Succinic Anhydride as an Enabler in Ethylene Carbonate-Free Linear Alkyl Carbonate Electrolytes for High Voltage Li-Ion Cells

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Long life and energy dense Li-ion cells are attractive to battery manufacturers and electric vehicle (EV) makers. Cycling a Li-ion cell to higher voltage increases its energy density but normally decreases cell lifetime. This is because electrolyte solvents are unstable at high voltages and the positive electrode/electrolyte interface becomes more reactive as the potential increases.1,2 Recent results have shown that ethylene carbonate (EC) itself is responsible for many issues associated with the operation of NMC/graphite cells to high potentials.3,4 Reactions involving EC at the positive electrode cause gas evolution and impedance growth, leading to cell failure. Such reactions become very problematic above 4.5 V vs. Li/Li⁺ regardless of the electrolyte additives used.5

The removal of EC has been shown to enhance high voltage performance of NMC(442)/graphite cells at both room temperature and high temperature.6 When used at small loadings, several cyclic carbonates including vinylene carbonate (VC), fluoroethylene carbonate (FEC) and difluoroethylene carbonate (DiFEC), can enable the use of linear alkyl carbonate-based electrolytes without ethylene carbonate.7 The cycling performance of these EC-free electrolytes was determined to be dependent upon the initial loading of passivating agent added, which must be high enough to passivate the graphite electrode, yet low enough to ensure low impedance (for VC and DiFEC) and low gassing during cell use. The addition of co-additives helps lower polarization growth during high voltage cycling.8

Problems with EC-free ethyl methyl carbonate (EMC)-based electrolytes include gas evolution during both cycling and storage at high temperatures. Figure S1 (supporting information) shows open circuit voltage (OCV) versus time as well as gas evolution during 500 h storage at 60 °C for NMC442/graphite cells containing EMC-based electrolyte with VC, FEC, and DiFEC as enablers. Compared to cells with a state-of-the-art electrolyte incorporating additives,9 cells containing linear alkyl carbonate electrolytes have similar voltage drop but higher gas evolution during 500 h storage tests at 60 °C. Therefore, it is important to find enablers that can reduce gas evolution at high temperature while providing similar or better performance to linear alkyl carbonate electrolytes with cyclic carbonate (VC, FEC or DiFEC) enablers.

In this paper, EMC-based electrolytes with different amounts of succinic anhydride (SA) were studied in NMC442/graphite Li-ion pouch cells. Experiments were made using ultra high precision coulometry (UHPC),7 a precision storage system,8 electrochemical impedance spectroscopy (EIS)9 and gas volume measurements. Gas evolution during formation and cycling, coulombic efficiency, charge end point capacity slippage during cycling and EIS spectra before and after cycling were examined and were compared to EC-based electrolytes with SA and some other promising additive blends.

Chemicals.—1 M LiPF6 in ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 wt% ratio, BASF, 99.99%) was used as the control electrolyte. 1 M LiPF6 in EMC was used as the studied electrolyte here. To this studied electrolyte, the enablers vinylene carbonate (VC) and succinic anhydride (SA) were added at 0.5 to 3% by weight. Figure 1a shows the structure of SA. A storage test showed that both control and 1% SA-99% EMC electrolyte (both had 1 M LiPF6) did not change color during three days of storage at 80 °C. This suggests SA in EMC is a stable system. A promising electrolyte additive combination which contains 2% prop-1-ene,1,3-sultone (PES) + 1% methylene...
methanesulfonate (MMDs) or 1,3,2-dioxathiolan-2,2-oxide (DTD) + 1% tris(trimethylsilyl) phosphate (TSPt) (PES211) in 1 M LiPF₆ EC:EMC (3:7 by wt) electrolyte was chosen for comparison in some of the experiments. Previous studies have been shown that PES211 can yield NMC(111)/graphite or NMC(442)/graphite pouch cells with excellent cycling or storage performance.⁶,¹⁺¹¹

