The effect of the nitrile electrolyte additives, succinonitrile (SN), adiponitrile (AN) and pimelonitrile (PN) was studied using High Precision Charger at Dalhousie University, automated cell storage and AC impedance. Li[Ni0.33Mn0.33Co0.33]O2/graphite (NMC111/graphite) cells containing the nitrile electrolyte additives showed no significant effect on the cycling between 2.8 V and 4.2 V and storage at 4.2 V at 60 ± 0.1°C. However, when the high cutoff voltage increased to 4.5 V in Li[Ni0.4Mn0.4Co0.2]O2/graphite (NMC442/graphite) cells, the addition of 2 wt% SN and 2 wt% vinylene carbonate (VC) reduced the reversible capacity loss and gas generation during storage experiments at 60 ± 0.1°C compared to 2 wt% VC alone. The addition of 2 wt% SN also caused a large impedance growth during the 4.5 V storage period, but that could be suppressed by the addition of 1 wt% ethylene sulfite (ES) + 1 wt% tris(trimethylsilyl) phosphite (TTSPi) or 2 wt% trimethylene sulfate (TMS) + 2 wt% TTSPi. This work shows that SN leads to meaningful improvements in storage properties at voltages higher than 4.4 V. This also suggests that SN can enhance the long-term cycle life of the high voltage NMC/graphite cells by suppressing electrolyte oxidation at the positive electrode.

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The incorporation of electrolyte additives is one of the approaches for improving the cycle life and calendar life of Li-ion cells.\textsuperscript{3−2} Recently, Burns et al. suggested that the addition of one or more electrolyte additives can lead to longer cycle life by suppressing electrolyte oxidation at the positive electrode.\textsuperscript{3} Burns et al. reported that electrolyte oxidation products created at the positive electrode migrate to the negative electrode and are reduced on the surface of the negative electrode as a solid layer of undesired material. As the layer becomes thicker during the cycle test, ion transport to the bulk of the negative electrode is reduced, which leads to “cycle life failure”.

Based on the results of reference 3, it is possible that nitriles as electrolyte additives can be potential candidates to improve cycle life because results in the literature showed that EC:DMC mixed with nitrile co-solvents has high electrochemical stability up to around 5.0 V and starts to be oxidized at around 5.5 V vs. Li/Li\textsuperscript{+}. While pure EC:DMC starts to be oxidized suddenly at around 4.5 V.\textsuperscript{3−7} Nigahara et al. reported that 1.0 M LiPF\textsubscript{6} in EC:DMC:sebacanitrile (25:25:50 by vol %) showed the best electrochemical compatibility with positive electrode materials such as LiMn\textsubscript{2}O\textsubscript{4} and LiCoPO\textsubscript{4} in experiments involving the nitriles: glutaronitrile, adiponitrile, pimelonitrile, sebanoitrile, sebacanitrile and dodecanenitrile at high voltage.\textsuperscript{4} Duncan et al. showed that dinitriles with shorter carbon chain length between nitrile groups gave higher capacities in Li-ion cells than dinitriles with longer carbon chain between nitrile groups because the shorter dinitriles showed higher ionic conductivity than the longer dinitriles.\textsuperscript{5} The possibility of using adiponitrile and glutaronitrile as electrolyte solvents was investigated thoroughly.\textsuperscript{6−8} However, the electrochemical characteristics of Li-ion cells, when nitriles are used as electrolyte additives (less than 5 wt%), have not been thoroughly investigated yet.

Here, the possibility of using 2 wt% of succinonitrile (SN), adiponitrile (AN) or pimelonitrile (PN) as an electrolyte additive is considered. Storage and cycling experiments at 60°C using Li[Ni0.33Mn0.33Co0.33]O2/graphite (NMC111/graphite) or LiCoO\textsubscript{2}/graphite (LCO/graphite) pouch cells were made using nitrile electrolyte additives. Higher voltage storage experiments at 4.5 V were also conducted using Li[Ni0.4Mn0.4Co0.2]O2/graphite (NMC442/graphite) pouch cells to compare with the 4.2 V storage results. The effect of adiponitrile as an electrolyte co-solvent (> 20 wt%) on 4.5 V storage properties was also explored for comparison with the conventional EC:EMC electrolyte system.

