Dioxazolone and Nitrile Sulfite Electrolyte Additives for Lithium-Ion Cells

David S. Hall, Toren Hynes, and J. R. Dahn

Abstract

Electrolyte additives are used in lithium-ion cells to achieve higher energy densities and longer lifetimes for electric vehicle and grid energy storage applications. This work tests a recently developed electrolyte additive, MDO (3-methyl-1,4,2-dioxazol-5-one) and introduces two new additives, PDO (3-phenyl-1,4,2-dioxazol-5-one) and BS (benzonitrile sulfite, 5-phenyl-1,3,2,4-dioxathiazole 2-oxide). The cell formation, high temperature storage and long-term cycling performance of lithium-ion NMC/graphite pouch cells prepared with these additives and binary blends thereof are presented. Differential capacity results indicate that MDO and PDO form passive solid-electrolyte interphase layers on the graphite electrode during cell formation, whereas BS does not. It is demonstrated that PDO is a highly promising new additive, especially when used as a binary blend with lithium difluorophosphate or ethylene sulfate. Future work is encouraged to explore the interactions between these additives and develop optimized solution chemistries, for example by adjusting the ratio of primary and secondary additives or through introducing ternary blends.

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To further progress the adoption of electric vehicles and grid energy storage applications, it is desirable to develop lithium-ion cell chemistries that offer longer lifetimes at high temperatures and high cell voltages, without significantly increasing cost. The introduction of sacrificial electrolyte additives on the order of a few weight percent is a practical method to form protective solid-electrolyte interphase (SEI) layers that limit electrolyte decomposition during cell storage and operation. In recent years, significant efforts have yielded a large number of such additives that may be used to improve cell performance for various applications. Examples are vinylene carbonate (VC), fluorothene carbonate (FEC), prop-1-ene-1,3-sultone (PES), ethylene sulfate (1,3,2-dioxathiolane-2,2-dioxide, DTD), and lithium difluorophosphate (LFO).

One recently developed additive is 3-methyl-1,4,2-dioxazol-5-one (MDO), which was demonstrated to passivate graphite anodes against exfoliation in the presence of propylene carbonate (PC). Based on these preliminary results, it is desirable to test the effects of MDO on the performance of various cell chemistries under stressful test conditions, such as long-term cycling to high voltages and high temperature storage. This compound was previously reported as an amidation reagent for organic synthesis, which may have significance for understanding its chemistry in passivating the graphite surface in a lithium-ion cell. Moreover, Park et al. also describe the preparation of related compounds with similar reactivities, but that contain aromatic phenyl constituents. Given the success of other phenyl-containing additives, such as diphenyl carbonate, it was here considered that these may also make good electrolyte additives.

The present work therefore studies the long-term cycling and high temperature storage behavior of MDO and two new additives: 3-phenyl-1,4,2-dioxazol-5-one (PDO) and benzonitrile sulfite (BS; 5-phenyl-1,3,2,4-dioxathiazole 2-oxide).

Additive synthesis.—MDO, PDO, and BS were synthesized based on the methods reported by Park et al. The synthetic routes used in the present work are summarized in Figure 2. All solvents and starting materials were used as received, without further purification. Thionyl chloride (1 M in CH2Cl2) and benzhydroxamic acid (98%) were purchased from Alfa Aesar. 1,1′-carbonyldiimidazole (CDI ≥ 98%) and

Figure 1. Chemical structures and DFT-optimized ball-and-stick geometries of the three additives discussed in this work: a) 3-methyl-1,4,2-dioxazol-5-one (MDO), b) 3-phenyl-1,4,2-dioxazol-5-one (PDO), and c) benzonitrile sulfite (BS, 5-phenyl-1,3,2,4-dioxathiazole 2-oxide).

Experimental

Additive synthesis.—MDO, PDO, and BS were synthesized based on the methods reported by Park et al. The synthetic routes used in the present work are summarized in Figure 2. All solvents and starting materials were used as received, without further purification. Thionyl chloride (1 M in CH2Cl2) and benzhydroxamic acid (98%) were purchased from Alfa Aesar. 1,1′-carbonyldiimidazole (CDI ≥ 98%) and

Figure 2. Synthetic routes used to prepare the three additives studied in this work; a) 3-methyl-1,4,2-dioxazol-5-one (MDO), b) 3-phenyl-1,4,2-dioxazol-5-one (PDO), and c) benzonitrile sulfite (BS).
acetaldehydeic acid (95%) were purchased from Oakwood Chemical Inc. Following preparation, additives were characterized by nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR). Full details of the syntheses and the characterization results are provided as supplemental material.

