to determine the optimum amount of VC for Li/graphite cells operated at between 30 and  $60^{\circ}$ C. The experiments reported show that no VC is required at  $30^{\circ}$ C, but that up to about 0.5% is not deleterious. Similarly, the experiments show that somewhere between 1 and 2% VC is optimum at  $60^{\circ}$ C. The length of the error bars in Figure 5 indicates that basically equivalent performance was obtained for VC contents within the range of the error bar.

It is important to remember that a full Li-ion cell contains two intercalation electrodes and does not contain any metallic lithium. Therefore, it is unclear what importance, if any, the results in Figures 2 – 5 may have for full Li-ion cells. The same type of experiments need to be performed for Li/positive-electrode half cells and for full cells. It is our opinion that the impact of VC at the negative electrode is relatively small compared to its impact at the positive electrode.<sup>7</sup> The span of CE variation between cells with 0% VC and cells with 1% VC is less than 0.0003 (slightly more than our experimental error of  $\pm 0.0002$ ) in Figure 4 over the range of cycles 20 to 35, showing that VC does not have a profound impact at 30°C. This must be compared to similar results for positive electrodes.

Figure 6 shows the specific capacity (bottom panel), CE (middle panel) and charge capacity endpoint (top panel) vs cycle number for Li/NMC (96:2:2) cells with 0%, 0.25%, 0.5% and 1 wt% VC at 30°C. The addition of VC greatly improves the CE and significantly



Figure 2. The specific capacity (mAh/g) (bottom panels), CE (middle panels) and charge capacity endpoint (mAh/g) (top panels) vs cycle number for Li/graphite (86:7:7) cells with 0, 1, 2, 3 and 4 wt % VC at 30, 40, 50 and 60°C.



Figure 3. The specific capacity (mAh/g) (bottom panels), CE (middle panels) and charge capacity endpoint (mAh/g) (top panels) vs cycle number for Li/graphite (95:3:2) cells with 0, 1, 2 and 4 wt % VC at 30, 40, 50 and 60°C.



Figure 4. The specific capacity (mAh/g) (bottom panels), CE (middle panels) and charge capacity endpoint (mAh/g) (top panels) vs cycle number for Li/graphite (95:3:2) cells with 0, 0.25, 0.5 and 1 wt % VC at  $30^{\circ}$ C.





**Figure 5.** An estimate of the optimum VC content for minimizing the total irreversible capacity and maximizing coulombic efficiency of Li/graphite cells based on a summary of the data in Figures 2–4 (see Table I).

decreases the charge endpoint capacity slippage rate. The coulombic efficiency of these cells is about 0.997 when there is no VC present and improves to about 0.9985 when 1% VC is present. Figure 6c shows that the capacity retention is not strongly impacted by the addition of VC, while Figure 6a shows that the charge endpoint capacity slippage is greatly reduced when VC is added. The results in Figures 6a and 6c strongly suggest electrolyte oxidation at the surface of the positive electrode is the cause for this poor CE and that the presence of VC slows this oxidation. The range of CE variation for these cells spans a range of 0.0015, at least 5 times larger than the impact of the same variation in VC content on the negative electrode as shown in Figure 4. This, along with the work in reference 7 suggests that the major impact of VC addition in improving Li-ion battery life is due to its effects at the positive electrode.

Figure 6. The specific capacity (mAh/g) (bottom panels), CE (middle panels) and charge capacity endpoint (mAh/g) (top panels) vs cycle number for Li/NMC (96:2:2) half cells with 0, 0.25, 0.5 and 1 wt % VC at  $30^{\circ}$ C.

### Conclusions

Additions of VC to Li/graphite cells increase irreversible capacity at all temperatures and only increase coulombic efficiency significantly at 50 and 60°C. However, adding small amounts of VC, less than about 1%, does not create significant negative impacts at either 30 or 40°C. At these temperatures there is little difference between the coulombic efficiency of Li/graphite cells containing either 0 or 1% VC. In fact, at 30°C, the CE's are within 0.0003. Significant further work, using surface-sensitive spectroscopies and careful analysis of electrolytes for possible reaction products, would be required to understand this temperature dependence of the impact of VC.

Li/NMC cells show an increase in CE of 0.0015 to  $0.9985 \pm 0.0002$ from 0.9970  $\pm$  0.0002 for cells containing 1% VC compared to cells with no VC, respectively. This change in CE is five times that which occurs in Li/graphite cells cycled at 30°C when 1% VC is added. This suggests the positive impact of VC in commercial Li-ion cells stems both from suppression of parasitic reactions at the positive electrode and from a "better" SEI at the negative electrode.

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