Gas Evolution during Unwanted Lithium Plating in Li-Ion Cells with EC-Based or EC-Free Electrolytes

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Unwanted lithium plating in lithium ion batteries with graphite negative electrodes can be a serious aging mechanism. Unwanted lithium plating is most likely at low temperatures and high charge rates.1–3 The deposited Li metal can react with electrolyte, consuming active lithium and electrolyte, thus resulting in fast capacity fade. Unwanted lithium plating can be caused by increased resistance of the solid electrolyte interface (SEI), sluggish charge transfer kinetics, insufficient ionic transport to the back of the graphite electrode and limited solid state diffusion,6,7 among others. All of these increase cell polarization and drive the lithiated graphite to or below the potential of metallic Li. Therefore, the propensity toward unwanted Li plating in LIBs has a close relationship not only with the charging conditions such as low temperature,8,9 high charging rates10 and overcharging,11,12 but also with the anode/cathode ratio,13,14 carbonaceous materials selected15,16 and the electrolyte used.17

The effects of different electrolyte systems on unwanted lithium plating behavior has been reported in several works. Smart and Ratnakumar showed that cells with high EC-content and SEI-stabilizing additives (like VC) were relatively prone to unwanted lithium plating probably due to the high-resistance SEI formed by VC.17 Yariv et al. showed that fluoroethylene carbonate (FEC) as a co-solvent could improve the low-temperature behavior of the lithiated graphite electrode and reduce the propensity for lithium plating.16

During recent years, electrolyte systems that are suitable for higher-voltage operation have been widely studied in order to improve the energy density of lithium-ion batteries. High-voltage NMC/graphite cells can be improved using appropriate electrolyte additives such as prop-1-ene-1,3-sultone (PES),18 pyridine boron trifluoride (PBF), pyridine phosphorus pentfluoride (PPF),19 fluorinated phosphate esters20 etc. and/or new solvents with high oxidation ability such as fluorinated solvents,21,22 sulfone-based electrolytes23,24 and room temperature ionic liquid-based electrolytes.25 Recently, Xia et al. found that EC-free electrolyte composed of EMC and selected additives could effectively improve the high-voltage performance of NMC442/graphite cells.26 Figure 1 shows the normalized capacity of NMC442/graphite cells containing 1 M LiPF6 EC:EMC (3:7) + 2% PES + 1% ethylene sulfate (DTD) + 1% tris-trimethylsilyl phosphate (TTSPi) (This additive triplet is called PES211D, here) or 1 M LiPF6 EMC:VC (98:2) + 1% PPF cycled to 4.4 V at 55°C and 20°C. Figure 1 clearly shows that cells with EC-free EMC based electrolyte have good high-voltage performance at room temperature and at elevated temperatures up to 55°C which provides a promising alternative to EC-based electrolyte.

While designing electrolytes that are suitable for high-voltage application, the effects of these electrolytes on the low-temperature and high-rate performance should be considered but are hardly mentioned in the literature. To the best of our knowledge, the impact of EC-free EMC-based electrolyte on low-temperature performance and unwanted lithium plating behavior has not been reported.

Unwanted platted lithium can react with electrolyte to produce gas and increase pouch cell volume. Pouch cell volume evolution can be accurately monitored using an In Situ Gas Analyzer based on Archimedes’ principle by measuring the buoyant force on a cell immersed in fluid. More details of this in-situ gas method can be found in reference.27 In-situ gas volume measurements have been used to help understand parasitic reactions occurring under different charging conditions during formation and cycling at different temperatures.28–30

Here, the effects of EC-based electrolytes and EC-free EMC-based electrolytes on unwanted lithium plating in NMC111/graphite pouch cells is probed. An in-situ gas analyzer and electrochemical measurements were used for these studies.

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Experimental

1 M LiPF₆ EC:EMC (3:7 wt% ratio) electrolyte, called control, was used as the EC-based electrolyte. Other EC-containing electrolytes were 2 wt% VC in control and 2% PES + 1% DTD + 1% TTSPi in control (called PES211D). The EC-free electrolyte systems included 1 M LiPF₆ in EMC:VC (98:2), EMC:VC (98:2) + 1% PPF, EC:EMC:FEC (95:5) and EC:EMC:FEC (95:5) + 1% PPF. PPF was added due to its beneficial impact on high-voltage performance as shown in Figure 1.