**Lithium-ion cells.—**Dry (no electrolyte), vacuum-sealed \( \text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_{2} \) (NMC532)/graphite and \( \text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_{2} \) (NMC622)/graphite pouch cells, with capacity of ~220 mAh and ~230 mAh, respectively, were received from LiFun Technology (Tianyuan District, Zhuzhou, Hunan, China). The NMC532 material was ‘single crystal’, as described previously,\(^{22,26}\) and the NMC622 was conventional polycrystalline material. The cells were cut below the heat seal in an argon-atmosphere glove box, dried under vacuum at 100°C, and immediately loaded into temperature-controlled boxes (−90 ± 1°C) sealed under vacuum (less than 0.1 mbar) and handled using ESD gloves. The cells were then increased in temperature to 60.0 ± 0.1°C and charged between 2.8–4.3 V twice and then held at 4.3 V for 1 h. All solutions in this work used 1.2 mol L\(^{-1}\) LiPF\(_6\) (BASF, ≥99.9%), DTD (Guangzhou Tinci Materials Tech. Co. Ltd., ≥98%), and LiPO\(_4\)F\(_2\) (abbreviated as “LFO”, Shenzhen CapChem Tech. Co. Ltd.) were added singly or as binary blends to this electrolyte solution in the indicated mass percentages. Cells were filled with 1.0 ± 0.1 g of solution, sealed at ~90 kPa gauge pressure using a compact vacuum sealer (MSK-115A, MTI Corp.) and immediately held at 1.5 V at room temperature (21–25°C) to prevent corrosion of the copper current collector during the ~24 h wetting period that followed. Cells were then loaded into temperature-controlled boxes (40.0 ± 0.1°C) and connected to a Maccor 4000 Series automated test system (Maccor Inc.). Because gas formation was expected to occur during formation, the pouch cells were clamped using soft rubber (at about 25 kPa gauge pressure), which has previously been observed to significantly improve the experimental precision.

**Electrochemical testing.—**SEI formation was performed by charging cells at C/20 to 4.3 V, holding at 4.3 V for 1 h, discharging at C/20 to 3.8 V, and then holding cells at 3.8 V for 1 h. Cells were weighed under water before and after formation, allowing the change in displacement volume to be determined using the Archimedes principle. Cells were then degassed by cutting the pouch open in an argon-atmosphere glove box, and resealed using the compact vacuum sealer. Cells were weighed again and electrochemical impedance spectroscopy (EIS) was then measured at 10.0 ± 0.1°C using a Biologic VMP3 instrument (100 kHz – 10 mHz, ± 10 mV sinusoidal amplitude). Following formation, cells were either taken for storage or long-term cycling.

For storage, cells were maintained at 40.0 ± 0.1°C while they were cycled between 2.8–4.3 V twice and then held at 4.3 V for 24 h. Cells were then increased in temperature to 60.0 ± 0.1°C and the cell voltage was recorded at open circuit for 500 h. Following storage, cells were charge-discharge cycled twice again and then charged to 3.8 V. EIS was then measured and cells were weighed under water again to determine gas evolution during storage.

For long-term cycling, cells were maintained at 40.0 ± 0.1°C and cycled by charging at C/3 to 4.3 V, and holding the voltage at 4.3 V until the charge current decreased below C/20. Cells were then discharged at C/3 to 2.8 V before being charged again. A slow charge-discharge cycle at C/20 was performed every 50 cycles.

**Density functional theory calculations.—**Density functional theory (DFT) calculations were performed using Gaussian (G09,2011)\(^{22}\) Geometry optimization and normal mode analyses were performed using the M062X hybrid functional,\(^{23,24}\) the IEPPCM-UFF implicit solvation model (\(\epsilon = 20\)),\(^{23,24}\) and the 6-31+ +G(2df,2pd) basis set. Whereas the B3LYP hybrid functional generally provides an excellent balance of speed and accuracy, the M062X double hybrid functional typically offers superior accuracy for molecules with charge separation.\(^{28,32,35}\) The polarizable continuum model (PCM) was selected to balance calculation speed and accuracy.\(^{24,25}\) This choice comes with an inherent loss of accuracy, because implicit solvation models do not account for factors such as solvation sheath structure and preferential solvation in binary solvents.\(^{36–39}\) however, a more detailed representation of solvation, such as hybrid DFT-MM-PCM models (MM = molecular mechanics) were considered beyond the scope of the present work. Therefore, the present work utilized the PCM but encourages future work to improve our capability to model solvation behaviors.\(^{40}\)

