Multifunctional electrolyte additive for improved interfacial stability in Ni-rich layered oxide full-cells

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ABSTRACT

Improving the interfacial stability between the electrode and the electrolyte at high voltage is a key to successfully obtain high energy-density Li-ion batteries. Therefore, this study is dedicated to a novel multifunctional electrolyte additive, methoxystriethylenoxypropyltrimethoxysilane (MTE-TMS), able to stabilize the interface of both Ni-rich layered LiNi 0.5 Mn 0.5 O 2 (NCM851005) cathode and graphite anode in a full-cell. Electrochemical tests reveal that the addition of 1 wt% MTE-TMS significantly improves the long-term cycling stability of the graphite|NCM851005 full-cell, with an achieved maximum capacity of 198 mAh g⁻¹ and its excellent capacity retention of 84% after 100 cycles at C/5 using upper voltage cut-off of 4.3 V vs Li⁺/Li. In contrast, the standard electrolyte in absence of MTE-TMS leads to a rapid performance fade. The significantly improved electrochemical performance is attributed to the formation of a stable surface protective film at both the cathode and the anode surfaces upon long-term cycling in elevated voltage window, and thus suppressing the electrolyte decomposition at and structural degradation of both cathode and anode, resulting in well as reduced transition metal transfer between the two electrodes.

1. Introduction

Lithium-ion batteries (LIBs) are widely used for portable devices, electrical vehicles, large-scale energy storage systems, and are subject to ongoing modifications to meet the growing demands for higher energy and power densities [1,2]. In recent years, nickel-rich layered oxides (LiNi x Mn y Co z O 2, x ≥ 0.6, x + y + z = 1, Ni-rich NCMs) [3], which are cheaper and contain significantly less of toxic cobalt, offer a higher specific capacity (≥ 180 mAh g⁻¹) with an average voltage of ≈3.8 V vs Li⁺/Li [4], as compared to traditional LiCoO 2 (145 mAh g⁻¹) and spinel-LiMn 2 O 4 (120 mAh g⁻¹) [5]. However, large-scale application of Ni-rich NCM cathodes is hindered by severe capacity fading during long-term cycling, which is mainly caused by the instability of the Ni-rich NCM cathode-electrolyte interface at high-voltage (above 4.2 V vs Li⁺/Li), utilization of which would lead to higher energy densities [6–10]. The highly oxidized state of Ni⁴⁺, formed upon Li⁺-deintercalation, is spontaneously reduced to Ni³⁺ and Ni²⁺ by accepting electrons from the electrolyte, causing severe oxidative decomposition of the electrolyte at the cathode-electrolyte interface [6–8,10]. This leads to the formation of nucleophilic fluoride (F⁻) species, which in turn can corrode the transition metals from Ni-rich NCM, causing the structure deterioration of cathode materials [11], when the standard LiPF 6 salt is used. In addition, the similar radius of Li⁺ (0.76 Å) to Ni²⁺ (0.69 Å) leads to the intermixing of Ni and Li layers, which results in the well-known phase transition from layered hexagonal structure (R3m) to spinel (Fd3m) and to cubic rock-salt (Fm3m), causing oxygen release and safety issues [8,12]. This electrochemically inactive rock-salt phase hinders the Li⁺ diffusion at the cathode-electrolyte interface, thus resulting in capacity fading. Additionally, crack formation, induced by internal stress in the secondary particles upon repeated Li⁺-(de)intercalation, provides new sites for the cathode-electrolyte interface reactions, accelerating layered-to-rock-salt phase transition, causing voltage fade [13]. Thus, the protection of the Ni-rich NCMs surface is a key to inhibit their structural deterioration, voltage fade, and achieve stable long-term performance. Effective methods to overcome the instability of the interface for the Ni-rich NCM cathodes are surface coating, bulk doping, and electrolyte additives. The surface coating layers, such as metal oxides [14–16] and metal fluorides [17,18], could prevent side reactions by avoiding the exposure of the Ni-rich NCM to the electrolyte, however, they hinder the Li⁺ diffusion due to their poor Li⁺ conductivity. Bulk doping [19–21] can reduce Li⁺/Ni²⁺ cation intermixing, stabilizing the layered structure, and blocking the generation of grain boundary cracks in secondary particles, but...
the decomposition of the electrolyte at higher voltage cannot be avoided using this strategy. In contrast, using electrolyte additives is a versatile, easy, and economical approach to mitigate these issues [6–8,11,22].

Recently, several kinds of electrolyte additives, such as borates [23], phosphates [24], sulfonates [25], nitriles [26], and fluorides [27], have been reported in the literature for improving stability and performance of Ni-rich NC cathodes. The Si-based electrolyte additives have recently received substantial attention as effective functional additives for Ni-rich NCM cathodes [11,22,28]. Deng et al. [28] demonstrated that the addition of 1 wt% diphenyldimethoxysilane (PDMS) could improve cycling performance of Li[Li0.38Co0.2Mn0.4O2] (NMC622) half-cells, as the siloxane structure provides active sites (Si–O) to remove HF from the electrolyte by affinity, and can, therefore, prevent metal-dissolution from NCM622 cathode. Wang et al. [22] proposed 3-isocyananopropyltriethoxysilane (IPTS) as a high-voltage electrolyte additive to improve Li[Li]NMC622 half-cell, finding that the –NCO group, and its derivatives, could form a stable and uniform surface film at the cathode–electrolyte interface. Jang et al. [11] reported that the silyl functional group, embedded in the organic additive of dimethoxydimethylsilane (DODS), improves the surface stability of NCM811 via a chemical HF scavenging, owing to the matched chemical reactivity of Si with F– and O with H+. Although these Si-based oxidative additives inhibit surface degradation of Ni-rich NC cathodes, they are mostly tested in the half-cell configurations without investigating their ability to reduce crack-formation and voltage fade of Ni-rich NCMs. Moreover, interface reaction mechanisms, causing performance degradation or improvements in full-cells, were not studied, including their effect on the performance of graphite anode.

In this work we present a novel multifunctional additive, methoxytriethyleneoxypropyltrimethoxysilane (MTE-TMS), possessing a unique functionality to simultaneously protect both Ni-rich NCM and graphite electrode surfaces. MTE-TMS improves the long-term cycling stability not only of individual half-cells of graphite and Ni-rich NCM but also of the full graphite||Ni-rich NCM cell. In this study we clarify MTE-TMS action mechanism on the interfacial stabilization and its correlation with the enhanced long-term cycling performance.