**Pouch cells, formation and degassing.**—The 402035-size pouch cells were manufactured by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The pouch cells had a capacity of 180 mAh and were balanced for 4.7 V operation. The negative electrode of these cells was composed of 96% artificial graphite particles (grade AML-400 from Kajjin, China, with an average particle size near 15–30 μm), 2% carbon black conductive diluent and 2% carboxymethylcellulose (CMC)/styrene butadiene rubber (SBR) binder. The positive electrode was composed of 96% Li[Ni₀.₄Mn₀.₄Co₀.₂]O₂ (NMC442, supplied by Umicore) particles (5–15 μm), 2% carbon black conductive diluent and 2% polyvinylidene fluoride (PVDF) binder. The pouch cells were sealed under vacuum without electrolyte in China, then shipped to our laboratory in Canada. Before filling with electrolyte, the cells were cut just below the heat seal and dried at 80°C under vacuum for 14 hours to remove residual water. Then the cells were transferred, without exposure to air, to an argon-filled glove box where they were filled with 0.75 mL (0.86 g for 1 M LiPF₆ in EMC, 0.90 g for 1 M LiPF₆ in EC:EMC 3:7) of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.) at a gauge pressure of −90 kPa.

After filling, the cells were placed in a temperature box at 40°C, where they were held at 1.5 V for 24 hours, to allow for the completion of wetting. Then the cells were charged at 9 mA/C(20)/C(3.5 V). This step is called “formation step 1”. After formation step 1 the amount of gas evolved in the cells was measured. Then the cells were transferred into the glove box, cut open to release any gas generated and vacuum sealed again. The NMC442/graphite cells destined for 4.5 V operation were charged to 4.5 V at C/20, gas evolution was measured and then the cells were degassed a second time at 4.5 V. These degassing voltages were selected based on the in-situ gas evolution experiments, which showed that most of the gas evolves in the formation cycle at voltages below 3.5 V and above 4.3 V. After the two degassing processes, cells were then discharged to 3.8 V impedance spectra were measured.

**UHPC barn-charge protocols.**—The “barn-charge” cycling procedure (see Figure S2 in the supporting information) was carried out using the Ultra-High Precision Charger (UHPC) at Dalhousie University.¹¹ The “barn-charge” protocol was designed so that the cells were exposed to higher potentials for significant fractions of their testing time, thereby highlighting the effects of electrolyte oxidation at high voltage. The “barn-charge” protocol consisted of a C/15 charge to 4.200 V, followed by a slower, C/40 charge to 4.500 V. The cells were then discharged, using a slow, C/40 current to 4.2 V, followed by a C/15 discharge to 2.800 V. The testing was done at 40°C. This process was repeated on the UHPC for 15 cycles where comparisons were made.

**Storage protocols.**—After formation step 2 (charge to 4.5 V), cells were first discharged to 2.8 V and charged to 4.5 V twice using currents corresponding to C/20. This was done at 40°C. Then the cells were held at 4.5 V for 24 h.

After this pre-cycling process, cells were carefully moved to the storage system which monitored their open circuit voltage every 6 hours for a total storage time of 500 h. Storage experiments were made at both 40 ± 0.1°C and 60 ± 0.1°C.

**In-situ and Ex-situ gas volume measurements.**—Both in-situ (dynamic) and ex-situ (static) gas measurements were used to measure gas evolution during formation and during cycling.¹²,¹₄ Both measurements were made using Archimedes’ principle with cells suspended from a balance while submerged in liquid. The changes in the weight of the cell suspended in fluid, before, during and after testing are directly related to the volume changes by the change in the buoyant force. The change in mass of a cell, Δm, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, by

$$\Delta v = -\Delta m/\rho$$  

[1]

Ex-situ measurements were made by suspending pouch cells from a fine wire “hook” attached under a Shimadzu balance (AW200D). The pouch cells were immersed in a beaker of de-ionized “nanopure” water (18 MΩ) that was at 20 ± 1°C for measurement. Before weighing, all cells were charged or discharged to 3.80 V. In-situ measurements were made using the apparatus and procedure described in Reference 15. This apparatus can measure the gas evolution in up to six pouch cells simultaneously during operation. During the in-situ measurements, the cells were suspended in silicone vacuum pump oil and the mass was measured using sensitive strain gauges (or load cells) while they were charged and discharged. All in-situ gas volume measurements were made in a temperature box at 40 ± 0.1°C. During these measurements, cells were charged and discharged without degassing.

**Electrochemical impedance spectroscopy.**—Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC442/graphite pouch cells after formation and also after cycling on the UHPC.⁹ Cells were charged or discharged to 3.80 V before they were moved to a 10 ± 0.1°C temperature box. Alternating current (AC) impedance spectra were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV at 10 ± 0.1°C. A Biologic VMP-3 was used to collect these data. The experimental setup did not allow for reproducible solution resistance measurements due to cable and connector impedance. Therefore, all impedance spectra were shifted to 0 on the real axis at the highest frequency measured.