The chemicals used in the electrolyte included LiPF₆ (purity 99.94%, BASF), EC:EMC (3:7, purity 99.99%, BASF), EMC (purity 99.92%, BASF), FEC (purity 99.94%, BASF), PES (purity 98.20%, Liaochuan Medicinal Chemistry Co.), DTD (purity 98%, Aldrich), TTSPi (purity >95%, TCI America) and PPF (purity 99.9%, 3 M).

This study used dry (no electrolyte) 220 mAh Li[Ni₀.₅Mn₀.₅Co₀.₅]O₂ (NMC111)/graphite pouch cells which were balanced to 4.4 V. Cells were manufactured by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000) and vacuum sealed without electrolyte before shipping to our laboratory in Canada. The pouch cells are 40 mm long × 20 mm wide × 3.5 mm thick. The electrode composition in the cells was as follows: Positive electrode - 96.2%; 1.8%:2.0% = Active Material:Carbon Black:PVDF Binder; Negative electrode - 95.4%; 1.3%:1.2%:2.2% = Active material:Carbon Black:CMC:SBR. The positive electrode had a total thickness of 105 μm and was calendared to a density of 3.55 g/cm³. The negative electrode had a total thickness of 110 μm and was calendared to a density of 1.55 g/cm³. The positive electrode coating had an areal density of 16 mg/cm² on (one side) and the negative electrode had an areal density of 9.5 mg/cm² on (one side). The positive electrode dimensions were 200 mm × 26 mm and the negative electrode dimensions were 204 mm × 28 mm. Both electrodes were coated on both sides, except for small regions on one side at the end of the foils. The overall active area of positive electrode is approximately 90.74 cm² and the overall active area of negative electrode is approximately 102.2 cm². The areal capacity of NMC111 material was measured at C/30 to be 2.50 mAh/cm² between 4.3 V and 2.8 V vs. Li⁺/Li. The reversible capacity of graphite was measured at C/30 to be 2.60 mAh/cm² between 1.5 V and 0.005 V vs. Li⁺/Li. Therefore, the calculated negative-to-positive capacity ratio at 4.1 V is about 1.17. To remove residual moisture, the cells were cut open and dried at 80°C for 14 h under vacuum before filling with electrolyte. The pouch cells were filled with 0.76 mL electrolyte and then vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp).

The formation process is described as follows. First, the pouch cells were held at 1.5 V for 24 h to ensure complete wetting of the electrolyte with the electrodes and separator. After constant current charging to 3.5 V at 11 mA (C/20) and holding at 3.5 V for 1 h (all at 40°C), the cells were degassed in argon-filled glove box. After degassing, these cells were charged to 4.1 V and discharged to 3.8 V at C/20 and 40°C for electrochemical impedance spectroscopy (EIS) measurements. The potential of 3.8 V was chosen for the EIS measurements because both graphite and NMC electrodes are at about 50% state of charge at this voltage.

EIS measurements were conducted on NMC111/graphite pouch cells after formation. All EIS spectra were measured using a Biologic VMP3 electrochemical test station at a temperature of 10.0 ± 0.1°C and collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV.

For 10°C cycling, cells were charged and discharged between 2.8 V and 4.1 V at different rates of C/10 (22 mA), C/5 (44 mA), C/3 (73 mA), C/2 (110 mA) and 1C (220 mA) using a Maccor Series 4000 battery test system. Ex-situ (static) gas evolution measurements were used to measure the gas production during cycling.

For the in-situ gas measurements, the pouch cells were put into the specialized apparatus. Cell volume changes were obtained during cycling. Cells were cycled between 2.8 V and 4.1 V with a 1 hour hold at 4.1 V every cycle. The cycle rates were 1C, 1.5C and 2C (20 cycles at each C-rate) at 22 ± 0.5°C using a Maccor system. Two C/2 cycles were used between each charge rate to measure the C/2 cell capacity. The 1 hour hold at 4.1 V was used to allow full completion of charging. The upper cutoff voltage was set to 4.1 V in order to ensure that the cells were far from having a fully loaded negative electrode which would occur at 4.4 V and to avoid gassing due to electrolyte oxidation at the positive electrode. Carbonate-based electrolytes can cycle up to 4.2–4.3 V with little anodic activity. Therefore, oxide electrolyte oxidation and metal dissolution at the cathode side are not expected to be problematic when cells are cycled only to 4.1 V.