Standard electrode potentials were calculated according to the following reactions for (1) oxidation and (2) reduction of a molecular species, \(M\):

\[
\begin{align*}
M & \rightleftharpoons M^+ + e^- \quad [1] \\
M + Li^+ + e^- & \rightleftharpoons LiM \quad [2]
\end{align*}
\]

The full details of the calculation of electrode half potentials from DFT-calculated free energies of reaction, including the conversion from the absolute to relative electrode potentials, has been described in detail previously.\(^{41}\)

**Results and Discussion**

During the initial portion of the first charging step, the potential of the positive electrode increases very slowly, whereas the potential at the negative electrode surface decreases relatively quickly. As a result, it is during this ‘formation’ step that the negative electrode SEI is produced, primarily by the electrochemical reduction of EC and/or electrolyte adducts at the graphite surface.\(^{42–44}\) The differential capacity versus voltage (dQ/dV vs. \(V\)) plots of the first charging step, shown in Figure 3, may therefore be used to consider whether the additives in this work directly produce negative SEI layers. The introduction of MDO into a cell leads to a broad reduction feature that onsets at ~2.1 V\(_{\text{cell}}\) for both cell types (Figures 3a,3b). Given the positive electrode potentials are initially ~3.5 ± 0.1 V vs Li/Li\(^+\), it is therefore estimated that this reduction feature onsets at ~1.4 V vs Li/Li\(^+\).\(^{24}\) It is noted that the reduction feature is quite small and only visible for cells that contained 2% MDO (see inset). An additional reduction feature is observed at ~2.6 V\(_{\text{cell}}\) (~0.9 V vs Li/Li\(^+\)) the origin of which is not clear. However, the reduction potential of MDO was calculated using DFT and found to be closer in value to the second feature, \(E_{\text{red,calc}} = 0.67 \text{~V vs Li/Li}^+\) (Table I). Finally, there is a small feature at 2.85 V\(_{\text{cell}}\) attributable to reduction of the EC cosolvents. The figure includes the formation of a ‘control’ cell, prepared with no additives for comparison. The feature at 2.85 V\(_{\text{cell}}\) has a larger area for the 1% MDO cell, indicating incomplete graphite passivation, whereas it is quite small in the 2% MDO cells. The results support the previous observation that MDO passivates graphite electrode surfaces.\(^{21}\)

Cells prepared with PDO display two clear features in the differential capacity plot (Figures 3c,3d). The first reduction feature onsets at ~2.1 V\(_{\text{cell}}\) in NMC622/graphite cells (~1.4 V vs Li/Li\(^+\)) and ~2.0 V (see inset) in NMC532/graphite cells (~1.5 V vs Li/Li\(^+\)). The second feature onsets at ~2.35 V\(_{\text{cell}}\) in both cell types (~1.15 V vs Li/Li\(^+\)). As with MDO, the latter of these is the closer match with the DFT-calculated reduction potential, 1.18 V vs Li/Li\(^+\) (Table I). The EC reduction feature is again weakly present in PDO-containing cells and its area is greater in 1% PDO than it is in 2% PDO cells. Moreover, the area of the EC feature is very small for all PDO-containing cells compared to additive-free cells. This demonstrates that PDO leads to the formation of a passive, or at least a partially passive, SEI on the graphite electrode.

Finally, cells prepared with BS also display two prominent features in the differential capacity plot (Figures 3e,3f). The area of these features, which is directly proportional to the charge associated with the corresponding reduction, is significantly greater than observed for MDO and PDO reduction. There is also more variability in the onset potential of these features, which range from 2.2–2.4 V\(_{\text{cell}}\) (~1.1–1.3 V vs Li/Li\(^+\)) and 2.4–2.6 V\(_{\text{cell}}\) (~0.9–1.1 V vs Li/Li\(^+\)) between
Figure 3. Differential capacity (dQ/dV) plots of cell formation in NMC622B/graphite (left) and NMC532/graphite (right) cells. Electrolyte solutions contained (a,b) MDO-, (c,d) PDO-, or (e,f) BS-based (bottom) additive blends, as indicated on the figure. A ‘control’ cell was prepared without any additives for comparison.