2. Materials and methods

2.1. Additive characterization

DFT calculations of the highest unoccupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were performed with the Gaussian 09 software package with a basis set of B3LYP/6–311+ (3df, 2p) [22]. Linear sweep voltammetry (LSV) was conducted to evaluate the anodic stability of electrolytes at a scan rate of 1 mV s−1 from open-circuit voltage (OCV) of ±3.0 to 6.0 V vs Li+/Li, with glassy carbon (Ø = 14 mm) as a working electrode, and lithium metal as the counter/reference electrode.

2.2. Electrode preparation

The cathode was made of 93 wt% LiNi0.88Co0.1Mn0.02O2 (NCM851005, BASF Germany), 1.5 wt% carbon black SC65 (Imerys Graphite and Carbon, Switzerland), 2.5 wt% graphite SFG6L (Imerys Graphite and Carbon, Switzerland) and 3 wt% polyvinylidene fluoride binder (PVDF/130, Solvay) suspended in an N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) solvent and cast onto aluminum foil. For full-cell assembly, commercial graphite anode on a copper foil was composed of 95.7 wt% graphite active material (Hitachi), 0.5 wt% carbon black SC65 (Imerys Graphite & Carbon, Switzerland) and 3.8 wt% binder (sodium carboxymethyl cellulose (CMC) mixed with styrene butadiene rubber (SBR)). The NMP was evaporated under vacuum at 80 °C for 8 h, and circular electrodes were punched out (Ø = 13 mm for NCM851005 and Ø = 14 mm for graphite) and dried overnight at 120 °C in vacuum in order to remove remaining NMP and absorbed water, before introducing electrodes into an argon-filled glove box. Average active mass loading of NCM851005 was 8.9 mg cm−2 in Li||NCM851005 half-cells and ≈12.3 mg cm−2 in graphite||NCM851005 full-cells, respectively. The loading mass of graphite was ≈9.0 mg cm−2. The capacity ratio of graphite anode to NCM851005 cathode was adjusted to ≈1.1.

2.3. Electrochemical performance

Coin-type electrochemical half-cells (PSI standard cells) [29] consisting of NCM851005 cathode as a working electrode, Li metal foil (0.75 mm thick, Alfa Aesar, United States) as a counter electrode, separator (Celgard 2400), and 500 μl standard electrolyte of 1 M LiPF6 in ethylene carbonate (EC):diethyl carbonate (DEC), 3:7 by weight (LP47, BASF SE) without and with an optimal amount of 1 wt% methoxytriethyleneoxypropyltrimethoxysilane (MTE-TMS, Fluorochem, Ltd., UK) were assembled in an argon-filled glove box, with water and oxygen content less than 1 ppm. The cyclic voltammetry (CV) measurements were carried out using an electrochemical workstation (VMP3, BioLogic Science Instruments) at a scanning rate of 0.05 mV s−1, and the voltage ranges for the Li||NCM851005 and the Li||graphite half-cells were 3.0–4.3 V and 0.05–3.0 V vs Li+/Li, respectively. Cells were as well galvanostatically cycled between 3.0 and 4.3 V at C/5 (42 mA g−1) rate after two formation cycles at slower C/10 (21 mA g−1) using an Arbin battery cycle. The AC impedance spectra were recorded during cycling in the frequency range of 10 mHz–100 kHz with an amplitude of 10 mV, using an impedance spectroscopic analyzer (VMP3, BioLogic Science Instruments), after a potentiostatic step of 5 h for equilibration. The impedance spectra were fitted with the use of the Z-View equivalent circuit modeling software. The GITT was used with a constant-current of C/10 for 10 min, followed by 3 h open-circuit relaxation between 3.0 and 4.3 V. The Li||graphite half-cells were cycled between 0.05 and 1.5 V with initial cycle at C/20 and subsequent cycles at 0.2 C (1 C = 372 mA g−1).

Coin-type electrochemical full-cells (PSI standard cells) [29], consisting of NCM851005 cathode, graphite anode, separator (Celgard 2400) and standard electrolyte without and with an optimal amount of 1 wt% MTE-TMS additive, were assembled in an argon-filled glove box. Their charge-discharge cycling performance was tested between 3.0 and 4.25 V (corresponding to 4.3 V vs Li+/Li) at C/5 (42 mA g−1) after two formation cycles at C/10 (21 mA g−1), using an Arbin battery cycler. All the electrochemical tests were carried out at room temperature. For additional experiment, determining our additive’s effectiveness in full-cells, the graphite anodes were pre-lithiated. For pre-lithiation the graphite anodes were assembled to the half-cells with metallic Li and charged to 0.05 V vs Li+/Li. Then these graphite anodes were washed in electrolyte and assembled into the full-cells with pristine NMC851005 cathodes.

2.4. Chemical and physical characterization

For differential scanning calorimetry (DSC) tests, the Li||NCM851005 half-cells were fully charged to 4.3 V at C/10. Then, the cells were disassembled, and the cathode materials were scraped from the electrodes, getting about 2–5 mg of powders. The powders were sealed in a high-pressure DSC sample pan. The DSC tests were performed on the Perkin-Elmer DSC 8000 in the range from 30 to 300 °C with a heating rate of 5 °C min−1.

Electrolyte-dependent crack formation for NCM851005 cathodes during cycling was examined using cross-sectional SEM. Cross-section samples of pristine and cycled cathodes were prepared using a Hitachi Ion Mill IM4000 at an acceleration voltage of 4 kV and an ion current of 120 μA. The milling time was 7 h. The cathodes were transferred to a scanning electron microscope (SEM, Zeiss Gemini) and imaged with an
acceleration voltage of 10 kV (in-lens and secondary electron detectors). Morphology changes on the cathodes and anodes surface were imaged using SEM (Zeiss Gemini) at 10 kV. The thickness and uniformity of surface film formed on the cathodes with cycling in different electrolytes were studied using transmission electron microscopy (TEM, FEI Tecnai G2) at 120 kV. Cycled cathode active materials were scraped off the electrodes (cycled in the full-cells) and dispersed in DMC before being transferred onto a lacey-carbon-supported Cu grid. Structural data for NCM851005 cathode after cycling were obtained ex situ by XRD analysis, by comparing the patterns of pristine and cycled NCM851005 cathodes. Pristine and cycled NCM851005 active materials were removed from the pristine and cycled electrodes, and filled into a capillaries with an outside diameter of 0.5 mm with 0.01 mm wall thickness. The capillaries were then sealed with wax inside an argon-filled glove box. X-ray powder diffraction measurements were performed in the 20 range of 20–80° at a scan rate of 1° min⁻¹ at 45 kV and 40 mA, using a PANalytical Empyrean diffractometer, equipped with a linear detector (X'Celerator) and using Cu–Kα radiation (λ = 1.5418 Å). Local structural changes in graphite anode material after cycling were investigated, using a Raman microscope (Labram HR800, Horiba-Jobin Yvon, Japan), equipped with a He–Ne laser (632.8 nm) at 2 mW. A typical spectrum was recorded in the range of 1000–1800 cm⁻¹ using a 50x objective (ULWDMs Plan 50, NA = 0.55, Olympus, Japan), accumulating 3 scans with an acquisition time of 20 s per scan.