**Symmetric cells.**—Symmetric cells were made from electrodes obtained from some of these pouch cells after cycling. Symmetric cells were made by the procedures described by Petibon et al. and Burns et al.⁹,¹⁶ The pouch cells were charged or discharged to 3.80 V (approx. 50% state of charge) before they were opened in an argon-filled glove box. Six coin-cell size (1.54 cm²) positive electrodes and six coin-cell size (1.54 cm²) negative electrodes were cut from the pouch cells electrodes with a precision punch. Two negative symmetric coin cells, two positive symmetric coin cells and two full coin cells were reassembled using one polypropylene blow microfiber separator (BMF—available from 3 M Co., 0.275 mm thickness, 3.2 mg/cm²). The electrolyte used for symmetric cell was the same as that used in parent pouch cell. A positive electrode symmetric cell was constructed using two positive electrodes, and a negative electrode symmetric cell was constructed using two negative electrodes. A full coin cell was constructed using one positive electrode and one negative electrode.

**Long-term cycling.**—Long-term cycling was done using Neware battery testing stations. Cells were housed at 40°C ± 1°C or 55°C ± 1°C in temperature controlled boxes. Cells were cycled between 2.8 – 4.4 V or 4.5 V using a constant current of C/2.2. A constant voltage step was added at the top of charge and applied until the current dropped below C/20.

**Results and Discussion.**

Figure 1a shows the differential capacity (dQ/dV) vs. V curves for NMC442/graphite pouch cells with different concentrations of SA during formation step 1. From the dQ/dV vs. V curves, one can determine at which potential the additives initially react with the graphite electrode. Figure 1a shows that cells containing control (1 M LiPF₆ in EC:EMC 3:7) electrolyte have a pronounced peak at 2.9 V (graphite electrode around 0.75 V vs. Li/Li⁺) which is due to the reduction of EC on the graphite surface.¹⁷–²⁰ Figure 1a shows that cells
with 1 M LiPF$_6$ in EMC have a large differential capacity peak around 3.2 V (graphite electrode around 0.45 V vs. Li/Li$^+$) which is caused by the reduction of EMC at the graphite electrode surface. The large area under the peaks indicates the poor passivation of the graphite electrode during formation. Figure 1a shows that the addition of 2% VC to EMC electrolyte totally eliminates the EMC peak at 3.2 V. Figure 1a shows adding 0.2% or 0.5% SA is not enough to passivate the graphite electrode since the 3.2 V peak is due to the reduction of EMC still exists. Figure 1a shows adding 1% or more SA can totally eliminate the EMC reduction peak. It is therefore concluded that the amount of SA should be higher than 0.5% in cells of this type.

In-situ gas measurements were performed to quantify how SA impacts the gas evolution during formation. Figure 1c shows the cell voltage versus time during the whole formation cycle for the NMC442/graphite pouch cells with different amounts of SA in EMC electrolyte. Figure 1c shows the in-situ gas volume versus time for the same pouch cells measured during in-situ gas measurements. Figure 1c shows that the cell containing 1 M LiPF$_6$ in EMC electrolyte continues to produce gas when charged to from 1.5 to 4.5 V. Figure 1c shows all the cells (except the cell containing 1 M LiPF$_6$ in EMC) have two main gas evolution steps during the first charge just below 3.5 V (formation step 1) and just below 4.5 V (formation step 2). The gas created during formation step 1 is caused by the passivation of graphite at the negative electrode while the gas during formation step 2 is caused by electrolyte oxidation and the passivation of the NMC electrode when the electrode is first charged to 4.5 V. Figure 1c shows adding 2% VC almost eliminated all the gas production during formation. Figure 1c shows that adding 0.5% SA to EMC electrolyte can decrease the amount of gas produced during formation, but not eliminate it entirely. When the concentration of SA was increased to 1%, the amount of gas evolved decreased to a quantity similar to that seen when VC was used. Further increasing the concentration of SA slightly decreased the amount of gas evolved, especially during formation step 2.