The quantity of gas produced following the full formation cycle to 4.3 V is summarized in Figure 4b. Whereas some gas production during formation is largely inevitable, it is desirable to develop solution chemistries that do not produce gas excessively. It is observed that PDO-containing cells produced the least amount of gas, whereas MDO-containing cells produced the most. It is interesting that the passivation behavior of MDO at the negative electrode, as discussed above, does not limit gas production. Since cells with control electrolyte produce about 1.2 mL of gas during formation due to EC reduction and cells with 2% MDO produce about 2 mL, it is clear that MDO must react with Li^+ + e^- to produce gaseous products. Gas evolution was not tracked in Reference 21 so this disturbing result was not discovered in that earlier work. Figure 3 shows that DTD mitigates gas production from MDO. However, cells with 1% DTD or 2% DTD as sole additives (in NMC111/graphite cells), as discussed in reference 16, yield 0.8 and 1.0 mL of gas during formation. Reference 24 showed that significant gas is also produced during formation in NMC532/graphite cells that contain just DTD and that this gas is primarily ethylene. Therefore there must be some synergy in the behavior of MDO and DTD that acts to limit gas production. This underscores yet again, how complex the understanding of combinations of electrolyte additives can be.

Following the formation and degassing protocols, cells were apportioned into two groups and taken for either high-temperature storage or long-term cycling. For the former, the terminal voltage was measured automatically every 6 hours for 500 h while the cells were maintained at 60°C (Figure 5). Some degree of self-discharge under such harsh conditions is inevitable, which provides a practical opportunity to compare the performance of various cell chemistries on a relatively short timescale. Figure 5 shows that MDO, PDO, and BS all display

Table I. Standard reduction and oxidation potentials of the four additives were calculated with DFT using M06-2X/6-31+g(2df,2pd)/IEF-PCM(ε = 20). The experimental reduction potentials, estimated from Figure 3, are provided for comparison.

| Additive | \(E_{\text{red}}^{0,\text{calc}}\) \(\text{V vs Li/Li}^+\) | \(E_{\text{red}}^{0,\text{exp}}\) \(\text{V vs Li/Li}^+\) | \(E_{\text{ox}}^{0,\text{calc}}\) \(\text{V vs Li/Li}^+\) |
|----------|-----------------|-----------------|-----------------|
| MDO      | 0.67            | 0.9             | 6.70            |
| PDO      | 1.18            | 1.15            | 5.97            |
| BS       | 1.16            | 0.9–1.1         | 5.73            |

\(^a\) Assuming \(E_{\text{ENMC,initial}} \sim 3.5\) V vs. Li/Li^+.
Figure 4. Cell volume change due to gas production during (a) 4.3 V storage for 500 h at 60°C and (b) cell formation to 4.3 V in NMC622/graphite (left) and NMC532/graphite (right) cells. Electrolyte solutions contained MDO-, PDO-, or BS-based additive blends, as indicated at the bottom of the figure.

Figure 5. Cell voltage in NMC622/graphite (left) and NMC532/graphite (right) cells was measured during open circuit storage at 60°C for 500 h. Electrolyte solutions contained (a,b) MDO-, (c,d) PDO-, or (e,f) BS-based additive blends, as indicated on the figure.
Figure 6. $R_{ct}$ after formation (a) storage for 500 h at 60 $^\circ$C and (b) cell formation to 4.3 V in NMC622/graphite (left) and NMC532/graphite (right) cells. Electrolyte solutions contained MDO-, PDO-, or BS-based additive blends, as indicated at the bottom of the figure.

poor storage behavior when used as standalone additives. Again the work in Reference 21 did not report storage results so those authors did not discover this disturbing result. This highlights the needs for a complete set of experiments when evaluating electrolyte additives. For all three additives, the performance was not improved by the introduction of DTD, whereas LFO offered some improvements for PDO and BS. During storage at high voltage and temperature, the production of significant gas volumes is often of concern.46–48 Figure 4a shows that significant gas evolution occurs in cells prepared with MDO, whereas PDO-containing cells produced the least gas in this work. EIS was also measured to observe whether there was significant impedance growth during storage. However, the results summarized in Figure 6 indicate that impedance growth is not a significant concern for any of the cells tested in this work. Overall, the best storage performance was observed in cells that contained VC as a co-additive and the storage results suggest that PDO is the most promising of the three additives.