The chemical analysis of leached Ni, Co and Mn amounts on anode was performed on inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Arcos). The ICP-OES samples were prepared with the following procedures: cycled graphite anodes were first washed with DMC for three times, then graphite active material was carefully scraped out from the cycled graphite anodes and dissolved into 0.6 M HCl (30%). The resulting transparent solution was subsequently diluted with milliQ water before being subjected to ICP-OES analyses.

The surface of NCM851005 and graphite were analyzed by ex situ XPS, using ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) with focused monochromatized Al Kα radiation (hv = 1486.6 eV). High resolution spectra were obtained at a power of 150 W under a base pressure of 2 × 10⁻⁹ mbar. The electrodes, cycled in the full-cells, were washed with DMC for the removal of residual electrolyte salt, followed by drying in the glove box at room temperature. They were transferred from the glove box to the XPS chamber without exposure to the air by using a vacuum-sealed transfer holder. The beam size was about 500 μm² and the pass energy was 30 eV. Binding energy was corrected based on the C-C bond in the C 1s level at 285 eV. Curve-fitting were conducted on the peaks with Gaussian (20%) and Lorentzian (80%) functions using XPSPEAK 4.1 program, till the goodness of fit is minimized, after having Shirley-type background correction. The full width half maximum (FWHM) of each component in one spectrum was set to be ±0.2 eV as the same.

3. Result and discussion

3.1. Oxidation and reduction behaviors of MTE-TMS

The oxidation and reduction behavior of MTE-TMS can be predicted by calculating the energy levels of the highest occupied molecular orbital (HOMO) and of the lowest unoccupied molecular orbital (LUMO). The calculation results show that the HOMO energy level of MTE-TMS is higher than those of EC and DEC solvents (Fig. 1a), indicating MTE-TMS can be oxidized on the cathode before the solvents of the standard electrolyte. These calculations are in good agreement with the results obtained from linear sweep voltammograms (LSV) shown in Fig. 1b, performed using glassy carbon as a working electrode. The electrolyte with MTE-TMS is preferentially oxidized as the oxidative current in LSV is larger than that for the cell without MTE-TMS, indicating that oxidation of electrolyte with the additive starts before the standard electrolyte (Fig. 1b), with specific MTE-TMS reduction at about 3.75 V (inset in Fig. 1b). The same tendency is also observed in the cyclic voltammograms (CVs) of the NCM851005 (Figs. 1c and S1). The onset oxidation potential (inset in Fig. 1c) is lower for the MTE-TMS-containing electrolyte as compared with standard electrolyte, confirming higher oxidation activity of MTE-TMS on the cathode surface. The difference between the redox peak potentials (ΔV) of NCM851005 becomes smaller with the presence of MTE-TMS additive by ≈24 mV (Fig. 1c). This suggests that MTE-TMS additive decreases the polarization and improves the reversibility of NCM851005 cathode during Li⁺(de)intercalation [30].

The reduction of MTE-TMS-containing electrolyte was investigated using the CV curves, recorded for the graphite electrodes. A clear reduction peak is observed at ≈1.5 V for the electrolyte with MTE-TMS (Fig. 1d), in agreement with lower LUMO of MTE-TMS in comparison to standard solvents, and this peak is likely to be a signature of the preferential reduction of MTE-TMS, suggesting that MTE-TMS participates in the formation of a solid electrolyte interface (SEI) layer on the graphite. Overall, theoretical calculations and experimental results reveal that MTE-TMS could be both oxidized at the cathode and reduced at the anode prior to the carbonate solvents, participating in formation a protective surface film on the cathode and the anode, preventing electrolyte decomposition in further cycles.

3.2. Electrochemical cycling of Li||NCM851005 half-cells

Firstly, the half-cells of Li||NCM851005 were tested with the standard electrolyte (1 M LiPF₆/EC:DEC) without and with an optimal amount of 1 wt% MTE-TMS additive (Fig. S2), and their cycling performance and impedance spectra changes during cycling are compared in Fig. 2. Without MTE-TMS, the cell exhibits the initial charge and discharge capacities of 243 and 202 mAh g⁻¹, respectively, with the initial Coulombic efficiency (ICE) of 83% (Fig. 2a). Discharge capacity decreases to 92 mAh g⁻¹ after 100 cycles, yielding a very low capacity retention of 46 % (Fig. 2g), which is accompanied by fading of redox peak intensities and their shifting positions, identifying the poor reversibility of the phase transition between hexagonal structures (H2–H3) at ≈4.2 V (Fig. 2b), and significantly increased interfacial resistances (Fig. 2c, 2f, 2i) with cycling. On the other hand, with MTE-TMS, a significantly improved cycling performance is observed: initial charge and discharge capacities are 230 and 206 mAh g⁻¹, respectively, corresponding to ICE of 90 % (Fig. 2d), and improved capacity retention of 89 % after 100 cycles (Fig. 2g) even under upper voltage cut-off of 4.3 V with a high mass NCM851005 loading of ≈8.9 mg cm⁻². The significantly improved long-term cycling stability is clearly due to the cathode–electrolyte interface stabilization by MTE-TMS additive, maintaining the redox peak positions upon multiple Li⁺(de)intercalations, resulting in reduction of H2–H3 phase transitions (Fig. 2e), with limited increase in the resistance (Fig. 2c, 2f, 2i) and overpotentials, as supported by galvanostatic intermittent titration technique (GITT) experiments (Fig. S3b).