After the in-situ gas measurement, cells were disassembled at 3.8 V within an argon-filled glove box to verify the presence of unwanted lithium plating when it was suspected.

Results and Discussion

Figure 2 shows the discharge capacity as a function of cycle number for the NMC111/graphite pouch cells with electrolytes of (a) 1 M LiPF₆ in EC:EMC (3:7) + 2% VC; (b) 1 M LiPF₆ in EC:EMC (3:7) + PES211D; (c) 1 M LiPF₆ in EMC:VC (98:2) + 1% PPF; and (d) 1 M LiPF₆ in EMC:FEC (95:5) cycled at 10°C. The various C-rates used are listed in the figure legend.
Figure 3. Cell volume change of NMC111/graphite pouch cells containing: (a) 1 M LiPF$_6$ EC:EMC (3:7) + PES211D; (b) 1 M LiPF$_6$ EMC:VC (98:2) + 1%PPF; (c) 1 M LiPF$_6$ EMC:FEC (95:5) and (d) 1 M LiPF$_6$ EMC:FEC (95:5) + 1%PPF after 10°C cycling and after cells were moved to 40°C for 24 h after 10°C cycling. The vertical scale for panel a) is vastly different than panels b), c) and d).

Figure 3 shows the volume change of cells after cycling at 10°C. The volume of the NMC111/graphite pouch cells was 2.35 mL on average which was measured based using Archimedes principle. When the volume change is greater than 0.2 mL (about 10% of the cell volume), gas production in pouch cell is obvious and can be detected (not quantified) by touch, in fact. For cells with 1 M LiPF$_6$ EC:EMC (3:7) + PES211 (Figure 3a), no obvious gas was produced even after cycling at C/2 where lithium plating had already occurred as speculated from the capacity fade. However, for cells with the EC-free EMC-based electrolyte 1 M LiPF$_6$ EMC:VC (98:2) + 1% PF (Figure 3b), gas evolution occurred at C/3. For cells with 1 M LiPF$_6$ EMC:FEC (95:5) and 1 M LiPF$_6$ EMC:FEC (95:5) + 1% PP (Figures 3c–3d), gas occurred at a charge rate of C/2. Unwanted lithium plating and gas production occurred at the same charge rate for cells with EC-free EMC-based electrolytes, suggesting gas production is caused by deposited lithium. After the 10°C cycles, cells were moved to a 40°C box for a 24 h rest and the cell volume was measured again. There was no gas production during the 24 h rest for cells that did not produce gas during the 10°C cycling. However, more gas was produced for cells that already produced gas during 10°C cycling when the cells were left at 40°C. The results in Figure 3 show that gas production was quite different for cells with different electrolytes when lithium plating occurred. Cells with EC-free EMC-based electrolytes were more prone to generate gas during lithium plating and the volume of gas increased during the high temperature rest, while no gas production occurred during lithium plating and high temperature rest for cells with EC-based electrolyte. Therefore, in-situ gas measurements could be a good method to detect lithium plating in cells with EC-free EMC-based electrolytes.

Figure 4 shows the voltage and volume change as a function of time for cells containing 1 M LiPF$_6$ EC:EMC (3:7) + 2% VC and 1 M LiPF$_6$ EMC:VC (98:2) cycling at low constant currents of C/20, C/10 and C/5 at 22°C. These two electrolytes are representatives of an EC-based electrolyte and an EC-free EMC-based electrolyte. The volume change versus time in Figures 4b and 4d showed a similar trend with cycling regardless of the electrolyte used: volume increases during charge, while reversibly recovers during discharge. This periodic volume change during low current cycling is caused by the expansion and contraction of the electrodes during lithiation and delithiation.18