Figure 2 summarizes the cycling data collected on the UHPC including coulombic inefficiency (CIE = 1 – CE), b) fade rate, c) charge end point capacity slippage and d) $\Delta V$ for NMC442/graphite pouch cells cycled to 4.5 V using barn-charge protocols shown in Figure S2.

points (cycles 11–15). The discharge capacity fade rate, charge end point capacity slippage and the increase in $\Delta V$/cycle were calculated from the slope of a best fit line to the final five points (cycles 11–15) of the data given in Figures S3 and S4. A CIE closer to 0 (CE is closer to 1.000) and a decrease in charge end point capacity slippage are indications of a reduction in parasitic reactions at both the positive and negative electrode which normally correlates with longer lifetime. Increases in $\Delta V$ are caused by increases in cell polarization during cycling and smaller values of $\Delta V$/cycle generally indicate lower impedance growth. Each data point in Figure 2 represents the average of two cells, and the error bars are the standard deviation of the results.

Figures 2 and S3 show that cells containing PES211 in EC:EMC electrolyte have significantly lower CIE, discharge capacity fade rate, charge end point capacity slippage and increase in $\Delta V$/cycle than cells containing control electrolyte, which agrees with previous results. Figures 2 and S3 show that cells containing 1 M LiPF$_6$ in EMC electrolyte have better performance than control but are not competitive to PES 211 in EC:EMC electrolyte. Figures 2 and S3 show that cells containing EMC:VC 98:2 electrolyte have lower CIE, lower charge end point capacity slippage and lower increase in $\Delta V$/cycle than cells containing PES211 in EC:EMC electrolyte. Cells containing 2% VC in EMC are then expected to have longer lifetime than cells with PES211 in EC:EMC electrolyte under these cycling conditions.

Figures 2 and S4 show adding 0.2 or 0.5% SA to EMC lead to larger CIE, charge end point capacity slippage and fade rate compared to cells containing 2% VC in EMC electrolyte. Figures 2 and S4 show the optimum SA loading is between 0.5% and 2% since the CIE, charge end point capacity slippage rate and fade rate improve going from pure EMC to SA:EMC (1:99) and then worsen going from SA:EMC (2:98) to SA:EMC (3:97). The improvement upon addition of 1% SA to pure EMC probably comes from a better passivation of the graphite surface while too much SA results in a thick SEI and high impedance.

Figures 3a and 3b show the typical open circuit voltage (OCV) versus time during 500 h storage at 40, ± 0.1 °C and 60, ± 0.1 °C, respectively, for NMC442/graphite cells with different amounts of SA in EMC electrolyte. Figure 3c shows a summary of the voltage drop points (cycles 11–15). The discharge capacity fade rate, charge end point capacity slippage and the increase in $\Delta V$/cycle were calculated from the slope of a best fit line to the final five points (cycles 11–15) of the data given in Figures 3a and 3b. Figure 3c shows a summary of the $V_{drop}$ data in Figures 3a and 3b.
EMC electrolyte at both 40°C and after UHPC cycling at 40°C for NMC442/graphite pouch cells with different electrolytes as indicated. $R_{ct}$ was measured at 3.8 V and 10°C.

(V$_{drop}$) during storage data shown in Figures 3a and 3b. V$_{drop}$ during storage indicates the oxidation of species at the positive electrode and has been shown to correlate well with charge end point capacity slippage. That is, cells with large charge end point capacity slippage during cycling normally have large voltage drops during storage. Figure 3 shows that cells containing 0.2% or 0.5% SA perform similarly to cells containing 1 M LiPF$_6$ in EMC electrolyte and much worse than cells with 2% VC in EMC electrolyte or PES211 in EC:EMC electrolyte at both 40°C and 60°C. Figure 3a shows that cells containing 1% SA have similar voltage drop to cells containing 2% VC in EMC electrolyte at both 40°C and 60°C. Further increasing the initial SA loading to 2% or 3% slightly reduces V$_{drop}$ at both 40°C and 60°C. The storage results again suggest the optimal amount of SA should be higher than 0.5%.