SN was recently introduced as an electrolyte additive for improving the thermal stability of LiCoO\textsubscript{2}. A paper about the effect of SN on impedance of LiCoO\textsubscript{2}/graphite pouch cells was also published.\textsuperscript{9} The molecular structures of SN, AN and PN are shown in Figure 1. PN has the longest chain between nitrile functional groups while SN has the shortest chain. Burns et al. have proposed that electrolytes with 1 or 2 wt% vinylene carbonate (VC) should be a “control” system showed no significant effect on the cycling of new electrolyte additives.\textsuperscript{10} Accordingly to this recommendation, 1.0 M LiPF\textsubscript{6} in EC:EMC (3:7 wt% ratio) containing 2% VC was used as the control electrolyte. The Ultra High Precision Charger (UHPC) and automated storage system at Dalhousie University were used for these studies.\textsuperscript{11−13}

**Experimental**

1.0 M LiPF\textsubscript{6} in EC:EMC (3:7 wt% ratio, BASF) with 2 wt% of vinylene carbonate (VC, BASF, 99.97%) was used as the control electrolyte. Two wt% of succinonitrile (SN, Acros Organics, 99.0±%), adiponitrile (AN, Sigma-Aldrich, 99%) or pimelonitrile (PN, Sigma-Aldrich, 98%) were added to the control electrolyte. Tris(trimethylsilyl) phosphite (TTSPi, 95%) was obtained from TCI

![Figure 1. Molecular structures of SN, AN and PN.](image-url)
The formation process was conducted at 40. Then discharged to 2.8 V at C/20 and charged again to 3.8 V at 15 mA. C/20 to the desired voltage for storage experiments (4.2 V–4.5 V) and complete wetting of electrolyte. The pouch cells were dried under vaccum at 80 °C overnight to re-measure coulombic efficiency (CE) with an accuracy of ±0.003%. During the formation process, the cells were charged at a rate of C/20 to the desired voltage for storage experiments (4.2 V–4.5 V) and then discharged to 2.8 V at C/20 and charged again to 3.8 V at 15 mA. The formation process was conducted at 40. ± 0.1°C. After formation, gas volume within the pouch cells was measured using Archimedes’ principle. After gas volume measurement, the cells were transferred into the glove box, and cut open to remove the gas generated during formation process and vacuum-sealed again.

Cycling experiments were performed on the Ultra High Precision Charger (UHPC) at Dalhousie University,11–12 which was built to measure coulombic efficiency (CE) with an accuracy of ±0.003%. The cells were cycled between 2.8 V and 4.2 V at C/20 in a 60. ± 0.1°C box for 15 cycles. Storage experiments at 4.2 V were conducted on an automated storage system. The storage experiment occurred as follows. The cells were first charged to 4.2 V, discharged to 2.8 V (D0), and charged back to 4.2 V at C/15 in a 60. ± 0.1°C box and then stored for 550 hours in the 60. ± 0.1°C box while their voltage was monitored every 6 hours automatically. After storage, the cells were discharged to 2.8 V (D1), charged 4.2 V and discharged to 2.8 V (D2) at C/15 in the 60. ± 0.1°C box. D0, D1, and D2 correspond to the initial capacity, the retained capacity and the recovered capacity, respectively, which are described in detail in reference 13. The storage experiments at 4.3, 4.4, and 4.5 V were conducted on an automated storage system in the 60 ± 0.5°C box using the same protocol used for the 4.2 V storage experiments, but discharge capacity before and after storage was measured in a 40. ± 0.1°C box connected to a Maccor series-4000 cycle.

