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Electrolyte Formulations Based on Dinitrile Solvents for High Voltage Li-Ion Batteries

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In this work, we have investigated the suitability of aliphatic dinitrile solvents with the chemical formula $N{\equiv}C\text{-}(CH_2)_n\text{-}C{\equiv}N$ where n varies from 3 to 8 in single, binary (mixed with ethylene carbonate, EC) or ternary (mixed with EC and dimethyl carbonate, DMC) electrolyte solutions for the high voltage (4.7 V) $LiMn_{1.5}Ni_{0.5}O_4$ cathode material in lithium batteries. We report that the conductivity of all the electrolyte solutions (with LiTFSI or LiBF$_4$ as salt) decreases as a function of "n", i.e. as the alkane chain become longer while the viscosity increases. The electrochemical stability window is about 7 V for the single electrolyte solutions and drops to 6–6.5 V for the binary and ternary ones. ATR IR spectra of all the electrolyte solutions indicate the presence of a strong interaction between Li ions and the different solvents. $Li/LiMn_{1.5}Ni_{0.5}O_4$ half cell batteries assembled using dinitriles as the main solvent (50% by volume), LiBF$_4$ salt and LiBOB co-salt show good performance only in the ternary solutions. Those with shorter alkane dinitriles with $n = 4$ and 5 retain the capacity better after 50 cycles than the longer ones with $n = 6$ and 8. Investigation of the surface of the cycled electrode by XPS reveals that DMC plays a great role in surface passivation at high voltages by preventing salt decomposition in ternary solutions.

There is an ever-increasing demand for higher power and energy density lithium batteries in rapidly-developing markets for consumer electronic and electric vehicles and also to meet the electrical storage needs of the electrical "smart" grid. The energy density can be increased by either increasing the capacity of the negative electrode "anode" and positive electrode "cathode" materials and/or increasing the voltage of the cathode material while keeping the voltage of the anode as low as possible. One high voltage cathode material that attracted attention since its first report in 1997[1] is a member of the spinel family $LiMn_{1.5}Ni_{0.5}O_4$ (hereafter LMNO) because of its high voltage (4.7 V), high capacity (148 mAh g^{-1}), facile ionic pathways and also because it does not use the expensive and toxic transition metal cobalt. It has been recently successfully commercialized by NEI Corporation under the trade name Nanomyte. However, increasing the voltage of the cathode material requires electrolyte formulations that are stable at such high voltages. In Li/LMNO half cells it was found that common electrolytes based on carbonates provide limited stability as they undergo oxidative decomposition that leads to a Cathode-Electrolyte Interface (CEI) passivation layer composed of organic and inorganic species such as carbonates, (ROCO$_2$Li), polyethers (-(CH$_2$O)$_n$-), LiF and Li$_x$PF$_y$[2–5] that do not completely protect the electrolyte solution under prolonged cycling conditions. This was found to have negative effect on the long-term stability of the battery due to rapid capacity fade and rise in total impedance. Solutions to this problem are centered around finding new optimized electrolyte formulations with new anodically more stable solvents and also additives that can properly passivate the cathode surface the same way they do to the anode. Electrolyte solutions based on molecular solvents with the sulfone functional group, -SO$_2$-, were reported by Xu and Angell[6] and Sun and Angell[7] to exhibit a large stability window reaching 5.8 V. Abouimrane et al.[8] demonstrated that tetramethylsulfone (TMS) can be used with ethyl-methyl carbonate (EMC) as co-solvent and LiPF$_6$ as salt in Li$_4$Ti$_5$O$_{12}$/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ full cells and reported good capacity. Sulfones, however, are not stable against graphitic carbon anodes and have in general a relatively high melting point (25°C for TMS) and viscosity, limiting their room temperature and high-rate battery performance. Room temperature ionic liquids have also been considered as a viable alternative due to their good anodic stability. Li/LMNO half cells made with Propyl-methyl-pyrrolidiunium bis(trifluoromethyl)sulfonimide (P13-TFSI) and LiTFSI salt have shown a stable capacity at room temperature and 55°C.[9] However, they show low high-rate battery performance, have high viscosity and are still expensive to make in large quantities.