Figure 4 shows a summary of the magnitude of the impedance ($R_{ct}$) after formation (green color), after 4.5 V storage at 40°C (cyan color), after 4.5 V storage at 60°C (red color), and after 600 h of UHPC cycling (blue color). Detailed EIS spectra for all of the cells tested after formation and after UHPC cycling are given in Figures S5a–S5d. All the EIS measurements were made at 3.80 V and at 10°C. $R_{ct}$ was calculated from the width of the semi-circle in the Nyquist representation of the electrochemical impedance spectra (see Figure S5). Smaller values of $R_{ct}$ as well as small increases in $R_{ct}$ are desired for cells cycled for the same period of time. Figure 4 clearly shows the benefit of using PES211 in EC:EMC electrolyte which has much less impedance growth than control during storage and cycling experiments. Figure 4 shows that adding 0.2% or 0.5% SA to EMC electrolyte leads to cells with lower impedance than cells containing 2% VC in EMC electrolyte or PES211 in EC:EMC electrolyte. Increasing the initial loading of SA higher than 1%, leads to cells with impedance after formation that is too high. However, the impedance of SA-containing cells greatly decreased during UHPC cycling and storage experiments. Cells containing SA:EMC 2:98 electrolyte have even smaller impedance than control or PES211 in EC:EMC electrolyte after storage experiments at 40°C or 60°C but their $R_{ct}$ are still larger than cells with SA:EMC 1:99.

To understand why the impedance decreases during cycling and where the high impedance comes from during formation, symmetric cells were made from the pouch cells after UHPC cycling as well as after formation. Figures 5a, 5c and 5e show the area-specific Nyquist plots of negative (5a) and positive (5c) electrode symmetric cells as well as full coin cells (5e) containing control (1 M LiPF$_6$ in EC:EMC 30:70), VC:EMC 2:98, SA:EMC 1:99 and SA:EMC 3:97, respectively. Figures 5b, 5d and 5f show the Bode plots of the real area-specific impedance as a function of frequency on a logarithmic axis for the same cells. The data in Figures 5a, 5b, 5c and 5d have been divided by two for easy comparison to the full cell data since it is expected that:

\[
\frac{1}{2}Z_n + \frac{1}{2}Z_p = Z_f
\]

where $Z_n$, $Z_p$ and $Z_f$ are the impedances of the negative electrode symmetric cell, the positive electrode symmetric cell and the full cell, respectively. These symmetric (or full) coin cells in Figure 5 were made from the pouch cells after the UHPC cycling experiments. Figure 5 shows that control cells have low impedance at the negative electrode and high impedance at the positive electrode mainly from electrolyte oxidation at high potential at the positive electrode interface. Figure 5 shows that compared to control cells, cells containing VC:EMC 2:98 or SA:EMC 1:99 electrolyte have similar negative electrode impedance but much smaller positive electrode impedance. Compared to cells containing SA:EMC 1:99, cells with SA:EMC 3:97 electrolyte showed much higher negative electrode impedance and slightly higher positive electrode impedance. Therefore, high concentrations of SA have a negative effect on the impedance of both graphite and NMC442 electrodes.

Figure S6 shows the area-specific Nyquist plots and Bode plots of negative (S6a, S6b) and positive (S6c, S6d) electrode symmetric cells as well as full coin cells (S6e, S6f) containing 3% SA after formation and after UHPC cycling. Figure S6 shows the extremely high impedance at the negative electrode after formation. Figure S6 clearly shows a large impedance decrease at the negative electrode during UHPC cycling while the positive electrode impedance slightly increases after UHPC cycling. The increase of the positive impedance during UHPC cycling presumably is caused by oxidation of species at the positive electrode. Again, Figure S6 shows that higher concentrations of SA have a negative impact on the impedance of both graphite and NMC442 electrodes.

Figure 6 shows that the volume of gas produced during formation step 1 (charge to 3.5 V), formation step 2 (charge to 4.5 V), 500 h storage at 40°C, 500 h storage at 60°C and UHPC cycling at 40°C. Figure 6 shows that control cells produced 0.15 mL, 1 mL and 0.1 mL gas during 500 h storage at 40°C, 500 h storage at 60°C and UHPC cycling.
cycling at 40 °C, respectively. The initial volume of the pouch cells was 2.2 mL. A volume change during cycling of less than 10% (0.22 mL) is desired in order to prevent pressure build up in hard-can cell designs and loss of stack pressure in cell designs with soft enclosures. The amount of gas produced during 60 °C storage for control cells is simply too large to be useful. Adding PES211 to control electrolyte greatly decreases the gas evolution during cycling or storage experiments. Figure 6 shows that cells containing 1 M LiPF6 in EMC electrolyte produced more gas than control cells during cycling or storage experiments due to the poor passivation of graphite electrode. Figure 6 shows that adding VC to EMC electrolyte greatly decreased the gas evolution during cycling or storage experiments. However, cells containing EMC:VC 98:2 electrolyte still produced about 0.5 mL gas during 60 °C storage which is not acceptable for practical use at high temperatures. Figure 6 shows that adding 0.2% or 0.5% SA to EMC electrolyte resulted in large amounts of gas being produced during storage and UHPC cycling tests due to incomplete passivation of the graphite electrode. Adding 1% SA to EMC electrolyte greatly decreased the gas evolution during storage and cycling experiments at 40 °C. However, the amount of gas evolved during storage at 60 °C was still large. Further increasing the content of SA to 2% or higher greatly decreased the gas evolution during cycling or storage at 40 °C or 60 °C to acceptable values. Therefore, 2% SA is more effective than 1% SA at high temperatures.