Electrochemical impedance spectroscopy (EIS) measurements for pouch cells and symmetric cells were conducted using a Bio-Logic VMP-3 equipped with 2 EIS boards. All the cells were charged or discharged to 3.8 V and then transferred to a 10. ± 0.1°C box before EIS measurements. AC impedance spectra were collected with ten points per decade from 100 kHz to 20 mHz with a signal amplitude of 10 mV at 10. ± 0.1°C. Symmetric cells were fabricated for EIS measurements to investigate the impedance changes on the positive and negative electrodes separately. The detailed procedures for making symmetric cells are described in reference 9.

In this paper, all experiments were conducted with a pair of cells, and when an average result was used, an error bar was shown to indicate repeatability. Table I summarizes all the experimental conditions and electrolytes used here.

### Results and Discussion

Figure 2 shows the effect of the gas generated during storage at 4.2 V in a 60. ± 0.1°C box for 550 hours on D0, D1, and D2 of LCO pouch cells containing 2% and 4% VC. After the storage period, the pouch cells expanded by around 30% due to gas generation. As shown in reference 13, D0 is the discharge capacity measured before the
storage and $D_1$ and $D_2$ are the first and second discharge capacities after the storage, respectively. Figures 2a–2c show the results for the cells which were immediately degassed after the storage, while Figures 2d–2f show the results for the cells which were not degassed. Cells with 2% VC and 4% VC contained around 0.5 mL and 1.2 mL of gas when storage was completed, respectively, as shown in Figure 6a. The 2% VC cells without degassing showed 90.17% $D_1$ and 92.35% $D_2$, which less than 91.56% $D_1$ and 97.81% $D_2$ for the 2% VC cells with degassing. Cells with 4% VC show more dramatic differences between the cells with and without degassing because the 4% VC cells contained more gas. The 4% VC cells without degassing showed 88.38% $D_1$ and 86.8% $D_2$, while the 4% VC cells with degassing showed 93.71% $D_1$ and 98.15% $D_2$. The smaller $D_1$ and $D_2$ of the cells without degassing are caused by the generation of gas. This gas caused the cells to bulge and reduced the stack pressure applied to the jelly rolls so that the contact between the positive electrode, the negative electrode and the separator became poor and some capacity was lost.

Figures 3a, 3b show the Bode plots of the area-specific real impedance of the 2% VC and the 4% VC LCO pouch cells shown in Figure 2, which was measured at 10 ± 0.1°C and at 3.8 V after $D_2$ was measured. Figure 3 shows that the cells without degassing showed much larger impedance than the cells that were degassed. It is not surprising that the 4% VC cells showed a larger difference between the cells with degassing and without degassing than that of the 2% VC cells due to the larger amount of gas generated in the 4% VC cells. Based on the results in Figures 2 and 3, it is obvious that the gas generated during storage greatly affects the electrochemical properties of pouch cells. Therefore every cell after storage was subjected to degassing as soon as the storage period was completed, and then the capacities $D_1$ and $D_2$ and the EIS spectrum were measured.
Figure 4 shows the amount of gas generated (a, b) and differential capacity (dQ/dV) versus voltage (V) (c, d) for pouch cells containing different electrolyte additives during the formation cycle. Figure 4 shows results for LCO pouch cells (a, c) and for NMC111 pouch cells (b, d). Figures 4a, 4b show that all LCO cells generate slightly more than 0.1 mL of gas (~4.3% of the cell volume), while all NMC111 cells generate less than 0.1 mL of gas (~4.8% of the cell volume). Less than 10% of gas is insufficient to make the cells expand significantly so that the electrochemical properties of the cells during formation itself are not significantly affected by the gas. Examination of the 2% VC LCO and NMC111 cells shows that the voltages at which the reaction of EC on graphite occurs are roughly 2.8 V (NMC111) and 2.9 V (LCO) as shown in Figures 4c, 4d. Small differences between dQ/dV for pair cells are of the same order as the differences between dQ/dV for cells with different additives. When nitrile electrolyte additives are added to 2% VC electrolyte for both LCO and NMC111 pouch cells, no significant changes to the EC reduction peaks occurred and no additional peaks appeared. This means that nitrile electrolyte additives are not reduced on graphite and do not significantly affect the EC reduction on graphite. Small differences between the cell voltages of the LCO and NMC111 cells where EC reduction occurs was caused by the different positive electrode potentials.