The remainder of the cells in this work were tested via long-term cycling at 40 $^\circ$C and at C/3 charge-discharge rate to 4.3 V. In NMC622/graphite cells, MDO-containing cells performed worse than cells made with 2% VC, which is a common additive that offers a good ‘standard’ comparison (Figures 7a, 7d). This is the opposite result than was reported in reference 21, which found that 2% MDO outperformed either 2% VC or 2% FEC. This difference may be ascribed to the very different electrolyte solutions employed in that work, 1M LiPF$_6$ in PC versus the 1.2M LiPF$_6$ in 3EC:7DMC used in the present study. The capacity retention of NMC622/graphite cells prepared with 2%PDO (including binary blends) is comparable to or better than the 2%VC cells. Of these, 2%PDO+1%MDO is the best-performing blend, which is in contrast to the poor storage behavior of this cell chemistry, relative to 2% VC (Figure 5c). It was also considered whether the superior cycling performance of the 2%PDO+1%MDO blend is primarily attributable to the introduction of DTD. Although cells made with 1%DTD as a single additive give very small $\Delta V$ growth rates, their capacity behavior is similar to 2%VC. It is therefore concluded that synergy between PDO and DTD give rise to the superior performance. Such synergy has been reported for DTD-containing blends previously, such as PES/DTD combinations.24 Finally, the cycling performance of BS in NMC622/graphite cells (Figures 7e and 7f) is only comparable to the 2%VC cell for the 2%BS + 2%VC blend. Of particular issue is the steep slope of $\Delta V$ versus cycle number ($\Delta V$ is the difference between average charge and average discharge voltages) for BS-containing cells (Figure 7f). This is often a negative sign for the longer-term performance of a cell. These results therefore support the previous observation that PDO is the most promising of the three additives developed in this work.

MDO-containing cells cycle considerably better in the NMC532/graphite cells, with comparable capacity retention to the 2%VC cells for 1%MDO, 2%MDO+1%MDO, and 2%MDO+2%VC (Figure 8a). However, there is considerable growth in $\Delta V$ versus cycle number for all of the MDO-containing cells. This indicates impedance growth and is often an early indication that a cell will eventually exhibit severe capacity fade and fail. Cells prepared with PDO as a standalone additive exhibit worse cycling performance than the 2%VC cells, in terms of both discharge capacity and $\Delta V$ (Figures 8b, 8e). However, the PDO-based blends all outperform 2%VC in terms of capacity retention. 2%PDO+1%MDO and 2%PDO+1%LFO additionally exhibit very little increase in $\Delta V$ versus cycle number, indicating these are both potentially good solution chemistries in NMC532/graphite cells. However, comparison between 2%PDO+1%LFO does not indicate a clear advantage to the blend relative to 1%LFO used as a single additive after ~800 cycles. Finally, all of the BS-containing cells underperform 2%VC in this cell type.

Finally, it was considered whether the storage performance of PDO-containing cells improves or deteriorates over multiple
charge-store cycles. Figure 9 shows the open circuit voltage of PDO-containing cells that had already been stored at 60°C for 500 h (Figure 5b) and that were then charged back to the 4.3 V upper voltage limit and stored for an additional 500 h. The results demonstrate a significantly smaller voltage drop during this second storage period, relative to the first. This finding is significant because it suggests that PDO performs well in storage but requires a sufficient SEI growth and maturation period. The long-term evolution of additive-derived SEI layers is a complex area of study that merits additional investigation to understand how the processes may be modeled for accurate cell lifetime and performance evolution predictions.

The cycling, gas evolution and storage performance therefore indicate that PDO is a promising new electrolyte additive, especially when used in combination with DTD and LFO co-additives. Future work is encouraged to understand the interactions between the additives and to develop more optimized blends and ratios of PDO in binary or ternary blends.

Conclusions

This work characterizes the high temperature storage and long-term cycling performance of lithium-ion NMC/graphite pouch cells...
Figure 9. The PDO-containing cells in Figure 5b were charged to 4.3 V and stored at open circuit at 60 °C for an additional 500 h. The cell voltage in a) NMC622/graphite and b) NCM532/graphite cells was measured during open circuit storage at 60 °C for 500 h. The PDO-based additive blends are indicated on the figure.

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