Impact of electrolyte solvent and additive choices on high voltage Li-ion pouch cells

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HIGHLIGHTS

- A $LaPO_4$-coating showed benefits above 4.5 V but not at 4.3 V or 4.4 V.
- $LaPO_4$-coated NMC442/graphite cells containing TAP performed best at 4.5 V.
- Uncoated NMC442/graphite cells with FEC:TFEC performed best at 4.5 V.

ARTICLE INFO

ABSTRACT

The effects that various electrolyte solvents and electrolyte additives had on both $LaPO_4$-coated $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ and uncoated $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$/graphite pouch cells were studied using automated storage, electrochemical impedance spectroscopy, gas production and long-term cycling experiments. Storage experiments showed that the voltage drop during storage at 4.3 or 4.4 V for both coated and uncoated cells was very similar for the same electrolyte choice. At 4.5 V or above, the $LaPO_4$-coated cells had a significantly smaller voltage drop than the uncoated cells except when fluorinated electrolytes were used. Automated charge discharge cycling/impedance spectroscopy testing of cells held at 4.5 V for 24 h every cycle showed that all cells containing ethylene carbonate:ethyl methyl carbonate electrolyte or sulfolane:ethyl methyl carbonate electrolyte exhibited severe capacity fade. By contrast, cells containing fluorinated electrolytes had the best capacity retention and smallest impedance growth during these aggressive cycling/hold tests. Long-term cycling experiments to 4.5 V confirmed that cells containing fluorinated electrolyte had the best cycling performance in the uncoated $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$/graphite cells while cells containing sulfolane:ethyl methyl carbonate electrolyte had the best cycling performance in coated $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$/graphite cells.

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1. Introduction

Since the first commercialization of $LiCoO_2$/graphite Li-ion batteries by Sony in 1991, intensive efforts have been aimed at developing new positive electrode materials with a higher operating voltage and higher discharge capacity [1,2]. Several high voltage electrode materials have been developed [3–8]. However, cycling performance of these materials is poor in conventional carbonate-based electrolytes due to increased electrolyte oxidation at high positive potentials, leading to cell failure stemming from gas generation and impedance growth [9–12].

It has been reported that electrolyte oxidation reactions can generate gaseous products, such as CO_2 and/or C_2H_4, and cause swelling problems and cell failure [13–15]. Some oxidation products can directly accumulate into a surface film on the positive electrode and contribute to impedance growth on the positive electrode [16,17]. Others can dissolve in the bulk electrolyte, migrate to the negative electrode where reduction occurs and generate a film on the negative electrode and therefore contribute to impedance growth on the negative side [18–20].

Using an automated EIS/cycling measurement, Nelson et al. [12] measured the charge transfer resistance as a function of voltage during cycling of $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$ (NMC442)/graphite cells. They demonstrated that impedance growth, especially at the positive electrode, was the main contributor to cell failure in high voltage NMC442 Li-ion cells. Based on ultra high precision

coulometry (UHPC) and symmetric cell studies, Xia et al. [21] found that electrolyte oxidation at the positive electrode, rather than Li consumption in the solid electrolyte interface (SEI) at the negative electrode was the dominant contributor to reducing the coulombic efficiency (CE) and increasing cell impedance when the upper cutoff potential was increased.

Two approaches are commonly used to limit electrolyte oxidation in high-voltage Li-ion cells. The first approach involves surface modification of cathode materials either by providing physical protection layers through material coatings or by the incorporation of electrolyte additives to form a solid electrolyte interphase (SEI). Surface coatings create a physical layer that can slow the rate of parasitic reactions between the charged electrode materials and electrolyte and thus improve the cycle life, calendar life and safety of Li-ion cells [22,23]. Although numerous studies [24–33] have shown that surface coating materials can improve electrochemical performance, recent publications by Nelson et al. [34] and Xia et al. [35] clearly showed that the expected benefit of a LaPO$_4$ coating in NMC442/graphite pouch cells was not present at 4.4 or 4.45 V when advanced electrolytes were used. At 4.5 V, the LaPO$_4$ coating provided benefit only when used in cells containing control electrolyte without additives. The results also indicated that the benefits due to the additives at 4.5 V far outweighed the benefits due to the coating at 4.5 V. Similarly, the formation or modification of the SEI layers on the surface of the positive or negative electrode due to electrolyte additives has been shown to be effective in improving cycle life, calendar life and safety of Li-ion cells [36,37]. Numerous publications [38–49] have shown that electrolyte additives can increase the usable voltage range of electrolytes by stabilizing the electrode/electrolyte interface. However, recent work by Ma et al. [11] showed that the benefit provided by electrolyte additives in traditional carbonate electrolyte above 4.5 V is diminished.

The second approach used to limit electrolyte oxidation in high voltage Li-ion cells involves solvents that are difficult to oxidize. Some organic solvents with strong electron-withdrawing groups, such as sulfones [50,51], nitriles [52,53], ionic liquids [54–57] and fluorinated compounds [58–61] apparently limit oxidation at high potentials. By decreasing the energy of the highest occupied molecular orbital (HOMO) relative to the vacuum level, such solvents normally limit electrolyte oxidation [62–64].