The layered to rock-salt phase transition as a result of cation mixing is known to cause not only capacity decay and overpotential increase but also voltage fade [13]. In order to evaluate the effect of MTE-TMS on the voltage fade, the variation of average charge–discharge voltages during cycling without and with MTE-TMS are compared in Fig. 2h, which were calculated by dividing the cell’s energy by the cell’s capacity [31]. Both electrolytes exhibit an increase of the average charge voltage due to overpotential growth with cycling, however, more in case of the standard electrolyte. The average discharge voltage decays only by 0.054 V after 100 cycles from the first average discharge voltage of 3.815 V with MTE-TMS, whereas voltage deteriorates by approximately 0.749 V from the first average discharge voltage of 3.822 V (more than 10 times) for the cathode with standard electrolyte. This result confirms that the role of MTE-TMS in stabilizing the cathode-electrolyte interface and cathode structure leads to reduced voltage fade and improved long-term cycling performance.
In addition to enhanced electrochemical performance, the MTE-TMS additive makes electrolyte safer as can be seen from DSC analysis of charged cathodes to 4.3 V (Fig. S4). The results show significantly enhanced thermal stability of NCM851005 cathode with MTE-TMS additive: charged cathode in the standard electrolyte exhibits a sharp exothermic peak at ±209 °C, with a heat generation of 415 J g⁻¹, while MTE-TMS shifts an exothermic peak to higher temperature (±213 °C), and a reduced heat generation by ±25% (295 J g⁻¹).

3.3. Electrochemical cycling of graphite‖NCM851005 full-cells

Considering the effects of MTE-TMS additive on the electrochemical performance of both Li‖NCM851005 (Fig. 2) and Li‖graphite (Fig. S5) half-cells, the full-cells of graphite‖NCM851005 were assembled and tested with standard electrolyte without and with 1 wt% MTE-TMS additive in a voltage window between 3.0 and 4.25 V (corresponding to 4.3 V vs Li⁺/Li⁻). Comparison of their electrochemistry is presented in Fig. 3. MTE-TMS additive in the full-cells, similarly to half-cells, causes a significant improvement in long-term cycling performance, as shown in Fig. 3e. The maximum capacity of 198 mAh g⁻¹ (Fig. 3c) with significantly higher capacity retention of 84 % at the 100th cycle and high Coulombic efficiency of 99.8% (Fig. 3e, f) were obtained. By contrast, lower capacities and Coulombic efficiencies, a rapid capacity fade (retention of 61 % at the 100th cycle) and larger voltage polarization were observed for the full-cell, cycled without MTE-TMS (Fig. 3a, b, c, f).

In the dQ/dV plots one can see that while redox peaks, due to charge and discharge processes, are well preserved in the presence of MTE-TMS additive (Fig. 3d), in the standard electrolyte (Fig. 3b), a substantial loss of redox peak stability and capacity with cycling occurs, which is associated with structural degradation of active materials. This emphasizes the critical role of MTE-TMS additive in stabilizing the electrolyte-electrode interface for improved full-cell cycling stability. Although cycling stability is improved by the presence of MTE-TMS, capacity retention (84%) is still lower than that of half-cell (Fig. 2g). The reasons behind can be: (i) effectiveness of MTE-TMS is reduced in full-cells, or (ii) lithium inventory loss during SEI formation on graphite anode during the first cycle [32]. To confirm that MTE-TMS is equally effective in full-cells, experiments with pre-lithiated graphite anode were performed. These results support our reasoning that less favorable capacity retention in full- as compared to half-cells is caused indeed by the loss of active Li in irreversible side reactions during the first cycle [32]. The full-cell with MTE-TMS and pre-lithiated graphite (Fig. S6) showed the same capacity retention (89%) as in case of the half-cell (Fig. 2), affirming effectiveness of MTE-TMS.

3.4. Cycling-induced morphological changes

Fig. 4 shows the cross-sectional and top-view SEM images of the pristine NCM851005, cycled without and with MTE-TMS additive in the full-cells for 100 cycles. The cross-sectional view (Fig. 4a) clearly
Fig. 2. Voltage profiles and their differential plots for Li|NCM851005 half-cells, cycled between 3.0 and 4.3 V in the standard electrolyte (a, b) without and (d, e) with MTE-TMS additive. Comparison of (g) cycling performance, (h) average charge-discharge voltages, (c, f) impedance evolution, and (i) changes in the interfacial resistances determined by fitting with the equivalent circuit in (c).

shows that pristine NCM851005 particles are crack-free, have smooth surface, and are compact. Cycling in the standard electrolyte without MTE-TMS results in the formation of internal cracks within secondary particles (Fig. 4c), generated along the grain boundaries from the core and propagating to the surface [8,33–35]. The crack formation is ascribed to strain due to the stress arising from the anisotropic lattice expansion and contraction of different grains inside secondary particles upon repeated Li^+-intercalation [8,12,35,36]. The cracks facilitate the penetration of the electrolyte into the cathode particles along the primary particle boundaries through the crack network, leading to expansion of cracks and formation of new cathode-electrolyte interface [37]. A thick surface film covers the whole surface of the primary particles (Fig. 4d), as a result of the electrolyte decomposition [8].

The crack formation and the degradation of the surface of primary particles lead to a loss of electrical contact between the primary particles [38–44], thus deteriorating the full-cell cycling performance (Fig. 3a and e). However, such crack formation is significantly reduced with the use of MTE-TMS additive, despite few hairline cracks still visible in Fig. 4e. Besides, the morphology of primary particles is sustained on the cycled cathode (Fig. 4f), and a very thin surface film, probably formed by additive decomposition products, is visible on the surface of the particles. This implies that MTE-TMS participates in the formation of a stable surface-protective film, avoiding the direct contact between NCM851005 particles and electrolyte, thus inhibiting the reactions at the cathode-electrolyte interface, and in such a way reducing the development and propagation of cracks.

The SEM images of graphite anodes, before and after cycling in the standard electrolyte without and with MTE-TMS additive, are shown in Fig. 5. The pristine graphite anode (Fig. 5a, b) has a uniform smooth surface. After cycling in the standard electrolyte without MTE-TMS (Fig. 5c, d), the graphite’s surface is completely covered by a thick polymer-like layer and surface is rougher than that of pristine. However, with MTE-TMS additive (Fig. 5e, f), the surface of graphite remains smooth with new nano- to sub-micrometer plate-like crystals, confirming the effectively passivating SEI. This indicates the role of MTE-TMS in protecting the graphite anode as well as reducing the electrolyte decomposition, thus improving the full-cell cycling performance (Fig. 3).