Figure 5 shows the open circuit voltage (OCV) versus time for LCO and NMC111 pouch cells containing different electrolyte additives during storage. The cells were stored for 550 hours at 60 ± 0.1°C after being charged to 4.2 V. Sinha et al. showed that the voltage drop during storage is caused by electrolyte oxidation or shuttle-type reactions at the positive electrode. 13 Figure 5a shows that the voltage drops are almost the same for all LCO cells except for the 2% VC + 2% SN LCO cells, which have a slightly larger voltage drop than the other LCO cells. Figure 5b clearly shows the smallest voltage drop for the 4% VC NMC111 cells. All the NMC111 cells with nitrile electrolyte additives showed slightly larger voltage drops than that of the 2% VC and 4% NMC111 cells. Among the nitriles electrolyte additives, 2% VC + 2% AN NMC111 cells showed the largest voltage drop while 2% VC + 2% SN NMC111 cells showed the smallest voltage drop.

Figure 6 shows the amount of gas generated (a, b), the reversible capacity loss (D2–D1) (c, d) and the irreversible capacity loss (D0–D2) (e, f) for the pouch cells containing different electrolyte additives during the storage testing shown in Figure 5. NMC cells show larger error bars than LCO cells apparently due to a small inconsistency of the NMC cells. Reversible capacity loss represents electrolyte oxidation at the positive electrode and shuttle type reactions, and irreversible capacity loss represents Li consumption by SEI growth on the negative electrode, which is described in detail in reference 13. Figure 6 shows results for LCO pouch cells (a, c, e) and NMC111 pouch cells (b, d, f). Figures 6a, 6b show that LCO cells generated more gas than NMC111 cells during the storage period. Cells with 4% VC generated the largest amount of gas and the addition of nitrile electrolyte additives to 2% VC LCO and NMC111 pouch cells reduced gas generation for both LCO and NMC111 cells. Figures 6c, 6d show that the reversible capacity loss of the 4% VC cells was the smallest and the addition of 2% SN or 2% AN to 2% VC resulted in almost the same reversible capacity loss compared to that of cells with 2% VC alone for both LCO and NMC111 cells. Adding 2% PN slightly decreased reversible capacity loss for LCO cells while it increased reversible capacity loss for NMC111 cells. Figures 6e, 6f show all the irreversible capacity losses were not greatly changed by the addition of nitrile electrolyte additives, which means nitrile electrolyte additives have little effect on the negative electrode. This is in good agreement with the results shown in Figures 4c, 4d.

Figure 7a, 7b show the Bode plots of the area-specific real impedance of LCO and NMC111 pouch cells with different electrolyte additives measured at 10 ± 0.1°C after the storage period as shown in Figure 5. Cells with 4% VC show the largest impedance of around 300 Ω·cm² for both LCO and NMC111 cells. For LCO, cells with 2% VC + 2% SN showed the largest impedance among the cells containing nitrile electrolyte additives and had smaller impedance than 4% VC cells. Cells with 2% VC + 2% SN or 2% AN to 2% VC showed almost the same and slightly larger impedance than cells with only 2% VC. For NMC111, cells with nitrile electrolyte additives showed almost same impedance around 150 Ω·cm², which was larger than that of cells with 2% VC and much smaller than that of cells with 4% VC. In order to investigate the effect of nitrile electrolyte additives on the impedance of the positive and the negative electrodes separately, symmetric cells were fabricated and EIS measurements were conducted.