Figure 5a shows the discharge capacity versus cycle number for NMC111/graphite pouch cells with the different electrolytes tested using the protocol described by in the Experimental section during in-situ gas measurement at 22°C. In order to compare the performance of cells cycled at different charge rates, the capacity was checked with a C/2 cycle between each charge rate. The capacity fade behavior at high C-rate charge depended strongly on the electrolyte used. During 1C cycling, capacity fade was very small and nearly the same for all cells, indicating little or no lithium plating occurred during 1C cycling. However, when charging at 1.5C, rapid capacity fade occurred for the cell with the EC-free electrolyte EMC:VC (98:2) + 1% PP. Rapid capacity loss occurred for cells with EMC:VC (98:2), FEC:EMC (95:5) and FEC:EMC (5:95) + 1%PPF during 2C cycling. This was permanent capacity loss (as indicated by the capacity at C/2 after cycling at 2C in Figure 5a) and indicated the occurrence of lithium plating as was verified by the images of the negative electrodes shown later. Cells containing EC:EMC (3:7) + 2%VC showed capacity loss beginning at 2C while those with EC:EMC (3:7) did not, indicating that lithium plating was more likely with the addition of 2 wt % VC as was reported by Smart and Ratnakumar.17 These results show that electrolyte selection strongly affects lithium plating and are consistent with the results of the 10°C cycling.

Figure 5b shows the impedance spectra of NMC111/graphite pouch cells, with different electrolytes as indicated in Figure 5a, after formation measured at 3.80 V and 10.0 ± 0.1°C. Figure 5b shows that cells with EC:EMC (3:7) + 2% VC had higher charge transfer impedance which explains the relatively poor rate performance of EC:EMC (3:7) + 2% VC compared to EC:EMC (3:7) electrolyte. Figure 5b shows that the addition of 1% PP to EMC-based electrolyte increased the cell impedance. Figure 5b also shows that cells containing EMC:FEC (95:5) have nearly the same impedance as cells containing EC:EMC (3:7) + 2% VC which cannot explain the more rapid capacity loss during 2C cycling for cells with EMC:FEC (95:5)
(as shown in Figure 5a). This rapid capacity loss for EC-free EMC-based electrolytes is caused by loss of stack pressure due to gassing caused by unwanted Li plating as will be explained later.

Figure 6 shows the cell volume change as a function of time for cells with EC-based electrolytes 1 M LiPF6 EC:EMC (3:7) and 1 M LiPF6 EC:EMC (3:7) + 2% VC during the charge-discharge cycling shown in Figure 5a. The cell volume increased during charging and reversibly decreased during discharging at each of the different charge rates similar to that shown for the low rate cycling in Figure 4. The volume change is caused by lithium insertion and deinsertion in the electrodes and there is no obvious gas produced. From the capacity loss versus cycle number in Figure 5a, the occurrence of lithium plating is predicted at 2C for cells with EC:EMC (3:7) + 2% VC. No obvious gassing is observed associated with this Li plating.

Figure 7 shows the volume change as a function of time for cells with a variety of EC-free electrolytes cycling at 1C, 1.5C and 2C as in Figure 5a. Cells containing 1 M LiPF6 EMC:VC (98:2) + 1% PPF cycled only 10 times per charge rate while the other three cells cycled 20 times per charge rate. It is very important that the reader appreciate that the vertical scale in Figure 7 is much larger than that in Figure 6. During 1C cycling, the volume change of all cells was reversible indicating no obvious gas production. Cells with EMC:VC (98:2) began to produce gas while cells with EMC:VC (98:2) + 1% PPF produced a large amount of gas during 1.5C cycling. Cells with EMC:FEC (95:5) and EMC:FEC (95:5) + 1% PPF electrolytes began to produce significant amounts of gas during 2C cycling. The charge C-rate where gas production initiates was the same as the C-rate of the onset of rapid capacity loss as shown in Figure 5a, indicating that rapid capacity fade was caused by a large amount of gas production associated with lithium plating in these EC-free electrolytes. A large amount of gas decreased the electrode stack pressure and can create gaps between the positive and negative electrodes in flat-wound pouch cells. This can result in rapid capacity loss. It has been reported that pouch cells without clamps during cycling have worse capacity retention compared with cells with clamps.39,40 In addition, cells with little stack pressure caused by gas production have local loss of electrode contact which accelerates capacity loss.41 This production of gas is due to lithium plating which was confirmed by pictures of the negative contact which accelerates capacity loss.41 This production of gas is due to lithium plating which was confirmed by pictures of the negative

![Figure 5](https://example.com/figure5.png)

Figure 5. a) Discharge capacity versus cycle number for NMC111/graphite pouch cells with 1 M LiPF6 EC-based electrolytes and 1 M LiPF6 EC-free EMC-based electrolytes during cycling with different rates at 22°C. b) Nyquist plots for NMC111/graphite cells with different electrolytes as indicated in panel a) after cell formation. The data in panel a) was collected during the in-situ gas measurements shown in Figures 6 and 7.