Recently, we have shown that electrolyte solutions based on aprotic aliphatic dinitrile solvents with the chemical formula NC-(CH$_2$)$_n$-CN with $n = 3$–8 have a wide electrochemical stability window of 7-8 V[10,11] and have very good thermal properties such as high flash point that surpasses those of carbonate solvents and hence can mitigate the flammability of lithium battery electrolyte solutions without the need for flame-retardant additives. We have also shown that their electrolyte solution mixture with carbonate solvents can be stable against graphitic carbon. Stable capacities were obtained in MCMB/LiCoO$_2$ half cells with an electrolyte solution consisting of EC:ADN 1:1 with 1 M LiTFSI and 0.1 M LiBOB.[10] It is believed that EC, BOB$^-$ anion and TFSI$^-$ anion permit the formation of a stable solid electrolyte interphase (SEI) at the surface of the MCMB graphitic electrode that protects the dinitrile solvent from undergoing reductive decomposition reactions. The use of TFSI$^-$ anion however limits the high voltage application of this particular mixture because it corrodes aluminum, the current collector for the cathode. Isken et al. reported that LiTFSI could be successfully substituted by LiBF$_4$[12] in a binary electrolyte solution consisting of 0.9 M LiBF$_4$ EC:ADN 1:1 and was cycled in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM, 4.3 V) cathode or graphite anode half cells for 50 cycles with low capacity fade and high coulombic efficiency. Nagahama et al.[13] reported earlier that the electrolyte solution can be modified by adding dimethyl carbonate (DMC) to decrease the viscosity and increase the conductivity and still be stable up to 7 V. This ternary electrolyte solution was prepared for dinitrile solvents with chain length $n = 3$ (Glutaronitrile) up to $n = 10$ (Dodecanitrile). Ultimately, they selected the composition 1 M LiBF$_4$ EC:DMC:Sebaconitrile ($n = 8$) in a ratio of 1:1:2 by volume to demonstrate successful cycling of commercial cathode materials (LiFePO$_4$, 3.4 V; LiMn$_2$O$_4$, 4.3 V) as well as under-R&D cathode materials with redox couples at and above 4.9 V (LiCoPO$_4$, Li$_2$NiPO$_4$F) but only for a few cycles. Very recently, Gmitter et al. investigated the addition of VC (Vinylene carbonate) and FEC (Fluoroethylene carbonate) additives to 1 M LiTFSI, 0.25 M LiBF$_4$ in single ADN electrolyte solution in MCMB half cells and MCMB/LiCoO$_2$ full cells and showed an evidence for the formation of a stable SEI and good capacity retention.[14]

In this work, the physical and chemical properties of single dinitrile (Adiponitrile (ADN), Pimelonitrile (PMN), Suberonitrile (SUN) and Sebaconitrile (SEN)), binary (EC:dinitrile) and ternary (EC:DMC:dinitrile) electrolyte solutions with LiTFSI or LiBF$_4$ salt and LiBOB co-salt were studied and were correlated to their components and dinitrile chain length. The testing of this type of electrolyte solutions for 50 cycles at voltages higher than 4.3 V, in this case at 4.7 V using Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ half cell is reported for the first time. A study of the nature of the surface layer (cathode-electrolyte interface, CEI) formed on cycled LMNO electrode was conducted using XPS

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technique to explain the superior performance of the ternary electrolyte solutions. Moreover, an IR study was conducted to shed light on the nature of interactions within the electrolyte solutions and their effect on battery performance.