3.5. Cycling-induced bulk structural changes

In order to compare the structural stability of NCM851005, cycled without and with additive, the full-cells after the 100th cycle were disassembled, and the NCM851005 cathodes were taken out for the ex situ XRD analysis. In case of pristine NCM851005 cathode (Fig. 6a-i), all the major peaks in the XRD patterns are identified to layered hexagonal structure (R3m). The a and c lattice parameters of pristine material
are 2.8713 and 14.1883 Å, respectively, with a c/a ratio of 4.9415 and unit cell volume of 101.2955 Å³. While after 100 cycles without MTE-TMS, the broadened (003) reflection is weakened and greatly shifted to lower 2θ region (Fig. 6b-ii) due to the loss of structural order and crystallinity, as compared to pristine (Fig. 6b-i). At the same time the (104) reflection (Fig. 6c-ii) is shifted to higher 2θ region, which suggests the decrease of ab-plane [23]. This correlates to the substantial loss of redox peak ordering and intensity in the dQ/dV plots after cycling (Fig. 3b). In comparison, the use of MTE-TMS additive lead to the significantly improved structural stability, as indicated by reduced magnitude in the shift of the (003) (Fig. 6b-iii) and the (104) (Fig. 6c-iii) reflections, as well as their reduced broadening and weakening after cycling, in agreement to well-maintained redox-peaks in the dQ/dV plots (Fig. 3d).

Fig. 6d shows the changes in the lattice parameters and cell volume of NCM851005 cathode with cycling. Both cycled cathodes exhibit lattice expansion along the c-axis and contraction along the ab-plane, however, to much higher degree in absence of MTE-TMS. Note that XRD patterns of cycled cathodes were collected from fully discharged full-cells, thus the changes in the lattice parameters are reflecting the Li inventory loss during cycling [8,23,45–47]. In case of the loss of active Li, the a parameter typically decreases due to the smaller ionic radius of the transition-metal ions as a result of oxidation [48]. In contrast, the c parameter increases due to the creation of Li-deficient state with a stronger electrostatic repulsion between the oxygen–oxygen layers across the Van der Waals gap [45,49]. As a result, a decrease of unit cell volume is observed for both cycled cathodes, consistent with ear-
The structural degradation of anode was investigated by Raman spectroscopy, it being very sensitive to graphite’s structural changes. Fig. 7 shows the Raman spectra of graphite anode: pristine and after 100 cycles in standard and in MTE-TMS-containing electrolyte. Raman spectrum of pristine anode consists of prominent G-band at 1582 cm$^{-1}$, and relatively weak D-band at 1335 cm$^{-1}$ [50]. Cycling of anodes in both electrolytes results in the growth of D-band at the expense of G-band, indicating a decrease in graphite structural ordering, along with the formation of sp$^3$-hybrid carbon-containing SEI species [51]. In general, the degree of disorder of carbon is evaluated using the relative intensity ratio of D-band to G-band (R = I_D/I_G). The higher the R value, the higher the structural disorder. The R increases from 0.344 for the pristine anode, to 0.439 after cycling with MTE-TMS additive, and to a significantly larger value of 0.706 for graphite cycled in the standard electrolyte. The lower R value with MTE-TMS additive indicates the greater structural preservation of graphite and relatively thin SEI layer, as observed in SEM images (Fig. 5c, 5f). In addition, a new shoulder at 1614 cm$^{-1}$ observed for both cycled anodes, the so-called D’-band, attributed to oxidized sp$^2$ carbon that represents surface defects [52], supporting the occurrence of structural disordering during cycling. The D’-band is relatively weak for the anode cycled with MTE-TMS additive, as compared to that cycled with standard electrolyte, again indicating structural preservation improvement when cycling in presence of MTE-TMS. This suggests that the use of our multifunctional electrolyte additive preserves better not only the structural stability of NCM851005 cathode but also structure of...
To better understand the surface chemistry changes due to the presence of additive, ex situ XPS was used to investigate the compositions of the surface on cycled NCM851005 and graphite electrodes, recovered from the full-cells.

Fig. 8A shows comparison of the XPS spectra of pristine and cycled cathodes, depending on the electrolyte composition. In the Ni 3p spectra, cycling without and with additive results in a significant difference: without MTE-TMS, the peaks of pristine material (Fig. 8A-a) are no longer visible after cycling (Fig. 8A-b) mainly because of a thick layer formed by electrolyte-degradation (Fig. 8B-b), as compared to the uncycled cathode (Fig. 8B-a). Spectral features are, however, well maintained for NCM851005 electrode, cycled with MTE-TMS additive (Fig. 8A-c), where Ni signal is clearly resolved. Peak of NCM851005 lattice (dark blue) M–O (M = Ni, Co, Mn) at 529.8 eV [27,53–57] in the O 1s spectrum is also still clearly visible for the cycled cathode with MTE-TMS additive, whereas it is completely shielded by other compounds on the electrode surface after cycling in the standard electrolyte due to the formation of thick surface film with high coverage, caused by severe electrolyte oxidation [58]. These results indicate that MTE-TMS induces formation of thinner surface film and prevent further electrolyte decomposition, consistent with our TEM results, where cathode cycled is covered with a thin and mostly uniform surface film (≈8 nm in thickness) (Fig. 8B-c). A new broad peak at 533.8 eV in the O 1s spectra (green), ascribed to various C–O-bond-containing compounds, and an enhanced peak at 532.4 eV, characteristic for C=O (dark yellow), can both be attributed to O-containing electrolyte decomposition products [53,54]. Higher concentration of C–O with MTE-TMS additive implies the accumulation of C–O containing decomposition products of the additive. In the C 1s spectra, new peaks of C–O (286.1 eV), C=O (288 eV) and CO$_3^{2–}$ (290 eV) functionalities from carbonate solvents decomposition are observed on both cycled cathodes, besides the peaks of C–H/C–C and C–F (PVDF) visible for pristine [53,54]. Higher concentration of C=O and CO$_3$ without MTE-TMS can be explained by the
more intense oxidative decomposition of carbonate solvents. In the F 1s spectra, both cycled cathodes show new peaks close to 687.8 and 685.5 eV, attributable to LiPF$_6$O$_2$ and LiF, respectively, from LiPF$_6$ decomposition in addition to the peak of PVDF at 688.8 eV, visible for pristine electrode [5,28,53,54,59]. Lower concentration of electrically resistive LiF on the cycled cathode with MTE-TMS additive might contribute to the decrease in the interfacial resistance and enhanced full-cell performance (Fig. 3c, e). In addition, features of PVDF binder, on cathode cycled with MTE-TMS additive, still remain clearly visible, contrary to their vague features for electrode cycled without MTE-TMS, confirming a thinner surface film formed with MTE-TMS additive, consistent with C 1s spectra results. In the P 2p spectra, higher concentration of Li$_6$PF$_5$ (137.1 eV) and Li$_4$PF$_6$O$_2$ (134.1 eV) species, which are the decomposition products of LiPF$_6$ (LiPF$_6$ → LiF + PF$_5$, PF$_5$ + H$_2$O → POF$_3$ + 2HF and POF$_3$ + ne$^-$ + nLi → Li$_4$PO$_3$F$_y$ + LiF) [22,28], are observed at the cycled cathode without MTE-TMS as compared to the one with MTE-TMS. These results indicate that MTE-TMS effectively scavenges the acidic species (e.g. HF, PF$_5$ and PF$_3$O) from the electrolyte, which is characteristic for Si–O functional group [11,60], leading to improved surface stability of the NCM851005 cathode. The most significant difference between the two electrolytes is revealed in the Si 2p spectra: the use of MTE-TMS additive results in the presence of Si–C [5,61], Si–O [22,28] and Si–F [22,62] features at 103.9, 103.3 and 102 eV, respectively, confirming that
the surface film is built from the oxidative decomposition products of MTE-TMS.