Figure 8 shows Bode plots of the area-specific real (a-d) and negative imaginary (e-h) impedance of positive electrode symmetric cells (a, e, g) and negative electrode symmetric cells with different electrolyte additives (b, f, h) measured at 10 ± 0.1°C after the storage period as shown in Figure 5. Figures 8a, 8b, 8e, 8f show the results for LCO cells gas. Figures 8c, 8d, 8g, 8h show the results for NMC111 cells. Figures 8a–8d show that the large impedance growth that 4% VC creates in LCO and NMC111 full cells is due primarily to the negative electrode. Figures 8b and 8d show that the real impedance of 4% VC
Figure 6. Volume of gas evolved (a, b), reversible capacity loss (c, d) and irreversible capacity loss (e, f) of LCO/graphite pouch cells (a, c, e) and NMC111/graphite pouch cells (b, d, f) charged to 4.2 V and stored at 60°C. The cells have different nitrile electrolyte additives as indicated in the legend.

Figure 7. Bode representation of the area-specific real impedance of LCO/graphite pouch cells (a) and NMC111/graphite pouch cells (b) charged to 4.2 V and stored at 60°C. The cells have different nitrile electrolyte additives as indicated in the legend. The EIS measurements were made at 3.8 V and 10°C.
cells at low frequency at the negative electrode is around 150 $\Omega \cdot \text{cm}^2$ and 200 $\Omega \cdot \text{cm}^2$ for LCO and NMC111 cells, respectively, which is much larger than the other cells which show an impedance around 50 $\Omega \cdot \text{cm}^2$ and 80 $\Omega \cdot \text{cm}^2$ for LCO and NMC111 cells, respectively. This is presumably because of the thick SEI growth that VC creates on the negative electrode.\textsuperscript{15–17} Petibon et al. have also published that the negative electrode impedance increases as the concentration of VC increases from 0.5% to 6%.\textsuperscript{16–17} However the impact of 4% VC on the positive electrode is smaller than that on the negative electrode for both LCO and NMC111 cells, as shown in Figures 8a and 8c.

Figures 8b, 8d, 8f, 8h show that the impact of the introduction of nitrate electrolyte additives to 2% VC cells on the negative electrode was small, while the addition of nitrate electrolyte additives to 2% VC cells increased the real impedance of the positive electrode as shown in Figures 8a, 8c, 8e, 8g. This means that the impedance growth of LCO and NMC111 full cells containing nitrate electrolyte additives shown in Figure 7 is caused by impedance growth at the positive electrode. The impedance increase of the positive electrode of NMC111 cells, the amount of gas generated was around 0.06 mL. For LCO cells, the amount of the gas was not affected by the addition of nitrate electrolyte additives to 2% VC cells. All cells generated around 0.1 mL of gas during cycling, which is much larger than the other cells which show an impedance around 50 $\Omega \cdot \text{cm}^2$ and 80 $\Omega \cdot \text{cm}^2$ for LCO and NMC111 cells, respectively.

Figure 8 shows the Bode representation of the area-specific real impedance (a, b, c, d) and negative imaginary impedance (e, f, g, h) of LCO/LCO positive electrode symmetric cells (a, c), graphite/graphite negative electrode symmetric cells (negative electrodes taken from LCO/graphite pouch cells) (b, f), NMC111/NMC111 positive electrode symmetric cells (c, g) and graphite/graphite negative electrode symmetric cells (negative electrodes taken from NMC111/graphite pouch cells) (d, h). The cells have different nitrate electrolyte additives as indicated in the legend.

Figures 9c, 9d show that it is difficult to evaluate differences between the capacity loss rates. All the LCO and NMC111 cells showed a capacity loss of around 10 mAh during the 15 cycles. Figures 9e, 9f show that the addition of nitrate electrolyte additives to 2% VC cells increases the slope of the charge end point capacity versus cycle curve for LCO and NMC111 cells. Only NMC111 cells with 2% VC + 2% AN showed a similar charge end point capacity slippage to that of 2% VC cells. Figures 9g, 9h show slightly lower coulombic efficiency when nitrate electrolyte additives were added to 2% VC cells for both LCO and NMC111 cells.