Recently, some studies of the effect of alternative solvents on NMC442/graphite pouch cells have been performed. Xia et al. [65] showed that sulfolane (SL)-based electrolytes with vinylene carbonate (VC) as an SEI-forming electrolyte additive could provide comparable cycling and storage performance to state-of-the-art electrolytes in NMC442/graphite pouch cells tested to 4.4 and 4.5 V. Xia et al. [66] also showed that fluorinated electrolytes containing fluoroethylene carbonate (FEC) and bis(2,2,2-trifluoroethyl) carbonate (TFEC) with prop-1-ene-1,3-sultone (PES) as an electrolyte additive outperformed all non-fluorinated electrolytes with all additives during continuous charge-discharge cycling tests to 4.5 V in NMC442/graphite pouch cells. Using isothermal electrochemical microcalorimetry, Downie et al. [67] showed that the parasitic heat flow from NMC442/graphite cells at high potential with FEC:TFEC electrolyte was much smaller than from cells with conventional electrolytes, suggesting that the fluorinated solvents limited electrolyte oxidation. Downie et al. [67] also observed that the separators extracted from NMC442 cells, tested to high voltage which contained FEC:TFEC electrolytes, were clean and white while those from extracted cells with conventional electrolytes were brown, suggesting electrolyte degradation.

Successfully operating Li-ion cells to high voltage may require the use of a combination of new electrolyte solvents, electrolyte additives as well as surface coatings. In this paper, the impact of different electrolyte solvents and electrolyte additives in high

voltage coated and uncoated NMC442/graphite cells were carefully studied and compared head-to-head using an automatic storage system (up to 4.7 V) and automated EIS/cycling measurements (up to 4.5 V). The voltage drop measured during storage experiments, impedance growth during cycling experiments as well as gas evolution during both cycling and storage experiments were compared to make an overall evaluation in both coated and uncoated NMC442/graphite Li-ion pouch cells. Long-term cycling experiments (to 4.5 V) were also performed to compare the charge-discharge cycling stability of cells containing these electrolyte systems.

2. Experimental

2.1. Electrolyte and electrolyte additives

1 M LiPF$_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 wt% ratio, BASF, 99.99%) was used as the control electrolyte. The other two electrolyte systems, 1 M LiPF$_6$ SL:EMC (3:7 wt % ratio) and 1 M LiPF$_6$ FEC:TFEC (1:1 wt% ratio), were used for comparison based on our previous publications [65]. Additives were included in the three electrolyte systems in a range of 0.5–2 wt%. These additives included vinylene carbonate (VC), prop-1-ene, 1,3-sultone (PES), methane methylenedisulfonate (MMDS), propanediol cyclic sulfate (trimethylene sulfate - TMS), 1,3,2-dioxathiolan-2,2-oxide (ethylene sulfate - DTD), tris trimethylsilyl phosphite (TTSPi), lithium bis(oxalate)borate (LiBOB) as well as triallyl phosphate (TAP). The purities and the suppliers of the solvents and additives used are listed in Table S1 and the structural information of these additives are given in Fig. S1 (supporting information). Figs. S2 and S3 show the voltage (V) vs. capacity (Q) (Figs. S2a and S3a) as well as the dQ/dV vs. V curves (Figs. S2b and S3b) during formation step 1 (charge to 3.5 V). Figs. S2 and S3 show that the different electrolytes have different reduction potentials that are affected by the solvent and additive choices. Figs. S2 and S3 show that the V vs. Q and dQ/dV vs. V curves are similar for the same electrolyte in both types of cells, indicating that the coating does not have an obvious impact on the reaction of the additives with Li$^+$ + e$^-$ at the graphite surface, which agrees with previous work [35].

The electrolyte solvents selected for this study are based on previous work [65,66,68]. The simple reason for choosing FEC-TFEC or SL-EMC:VC is to combine a high dielectric constant solvent with a low viscosity solvent. One component (FEC or SL:VC) can help to form the SEI on the negative electrode and dissolve the lithium salt due its high dielectric constant while the other component (TFEC or EMC) lowers the viscosity and the melting point.

The additives selected for this study are well-known in the literature and apparently improve the quality of the negative electrode SEI or reduce parasitic reactions at high voltage in NMC442/graphite cells. As examples, VC [69] and PES [70] are SEI forming additives and gas reducers during formation. MMDS [71], ES [72], TTSPi [73] have been shown to be effective impedance reducers. Both DTD [74] and TAP [48] can improve the coulombic efficiency (CE) and charge-discharge cycle life. The additive, TAP, can be polymerized through a cross-linked electro-polymerization of its three allyl groups at the surface of both graphite and coated NMC442 electrodes, leading to higher cell impedance [48]. The additive combination 2% PES + 1% DTD + 1% TTSPi, called PES211, was chosen based on previous work which showed cells with PES211 had the best cycling performance among the 110 additive blends studied [75].

2.2. Pouch cell construction

The 402035-size pouch cells used in this study were uncoated-NMC442/graphite cells with a capacity of 240 mAh and LaPO$_4$-