Surface chemistry studies of cycled cathodes have shown that, after cycling in the standard electrolyte, the surface film is mainly composed of LiPF$_6$-derived inorganic species including LiF, Li$_x$PF$_y$, Li$_x$PF$_y$O$_z$, and Li$_2$CO$_3$ at a relatively high concentration, originating from carbonate solvents. In contrast, the surface of the cathode, cycled with MTE-TMS additive, is covered with organic compounds, along the MTE-TMS decomposition products, forming a relatively thin and mostly uniform surface film, as the Ni and metal–oxygen bonds can be still detected.

Fig. 9 shows XPS spectra illustrating the chemical changes of graphite anode surface after prolonged cycling. The C 1s spectrum of pristine anode (Fig. 9a) contains a strong peak at 285 eV, corresponding to C–C/C–H bonds in carbon, tiny peaks at 286.7 and 288 eV from C=O and CO$_2$ of CMC binder, and at 285.7 eV characteristic to SBR [51,53,54,63,64].

The O 1s spectrum shows two peaks at 533.8 and 531.8 eV, arising from the CMC binder due to the presence of C–O and C=O functional groups, respectively [51,59,64]. After cycling, changes on de-lithiated graphite electrodes are observed on both cycled anodes (Fig. 9b,c) and are mainly due to the formation of the SEI. New peaks, characteristic to C–O (286.1 eV), C=O (288 eV) and CO$_3^{2-}$ (290 eV) functionalities, are present in the C 1s spectra, while the corresponding O 1s peaks are observed at 532.4 and 533.7 eV [58,65]. These contributions are attributed
to Li$_2$CO$_3$, alkyl carbonate and carboxylate salts from electrolyte decomposition products [51,58,65], and are more intense for electrodes cycled without MTE-TMS. A new shoulder at ≈282.6 eV in the C 1s spectrum from the electrode, cycled in standard electrolyte (Fig. 9c), is of particular importance, as it is due to the presence of lithiated graphite species (LiC$_x$) [59], implying that not all Li$^+$ ions could de-intercalate from graphite and return to the cathode. This lithium loss to the anode is most likely due to a high overpotential [46], as observed with full-cell cycling results shown in Fig. 3a. Differences are also observed in the F 1s and P 2p spectra. Peaks characteristic of Li$_x$PF$_y$, Li$_x$PF$_y$O$_z$, and LiF, are observed in the F 1s spectra at 687.4 and 685.5 eV, while peaks are present in the P 2p spectra at 137.1 and 134.1 eV for Li$_x$PF$_y$ and Li$_x$PF$_y$O$_z$ [5], for cells cycled both with and without additive. These originate from the decomposition of LiPF$_6$ salt, supported by the Li 1s spectra. However, the use of MTE-TMS additive leads to a notable decrease in the concentration of both P–F–O and Li–F compounds, confirming the role of MTE-TMS in scavenging the acidic species. The evidence of the Si-containing species generated via reductive decomposition MTE-TMS are observed in the Si 2p spectrum of anode cycled with MTE-TMS additive (Fig. 9c), similarly to the case of NCM85105 cathode. The XPS results of the graphite anodes indicate that while the SEI layer, formed in the standard electrolyte, includes relatively high concentrations of LiF, Li$_x$PF$_y$/Li$_x$PF$_y$O$_z$, 

Fig. 9. XPS spectra for chemical surface composition determination of (a) pristine graphite anode and cycled anodes taken from graphite|NCM851005 full-cells, cycled between 3.0 and 4.25 V in the standard electrolyte (b) without and (c) with MTE-TMS additive for 100 cycles.
and Li$_2$CO$_3$, MTE-TMS reductive decomposition products are present as the SEI species at the surface of anode cycled with MTE-TMS additive. Note that MTE-TMS oxidizes and reduces before the standard electrolyte, as shown in LSV and CV (Fig. 1). MTE-TMS additive might undergo earlier decomposition during early cycles, forming the relatively thin surface film/SEI layer, composed of Si-containing species and providing surface structural robustness to NCM815005 as well as graphite. The summary of MTE-TMS additive working principle is illustrated in Scheme 1b.

4. Conclusions

The MTE-TMS dual action electrolyte additive, able to protect both cathode and anode, has been studied and its working mechanism clarified. LSV and CV electrochemical experiments confirmed the hypothesis, raised from results of density functional theory calculations, that MTE-TMS is oxidized and reduced prior to the standard carbonate solvents. Ex situ analysis showed that MTE-TMS forms a stable and thin surface protective film on the NCM815005, containing Si species, which effectively reduced crack formation, metal-dissolution, and structural degradation of the cathode. MTE-TMS also forms a stable SEI layer on the graphite anode, stabilizing graphite structure and preventing thickening of the SEI.

MTE-TMS’ effectiveness, on both anode and cathode, results in superior cycling performance of the full-cells, with 1 wt% MTE-TMS in electrolyte, delivering high capacity of 198 mAh g$^{-1}$, along with an excellent capacity retention of 84% after 100 cycles at C/5, while cycled to upper cut-off voltage of 4.25 V (4.3 vs Li$^+/\text{Li}$). Our results demonstrate that MTE-TMS has a potential to help the realization of high-energy density Li-ion batteries through enabling wider working voltage range for Ni-rich oxide cathodes.

Data availability

The raw/processed data can be provided by authors upon reasonable request.

Author contributions

H.Q.P. and S.T. designed the study and wrote the manuscript. M. M. and M. E. K. performed the XPS measurements. M. T. conducted the ICP-OES characterizations. S.T. supervised the project. All authors discussed the results, and commented on this manuscript.

Declaration of competing interest

None

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2020.08.026.