Figure 10 shows the Bode plots of the area-specific real impedance of LCO and NMC111 pouch cells with different electrolyte additives measured at 10. ± 0.1 °C after the cycling shown in Figure 9. This result shows a similar trend to the result of impedance after storage as shown in Figure 7. For both LCO and NMC111 cells, the addition of nitrate electrolyte additives to 2% VC cells leads to larger impedance growth during cycling compared to 2% VC cells. Cells with SN show the largest impedance growth, while cells with PN show the smallest impedance growth.

From the results of Figures 4–10, it is clear that the cycling and storage properties between 2.8 V and 4.2 V at 60 °C are almost the same or slightly worse when nitrate electrolyte additives were added to 2% VC LCO and NMC cells. Experiments were conducted at higher voltages to look for redeeming features of the nitrate additives.

Figure 11 shows the OCV versus time for NMC442 pouch cells containing different electrolyte additives. The cells were cycled at 60 °C at currents corresponding to C/20 between 2.8 V and 4.2 V. Figure 9 shows: the amount of gas generated during cycling (a,b); the discharge capacity (c,d); the charge end point capacity (e,f); and the coulombic efficiency (g,h), all plotted versus cycle number except for the Figures 9a, 9b. Figures 9a, 9c, 9e, 9g show the results for LCO cells and Figures 9b, 9d, 9f, 9h show the results for NMC111 cells. All cells generated around 0.1 mL of gas during cycling, which was small enough so the cycling data were not affected by the gas. For LCO cells, the amount of the gas was not affected by the addition of nitrate electrolyte additives except for 2% PN. Cells with 2% VC + 2% SN showed the smallest amount of gas, around 0.05 mL. For NMC111 cells, the amount of gas generated was around 0.06 mL.
Figure 9. Cycling data collected on the UHPC at 60°C between 2.8 V and 4.2 V including the volume of gas evolved (a, b), the discharge capacity (c, d), the charge end point capacity (e, f) and the coulombic efficiency (g, h) of LCO/graphite pouch cells (a, c, e, g) and NMC111/graphite pouch cells (b, d, f, h). The cells have different nitrile electrolyte additives as indicated in the legend.

when it is used at higher voltages than 4.4 V. Figure 11d shows that SN is the best choice to suppress electrolyte oxidation among these nitrile electrolyte additives. NMC442 cells with 2% VC and 2% PN cells showed the largest voltage drop among these cells with nitrile electrolyte additives which is larger than cells with 2% VC alone. NMC442 cells with 2% VC + 2% AN show similar voltage drop to cells with 2% VC alone. Kim et al. showed that the addition of SN suppressed electrolyte oxidation by cyclic voltammetry experiments and that SN was complexed with transition metal ions. It is suggested that these surface metal/SN complexes may suppress the reduction of

Figure 10. Bode representation of the area-specific real impedance of LCO/graphite pouch cells (a) and NMC111/graphite pouch cells (b) after cycling at 60°C between 2.8 V and 4.2 V. The cells have different nitrile electrolyte additives as indicated in the legend. The EIS measurements were made at 3.8 V and 10°C.
transition metal ions needed for electrolyte oxidation at the surface of the positive electrode. Therefore electrolyte oxidation can be suppressed by surface metal/SN complexes.

Figure 12 shows the Bode plots of the area-specific real impedance of NMC442 pouch cells containing different electrolyte additives measured at 10. ± 0.1 °C after the storage test shown in Figure 11. Figures 12a–12c show that the impedance of cells with 2% VC significantly increases from 150 Ω · cm² to 250 Ω · cm², while the impedance of 2% SN cells increases from 250 Ω · cm² to 850 Ω · cm² as the storage voltage increases from 4.2 V to 4.5 V. Figure 12d shows that the impedance growth of cells with 2% VC + 2% PN was almost same as cells with 2% VC + 2% SN cells. Cells with 2% VC + 2% AN have an impedance growth with storage voltage intermediate between that of cells with 2% VC and cells with 2% VC + 2% SN. Figure 12e shows that the impedance starts to increase at high frequencies, around 100 kHz, when cells were stored at 4.5 V, while the impedance starts to increase at around 100 Hz when the cells were stored at 4.2 V as shown in Figure 7. This indicates that contributions to the full cell impedance depend on the storage voltage. Further experiments are required to understand what these contributions are.