Figures 7a and 7c show the cycling data (capacity retention and ΔV) for NMC442/graphite cells with different electrolytes during long-term cycling at 40 °C (2.8 to 4.5 V) with a current density of C/2.2 (80 mA). Figures 7b and 7d show the cycling data (capacity retention and ΔV) for NMC442/graphite cells with different electrolytes during long-term cycling at 55 °C (2.8 to 4.4 V) with a current density of C/2.2 (80 mA). Figure 7 shows that cells containing 1% SA in EMC electrolyte have a slightly worse capacity retention than cells containing PES211 in EC:EMC 3:7 or 2% VC in EMC electrolytes at 40 °C. However, at 55 °C, these SA-containing cells have slightly better capacity retention and less impedance growth. Our previous work showed that co-additives such as triallyl phosphate or phosphorous pentfluoride limit impedance growth during high voltage cycling of cells with EC-free-EMC-based electrolytes using VC as the graphite passivating agent. It may very well be that these same co-additives could help limit impedance growth when SA is used as enabler.

Figure 8 shows a comparison between 2% SA in EC:EMC and 2% SA in EMC electrolytes: a) coulombic efficiency vs. cycle number during “barn-charge” cycling protocol (see Figure S2) to 4.5 V on UHPC at 40 °C; b) charge end point capacity vs. cycle number during “barn-charge” cycling protocol on UHPC at 40 °C; c) open-circuit voltage versus storage time during storage at 60 °C; d) capacity vs cycle number during long-term cycling at C/2.2 (80 mA) between 2.8 V and 4.5 V at 40 °C using CCCV protocol; e) Nyquist plots after UHPC cycling; f) volume change due to gas evolution during UHPC cycling and storage tests.
electrolyte during UHPC cycling at 40 °C. Figures 8c, 8d and 8e show that cells containing 2% SA in EMC electrolyte have smaller \( V_{\text{drop}} \) during 500 h storage at 60 °C, better capacity retention during long-term cycling as well as lower impedance after UHPC cycling than cells containing 2% SA in EC:EMC 3:7 electrolyte. Figure 8f shows that cells containing 2% SA in EMC or 2% SA in EC:EMC 3:7 electrolytes have no swelling problem during UHPC cycling at 40 °C. However, at 60 °C, the EC-containing electrolyte produced a large amount of gas while the EC-free electrolyte produced almost no gas. This again confirms the disadvantages of using EC-containing electrolyte at high voltages. The removal of EC significantly improved the cycling and storage performance at high voltages and high temperatures.

Conclusions

EC-free electrolytes containing 1 M LiPF\(_6\) dissolved in ethyl methyl carbonate containing small amounts of SA as the passivating additive were studied in NMC(442)/graphite pouch type Li-ion cells during cycling and storage experiments. The results showed that SA could successfully passivate the graphite electrode at loading levels higher than 0.5%. Lower concentrations of SA generally produced more gas due to the unsuccessful passivation of the graphite electrode while higher concentrations of SA led to lower gas generation but higher impedance during formation. UHPC cycling showed that 1% or higher SA content could provide similar CE and charge end point capacity slippage to cells containing PES211 in EC:EMC 3:7 or 2% VC in EMC electrolytes. Storage experiments showed that increasing the amount of SA in EMC electrolyte led to smaller \( V_{\text{drop}} \) at both 40 °C and 60 °C. Gas evolution data showed that 2% SA is more effective than 1% in reducing gas production at high temperatures, EIS measurements showed higher concentrations of SA led to higher impedance during formation. Symmetric cell studies showed the high impedance of SA-containing cells came from a highly resistive SEI film formed on the negative electrode. Interestingly, the impedance of these SA-containing cells decreased significantly during UHPC cycling and this is mainly due to the decrease in impedance of the negative electrode.