References

[1] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367, doi:10.1038/35104644.
[2] M. Armand, J.-M. Tarascon, Building better batteries, Nature 451 (2008) 652–657, doi:10.1038/451652a.
[3] S.T. Myung, F. Maglia, K.J. Park, C.S. Yoon, P. Lamp, S.J. Kim, Y.K. Sun, Nickel-Rich Layered Cathode Materials for Automotive Lithium-Ion Batteries: Achievements and Perspectives, ACS Energy Lett 2 (2017) 196–223, doi:10.1021/acsenergylett.6b00594.
[4] J. Li, L.E. Downie, L. Ma, W. Qiu, J.R. Dahn, Study of the Failure Mechanisms of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Cathode Material for Lithium-Ion Batteries, J. Electrochem. Soc. 162 (2015) A1401–A1408, doi:10.1149/2.111507jes.
[5] Q. Zheng, L. Xing, X. Yang, X. Li, C. Ye, K. Wang, Q. Huang, W. Li, N-N-Allyl-, N-Bis(trimethylsilyl)amine as a Novel Electrolyte Additive to Enhance the Interfacial Stability of a Ni-Rich Electrode for Lithium-Ion Batteries, ACS Appl. Mater. Interfaces 10 (2018) 16843–16851, doi:10.1021/acsami.8b00913.
[6] H.Q. Pham, E.-H. Hwang, Y.-G. Kwon, S.-W. Song, Approaching the maximum capacity of nickel-rich LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ cathodes by charging to high-voltage in a non-flammable electrolyte of propylene carbonate and fluorinated linear carbonates, Chem. Commun 55 (2019) 1256–1258, doi:10.1039/c8cc10017a.
[7] K. Kim, Y. Kim, S. Park, H. Ji, S. Ji, K. Shin, J. Woo, S. Kim, S. You, N. Choi, Dual-function ethyl 4,4,4-trifluorobutylate additive for high-performance Ni-rich cathodes and stable graphite anodes, J. Power Sources 396 (2018) 276–287, doi:10.1016/j.jpowsour.2018.06.046.
[8] H.Q. Pham, Y.H. Thi Tran, J. Han, S.W. Song, Roles of Nonflammable Organic Liquid Electrolyte in Stabilizing the Interface of the LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Cathode at 4.5 V and Improving the Battery Performance, J. Phys. Chem. C 124 (2019) 175–185, doi:10.1021/acs.jpca.8b09690.
[9] B.J. Chae, T. Yim, Sulfonate-immobilized artificial cathode electrolyte interphases layer on Ni-rich cathode, J. Power Sources 360 (2017) 480–487, doi:10.1016/j.jpowsour.2017.06.037.
[10] T. Yim, S.H. Jang, Y.K. Han, Triphenylborate as a bi-functional additive to improve surface stability of Ni-rich cathode material, J. Power Sources 372 (2017) 24–30, doi:10.1016/j.jpowsour.2017.04.044.
[11] S.H. Jang, T. Yim, Effect of Silyle Ether-functionalized Dimethoxydimethylsilane on Electrochemical Performance of a Ni-rich NCM Cathode, ChemPhysChem 18 (2017) 3402–3406, doi:10.1002/cphc.201700921.
[12] H.H. Ryu, K.J. Park, C.S. Yoon, Y.K. Sun, Capacity fading of Ni-rich Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ (0.6 ≤ x ≤ 0.95) Cathodes for High-Energy-Density Lithium-Ion Batteries: Bulk or Surface Degradation? Chem. Mater. 30 (2018) 1155–1163, doi:10.1021/acs.chemmater.7b05269.
[13] P. Yan, J. Zheng, J. Liu, B. Wang, X. Cheng, Y. Zhang, X. Sun, C. Wang, J. Zhang, Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries, Nat. Energy 3 (2018) 600–605, doi:10.1038/s41560-018-0191-3.
H.Q. Pham, M. Mirolo and P. Mirolo.

Energy Storage Materials 33 (2020) 216-229

H.Q. Pham, K.-J. Park, M.-J. Choi, F. Maglia, S.-J. Kim, K.-H. Kim, C.S. Yoon, Y.-K. Sun, High-Capacity Concentration Li2MnO3 Cathode for Lithium-Ion Batteries, Adv. Energy Mater. 8 (2018) 1703612, doi:10.1002/aenm.201703612.

A.O. Kondrakov, A. Schmidt, J. Xu, H. Gellweiler, R. Möng, P. Hartmann, H. Sommer, T. Brezesinski, J. Janek, Anisotropic Lattice Strain and Mechanical Degradation of High-Capacity Low-Nickel Cathode Materials for Lithium-Ion Batteries, J. Phys. Chem. C 121 (2017) 3286–3294, doi:10.1021/acs.jpcc.6b11319.

H. Maleki Kheirnejad, S. Li, Controllable Cathode-Electrolyte Interface of LiNi0.5Mn1.5O4 for Lithium-Ion Batteries: A Review, Adv. Energy Mater. 9 (2019) 1901097, doi:10.1002/aenm.201901097.

M.M. Bessi, S. Xia, K. Kuppan, Y. Huang, M. Metzger, A.K. Shukla, G. Schneider, S. Hellstrom, J. Christensen, M.M. Doeff, Y. Liu, Mesostructural Chemomechanical Interplay of the LiNi0.5Mn1.5O4 Cathode in Solid-State Polymer Batteries, Chem. Mater. 31 (2019) 53–68, doi:10.1021/acs.chemmater.8b05063.

H.H. Sun, A. Mantiram, Impact of microcrack generation and surface degradation on a nickel-rich Li[Ni0.8Co0.19Mn0.01]O2 Cathode for Lithium-Ion Batteries, Chem. Mater. 29 (2017) 8486–8493, doi:10.1021/acs.chemmater.7b03266.

J. Zheng, F. Yan, L. Estevéz, C. Wang, J.G. Zhang, Effect of calcination temperature on the electrochemical properties of nickel-rich Li[Ni0.5Mn1.5O4] cathodes for lithium-ion batteries, Nano Energy 49 (2018) 538–548, doi:10.1016/j.nanoen.2018.04.077.

H.H. Ryu, G.T. Park, C.S. Yoon, Y.K. Sun, Microstructural Degradation of Ni-Rich Li[Ni0.5Mn1.5O4] Cathodes During Accelerated Calendar Aging, Small 14 (2018) 1803179, doi:10.1002/smll.201803179.