Figure 13 shows the OCV versus time for NMC442 pouch cells containing 2% VC + 1% ES + 1% TTSPi (211 additive) and 2% VC + 2% TMS + 2% TTSPi (222 additive). The cells were stored for 550 hours at 60. ± 0.1 °C after being charged to 4.5 V. The 211 additive was used to suppress the impedance growth during storage, and the 222 additive was used to compare the voltage drop with that of cells with 2% VC + 2% SN cells. NMC442 cells containing 2% SN combined with the 211 additive or the 222 additive were also studied for comparison. Figure 13a shows the voltage drop of the 211 additive cells was larger than cells with 2% VC + 2% SN and Figure 13b shows that the 222 additive cells show smaller voltage drop than cells with 2% VC + 2% SN. The voltage drop of the cells with ternary additive blends was not affected by the addition of SN.

Figure 14 shows the Bode plots of the area-specific real impedance of NMC442 pouch cells measured at 10. ± 0.1 °C after the storage period shown in Figure 13. Figures 14a, 14b show that when 1% ES + 1% TTSPi or 2% TMS + 2% TTSPi was added to cells with 2% VC + 2% SN, the impedance decreased significantly to 300 Ω · cm² and 350 Ω · cm² for the 211 additive + 2% SN cells and the 222 additive + 2% SN cells, respectively. But these impedances are still larger than those of cells with 2% VC and the corresponding cells with the ternary additives without SN. The results in Figure 14 indicate that the large impedance growth of cells with 2% VC + 2% SN at 4.5 V can be suppressed by the addition of 1% ES + 1% TTSPi or 2% TMS + 2% TTSPi.

Figure 15 shows the amount of gas generated (a), and reversible capacity loss (D₂-D₁) and irreversible capacity loss (D₀-D₂) for the NMC442 pouch cells (b) after the storage periods shown in Figures 11 and 13. Figure 15a shows that the addition of 2% SN always reduced the amount of gas generated during the storage at 4.5 V compared to corresponding cells without SN. The gas volume also became smaller as the chain length of the nitrile electrolyte additives increased. Figure 15b shows when 2% SN was added, the reversible capacity loss decreased from 15.8% to 10.4%, 15.3% to 14.4% and 12.7% to 11.6% for the cells containing 2% VC, the 211 additive and the 222 additive, respectively. Cells with 2% VC + 2% PN cell show the almost same reversible capacity loss as that of cells with 2% VC. Figure 15b also shows that when nitrile electrolyte additives were added to 2% VC, 211 additive and 222 additive cells, the irreversible capacity loss slightly increased. Figure 15b also shows that the addition of 1% ES + 1% TTSPi or 2% TMS + 2% TTSPi decreased the irreversible capacity loss compared to 2% VC cells. The results in Figure 15b indicate that the nitrile electrolyte additives suppress electrolyte oxidation and shuttle type reactions at the positive electrode.

Figure 16 shows the OCV versus time for NMC442 pouch cells containing 20%, 40% and 60% AN as an electrolyte solvent and with different concentrations of LiPF₆ and LiBF₄ as the salt. 1.0 M LiPF₆ in EC:EMC (3:7) (with no VC) was used as the control electrolyte for these experiments. The cells were stored for 550 hours at 60. ± 0.1 °C after being charged to 4.5 V. When 20 wt% AN was added to the control cells, LiPF₆ could not be dissolved more than 0.3 M. Cells with 0.3 M LiPF₆ in EC:EMC:AN (24:56:20) showed a larger voltage
Figure 12. Bode representation of the area-specific real impedance of NMC442/graphite pouch cells charged to 4.3 V (a), 4.4 V (b) and 4.5 V (c, d) and stored at 60°C. The cells have different nitrile electrolyte additives as indicated in the legend. The EIS measurements were made at 3.8 V and 10°C.