This work confirms that there are enablers other than cyclic carbonates can function well in EMC-based electrolytes. The SA-EMC electrolyte system showed similar performance to VC-EMC electrolyte system at 40 °C but better cycling (55 °C) and storage performance (60 °C) at high temperatures. The SA-EMC electrolyte system showed much better cycling performance than the SA-EC-EMC system at 55 °C. This further indicates the importance of removing EC from the electrolyte for high voltage Li-ion cells.

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References

1. L. Yang, B. Radvel, and B. L. Lucht, Electrochem. Solid-State Lett., 13, A95 (2010).
2. M. Kunduraci and G. G. Amatucci, J. Electrochem. Soc., 153, A1345 (2006).
3. J. Xia, R. Petibon, D. Xiong, L. Ma, and J. R. Dahn, J. Power Sources, 328, 124 (2016).
4. R. Petibon, J. Xia, L. Ma, M. K. G. Bauer, K. J. Nelson, and J. R. Dahn, J. Electrochem. Soc., 163, A2571 (2016).
5. J. Xia, K. J. Nelson, Z. Lu, and J. R. Dahn, J. Power Sources, 329, 387 (2016).
6. D. Y. Wang, J. Xia, L. Ma, K. J. Nelson, J. E. Harlow, D. Xiong, L. E. Downie, R. Petibon, J. C. Burns, A. Xiao, W. M. Lamanna, and J. R. Dahn, J. Electrochem. Soc., 161, A1818 (2014).
7. T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn, and J. R. Dahn, J. Electrochem. Soc., 160, A521 (2013).
8. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, J. Electrochem. Soc., 158, A1194 (2011).
9. R. Petibon, C. P. Aiken, N. N. Sinha, J. C. Burns, H. Ye, C. M. VanElzen, G. Jain, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 160, A117 (2013).
10. J. Xia, L. Ma, and J. R. Dahn, J. Power Sources, 287, 377 (2015).
11. L. Ma, J. Xia, and J. R. Dahn, J. Electrochem. Soc., 161, A2250 (2014).
12. C. P. Aiken, J. Self, R. Petibon, X. Xia, J. M. Paulsen, and J. R. Dahn, J. Electrochem. Soc., 162, A760 (2015).
13. J. Xia, M. Nie, L. Ma, and J. R. Dahn, J. Electrochem. Soc., 161, A230 (2014).
14. J. Xia, J. Self, L. Ma, and J. R. Dahn, J. Electrochem. Soc., 162, A1424 (2015).
15. C. P. Aiken, J. Xia, D. Y. Wang, D. A. Stevens, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 161, A1548 (2014).
16. J. C. Burns, L. J. Krause, D. -B. Le, L. D. Jensen, A. J. Smith, D. Xiong, and J. R. Dahn, J. Electrochem. Soc., 158, A1417 (2011).
17. J. G. Besenhard, M. Winter, J. Yang, and W. Biberacher, J. Power Sources, 54, 228 (1995).
18. D. Aurbach, K. Gamovskiy, B. Markovsky, Y. Gofer, M. Schmidt, and U. Heider, Electrochim. Acta, 47, 1423 (2002).
19. G. Y. Zhuang, K. Xu, H. Yang, T. R. Jow, and P. N. Ross, J. Phys. Chem. B, 109, 17567 (2005).
20. Y. Zhu, M. D. Casselman, Y. Li, A. Wei, and D. P. Abraham, J. Power Sources, 246, 184 (2014).
21. J. Self, C. P. Aiken, R. Petibon, and J. R. Dahn, J. Electrochem. Soc., 162, A796 (2015).
22. J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way, and J. R. Dahn, J. Electrochem. Soc., 160, A1451 (2013).
23. J. Xia, N. N. Sinha, L. P. Chen, and J. R. Dahn, J. Electrochem. Soc., 161, A264 (2013).
24. R. Petibon, L. Madec, D. W. Abarbanel, and J. R. Dahn, J. Power Sources, 300, 419 (2015).
25. J. Xia, S. L. Glazier, R. Petibon, and J. R. Dahn, Improving linear alkyl carbonate electrolytes with electrolyte additives, J. Electrochem. Soc., 164, A1239 (2017).