![Figure 6](https://example.com/figure6.png)

Figure 6. In situ gas evolution of NMC111/graphite cells with (a) 1 M LiPF6 EC:EMC (3:7) and (b) 1 M LiPF6 EC:EMC (3:7) + 2% VC during cycling at different charge rates and at 22°C. The capacity versus cycle number data for these cells is shown in Figure 5a.

![Figure 7](https://example.com/figure7.png)

Figure 7. In situ gas evolution of NMC111/graphite cells with 1 M LiPF6 in (a) EMC:VC (98:2), (b) EMC:VC (98:2) + 1% PPF, (c) EMC:FEC (95:5), (d) EMC:FEC (95:5) + 1% PPF during cycling with different rates at 22°C. The capacity versus cycle number data for these cells is shown in Figure 5a.
EC-free EMC-based electrolytes while no obvious gas was produced and there was relatively slow capacity loss for cells with EC:EMC (3:7) electrolyte. This reason for gas production in EC-free electrolytes can be easily explained. Freshly deposited Li is very unstable in organic solvents and reacts with electrolyte until a sufficient passivation film is formed on the deposited Li. EC can preferentially react with Li and form a stable SEI on the deposited Li in EC-containing electrolytes. However, in EC-free electrolyte, fresh Li keeps reacting with EMC which produces large amounts of gas. Therefore, the in-situ gas analyzer can be used to detect lithium plating in cells with EC-free electrolytes.

Figure 8 shows photographs of the negative electrodes (dismantled in an argon-filled glove box at 3.8 V, about 50% state of charge) of the cells after the in-situ gas test. The photographs were taken through the glove box window. These images confirm that lithium plating had occurred as speculated by the capacity loss and gas evolution results. For example, obvious lithium plating on the negative electrode occurred at 2C for cells with FEC:EMC (5:95) which is confirmed by the rapid capacity fade and large gas production at 2C.

Figure 9 summaries the effects of charge rate, electrolyte type and temperature on lithium plating and gas production. Lithium plating was detected by gas evolution, the rate of capacity fade and subsequent cell opening. The charge rate that initiates lithium plating is quite different for the different electrolytes and is lower at lower temperature. Lithium plating is more prone to occur when electrolyte additives such as VC and PES211 are used in EC:EMC(3:7) and when PPF is used in EMC-based electrolyte. 2% VC and PES211 are known to increase the resistance of the negative electrode SEI43–45 which apparently increases the propensity for plating. Figure 9 also shows that gas production accompanies lithium plating for cells with EMC-based EC-free electrolytes which is a possible bottleneck for cells with EC-free electrolytes cycling at low temperatures and high rates. The charge rate for cells with EC-free EMC-based electrolytes should be well-controlled to avoid lithium plating and the associated gas production at low temperatures.

**Conclusions**

The effect of electrolytes including EC:EMC (3:7) and EC-free EMC-based electrolyte on unwanted lithium plating and associated gas production was investigated through 10 C cycling and in-situ gas measurements at 22 °C. Lithium plating is the main mechanism for rapid capacity degradation at higher charge rates. The occurrence of lithium plating is highly dependent on the electrolyte type. The addition of 2% VC or PES211 in EC:EMC (3:7) electrolyte and 1% PPF in EMC-based electrolytes increases the tendency for lithium plating. Although EMC-based electrolytes without EC show outstanding performance at high voltage and high temperature, gas production occurs simultaneously with unwanted lithium plating in NMC/graphite cells at sufficiently high charge rate. A variety of other EC-free electrolytes have recently been proposed including those with highly concentrated salts like 5 M LiFSI in acetonitrile (AN)46 and 5 M LiFSI in ethyl acetate (EA).47 It is quite likely that cells using such electrolytes would show gassing during unwanted Li plating because AN and EA do not passivate Li well.
In-situ gas measurements show that obvious volume increases occur for cells with EC-free electrolytes at high current rates when lithium plating occurs. The irreversible volume increase is caused by the reaction of freshly deposited Li with EMC and results in cell expansion and rapid capacity fade. Cells with EC-free EMC based electrolyte should be charged at moderate rates, especially at low temperature, to avoid lithium plating and simultaneous gas production.

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