Figure 13. Open circuit voltage versus time of NMC442/graphite pouch cells charged to 4.5 V and stored at 60°C. The effect of 1% ES + 1% TTSPi (a) and 2% TMS and 2% TTSPi (b) on voltage drop during the storage experiment was investigated.

Figure 14. Bode representation of the area-specific real impedance of NMC442/graphite pouch cells charged to 4.5 V and stored at 60°C. The effect of 1% ES + 1% TTSPi (a) and 2% TMS and 2% TTSPi (b) on impedance growth during the storage experiment was investigated.
Figure 15. Volume of gas evolved (a), reversible capacity loss and irreversible capacity loss (b) of NMC442/graphite pouch cells charged to 4.5 V and stored at 60°C. The cells have different electrolyte additives as indicated in the legend.

Figure 16. Open circuit voltage versus time of NMC442 pouch cells charged to 4.5 V and stored at 60°C containing different types of salt (a) and different concentrations of AN (b) as indicated in the legend.

It was found that 0.7 M LiBF₄ could be additionally dissolved to make up a total of 1.0 M of salt. However, 0.3 M LiPF₆ + 0.7 M LiBF₄ showed an even larger voltage drop than 0.3 M LiPF₆ in EC:EMC:AN (24:56:20) and 1.0 M LiBF₄ in EC:EMC:AN (24:56:20) showed the largest voltage drop. This indicates that LiBF₄ increases electrolyte oxidation and shuttle type reactions at the positive electrode compared to LiPF₆ during 4.5 V storage experiments. Figure 16b shows the voltage versus time for the cells with different concentrations of AN using 1.0 M LiBF₄ as the salt. Figure 16b clearly shows that the voltage drop decreased as the concentration of AN increases from 20% to 60%. This means AN can suppress electrolyte oxidation at the positive electrode which is in good agreement with the results of the references 3 and 6. However, the voltage drop of cells with 60% AN is still larger than that of cells with 2% VC alone. The results of Figure 16 suggest that using these nitriles as co-solvents is not effective to suppress voltage drop during storage due to the salt solubility problem.

Conclusions

Three nitrile electrolyte additives, SN, AN and PN, combined with VC were studied using NMC111, LCO and NMC442 pouch cells. The role of nitrile electrolyte additives in Li-ion cells can be summarized:

1. At 4.2 V, the cycling and storage properties of NMC111 and LCO cells containing nitrile electrolyte additives combined with
2% VC at 60°C are almost the same or slightly worse compared to 2% VC cells. There is no apparent benefit to these nitrile additives below 4.2 V in LCO and NMC111 cells.

2. At 4.5 V, NMC442 cells with 2% VC + 2% SN show a smaller voltage drop than cells with 2% VC alone during storage experiments. The voltage drop of cells with 2% VC + 2% AN is almost the same as that of cells with 2% VC. Cells with 2% VC + 2% PN show larger voltage drop than cells with 2% VC alone.

3. The impedance of cells with 2% VC + 2% SN increases greatly during 4.5 V storage at 60°C, however, this can be suppressed by the addition of 1% ES + 1% TTSPi or 2% TMS + 2% TTSPi.

4. The addition of SN always: increases impedance, reduces reversible capacity loss and reduces gas generation during 60°C storage at 4.5 V.

5. When LiBF₄ is used as a salt, electrolyte oxidation at the positive electrode increases during 4.5 V storage. The electrolyte oxidation can be somewhat suppressed as the concentration of AN increases, however, the voltage drop of cells with 60% AN is still larger than that of 1.0 M LiPF₆ in EC:EMC (3:7) without AN.

This work suggests that the addition of 2% SN might improve 60°C cycle life at 4.5 V by reducing the rate of electrolyte oxidation, while additions of SN have no measurable impact on cycle life and storage at 4.2 V.

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