S.-K. Jung, H. Gwon, J. Hong, K.-Y. Seo, D.H. Seo, H. Kim, J. Hyun, W.-Y. Kang, K. Ko, Understanding the Role of Ni in Li[Ni0.5Mn1.5O4] O2 Cathodes for Lithium-Ion Batteries, Adv. Energy Mater. 4 (2014) 1300787, doi:10.1002/aenm.201300787.

M. He, C.C. Su, Z. Feng, L. Zeng, J.W. Wu, M.J. Bedeyk, F. Fenter, Y. Wang, Z. Zhang, High Voltage Li[Ni0.5Mn1.5O4]/Graphite Cell cycled at 4.6 V with a FEC/HEDEC-Based Electrolyte, Adv. Energy Mater 7 (2017) 1–9, doi:10.1002/aenm.201700109.

H.R. Kim, S.G. Woo, J.H. Kim, W. Choi, Y.J. Kim, Capacity fading behavior of Ni-rich layered cathode material, Chem.ElectroChem. 7 (2020) 474–483, doi:10.1002/celc.201900107.

J.-Y. Kang, X. Yao, Suppressing the Phase Transition of the Layered Ni-Rich Cathode through High-Voltage Cycling by Introducing Low-Content LiMnO2, ACS Appl. Mater. Interfaces 8 (2016) 2973-2980, doi:10.1021/acsami.5b10892.

R. Robert, C. Bunzi, E.J. Berg, P. Novak, Activation Mechanism of Li[Ni0.8Mn0.19Co0.01]O2 Surface and bulk operando electrochemical, differential electrochemical mass spectrometry, and X-ray diffraction analyses, Chem. Mater. 28 (2016) 3561–3574, doi:10.1021/acs.chemmater.6b00317.

A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information, Carbon 43 (8) (2005) 1731-1742, doi:10.1016/j.carbon.2005.02.018.

H.Q. Pham, B.J. Kim, H. Jo, S.Kang, S-J. You, S.W. Song, Material Characteristics-Dependent Solid Electrolyte Interphase Formation Behavior of Artificial Graphite Anodes, J. Electrochem. Soc. 164 (2017) A3045–A3053, doi:10.1149/2.006171jes.

Y.S.-Park, T.-W. Lee, M.-S. Shin, S.-H. Lim, S.-M. Lee, Modification for Improving the Electrochemical Performance of Hypoatomically-Spaced Natural Graphite as Anode Material for Lithium-Ion Batteries, J. Electrochem. Soc. 163 (2016) A3078–A3086, doi:10.1149/2.006161jes.

NIST X-Ray Photoelectron Spectroscopy Database, http://srdata.nist.gov/xps/VC

C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muleenberg (Ed.), Perk-inElmer Corp, Minnesota, 1979.

J.A. Gilbert, J. Barelo, T. Spila, S.E. Trask, D.J. Miller, B.J. Polzin, A.N. Jensen, D.N. Haldeman, Cycling Behavior of NMC (NiMnCo) Cathode Lithium-Ion Cells in the 3-4.4 Voltage Range: Diagnostic Studies of Full Cells and Harvested Electrodes, J. Electrochem. Soc. 164 (2017) A605-6065, doi:10.1149/2.008170jes.

M. He, C.-C. Su, C. Peebles, Z. Feng, J.G. Connell, C. Liao, Y. Wang, L.A. Shkrob, Z. Zhang, Mechanistic Insight in the Use of Phosphite Additives for Protection of Li[Ni0.5Mn1.5O4] Cathode in High Voltage Li-Ion Cells, ACS Appl. Mater. Interfaces 8 (2016) 11450–11458, doi:10.1021/acsami.6b02401.

K.R. Prakash, K. Madassamy, M. Kathiresan, A.S. Paskash, Ethylenebis(hexamethyl-1,3-dioxolane) as Electrolyte Additive for High Voltage Nickel-Rich Layered Cathode, J. Phys. Chem. A 123 (2019) 28604-28610, doi:10.1021/acs.jpca.8b09811.

H. Rong, M. Xu, Y. Zhu, B. Xie, H. Lin, Y. Liao, X. Xing, W. Li, A novel imidazolide-based electrolyte additive for LIBs having excellent electrochemical performance of high voltage nickel-rich electrode coupled with graphite anode lithium battery, Power Sources 302 (2019) 312–321, doi:10.1016/j.powsour.2016.09.016.

K. Beltrop, S. Klein, R. Nölle, A. Wilken, J.J. Lee, T.-K. Köster, J. Reiter, L. Tao, C. Liang, M. Winter, X. Q. Plackis, Triphenylphosphine as Highly Effective Electrolyte Additive for Graphite/NMC811 Lithium-Ion Cells, Chem. Mater. 8 (2018) 2726–2741, doi:10.1021/acs.chemmater.7b02585.

K. Wang, L. Xing, Y. Zhu, X. Zheng, D. Cai, W. Li, A comparative study of calcination temperature and stabilizing additives for lithium-ion battery: Which one is better and why is it better, J. Power Sources 342 (2017) 677–684, doi:10.1016/j.jpowsour.2016.12.112.

T. Yim, Y.K. Han, Tri(athymethyl) Phosphine as an Effective Electrolyte Additive to Improve the Surface Transmission of Nickel-Rich Anodes, ACS Appl. Mater. Interfaces 9 (2017) 32851–32858, doi:10.1021/acsami.7b10359.

H.J. Song, S.H. Jang, A.H. Oh, T. Yim. Artificial cathode-electrolyte interphases on nickel-rich cathode materials modified by stř displacement group, J. Power Sources 416 (2019) 1–8, doi:10.1016/j.jpowsour.2019.01.050.
[63] H. Jo, J. Kim, D.-T. Nguyen, K.K. Kang, D.-M. Jeon, A.-R. Yang, S.-W. Song, Stabilizing the Solid Electrolyte Interphase Layer and Cycling Performance of Silicon–Graphite Battery Anode by Using a Binary Additive of Fluorinated Carbonates, J. Phys. Chem. C. 120 (2016) 22466, doi:10.1021/acs.jpcc.6b07570.

[64] C.C. Nguyen, B.L. Lucht, Comparative Study of Fluoroethylene Carbonate and Vinylene Carbonate for Silicon Anodes in Lithium Ion Batteries, J. Electrochem. Soc. 161 (2014) A1933–A1938, doi:10.1149/2.0731412jes.

[65] T. Liu, A. Garsuch, F. Chesneau, B.L. Lucht, Surface phenomena of high energy Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2/graphite cells at high temperature and high cutoff voltages, J. Power Sources 269 (2014) 920–926, doi:10.1016/j.jpowsour.2014.07.051.