Experimental

The $LiMn_{1.5}Ni_{0.5}O_4$ was prepared by a co-precipitation method as described by Deng et al.[15] In a typical synthesis, a 2 M solution of manganese and nickel sulfates (Aldrich) with Mn:Ni 3:1 ratio was added simultaneously into a beaker with a solution of 2 M Na_2CO_3 (Aldrich) and 0.2 M NH_4OH (Fisher) using peristaltic pumps. All solutions were kept at $60°C$ during precipitation and stirred at 600 rpm. The precipitate was filtered, washed several times with deionized water and the powder was dried at $110°C$ overnight. A stoichiometric amount of Li_2CO_3 was added and mixed thoroughly with the obtained $Ni_{0.25}Mn_{0.75}CO_3$ powder and calcined under flowing air at $600°C$ for 15 h to decompose the carbonate precursor then at $900°C$ for 15 h to promote crystallite growth. Commercial $LiCoO_2$ (LCO, Umicore) was used as received.

Battery investigations were carried out using coin cell CR2325 (NRC Canada) assembled in a glove box. The electrode was prepared by casting a slurry consisting of 75% $LiMn_{1.5}Ni_{0.5}O_4$ with 15% Super S and 10% PVDF binder dissolved in N-methyl pyrrolidinone (NMP) on an aluminum foil. The casts of $LiCoO_2$ consisted of 75% $LiCoO_2$, 7.5% Super S, 7.5% KS-4 graphite and 10% PVDF. The casts were dried at $80°C$ under vacuum overnight, pressed at 100 psi in a calendar machine and punched into disks of 1.27 cm in diameter. Lithium disks of 1.72 cm in diameter were used as counter electrodes. The electrolytes were prepared in an argon-filled glove box by dissolving the appropriate amount of salts (lithium bis(oxalato)borate LiBOB (Chemetall), lithium tetrafluoroborate $LiBF_4$ (Aldrich), lithium bis(trifluoromethanesulfonyl)imide LiTFSI (Aldrich) or hexafluorophosphate $LiPF_6$ (Aldrich) in the single, binary or ternary mixture of solvents containing: ethylene carbonate (Aldrich), dimethyl carbonate (Aldrich), diethyl carbonate (Aldrich), glutaronitrile (Aldrich), adiponitrile (Aldrich), pimelonitrile (Aldrich), suberonitrile (Aldrich) or sebaconitrile (Fluka). Two Celgard 3501 microporous layers were used as separators. All solvent ratios in the mixtures (1:1, 1:1:2) were by volume.

The cells were cycled using an Arbin cycler between 3.5 V and 4.9 V when LMNO was used and between 2.5 V and 4.2 V when LCO was used at a rate of C/12, unless otherwise noted, using 148 mAh g^{-1} as the theoretical capacity for LMNO and 137 mAh g^{-1} for LCO. The cells were cycled in a temperature controlled chamber at $30 ± 0.1°C$.

DSC analysis was carried out using a TA instrument DSC2920. Aluminum pans were sealed in the Ar-filled glove box and transferred to the DSC apparatus and then scanned from $-50°C$ to $80°C$ at a rate of $5°C$ min^{-1} with He flowing gas. The viscosity measurements were carried out inside the glove box using a CANNON viscometer No. 200 and a Brookfield DV-I+ viscometer. For the conductivity measurements, the electrolyte was poured into a two-platinum-electrode conductivity cell (K = 1 cm^{-1}) in a glove box and the AC impedance spectra was measured in a range of temperature between $-20°C$ to $80°C$ with increments of $10°C$. The frequency range was 1 kHz – 1 Hz swept using a Solartron frequency response analyzer (FRA) 1255B coupled with a Princeton Applied Research (PAR) 263A potentiostat. Dielectric constant measurements of solvents and mixtures were carried out using BI-870 dielectric constant Meter from Brookhaven Instruments. Linear sweep voltammetry was performed with the PAR 263A potentiostat at a sweep rate of 10 mV s^{-1} with a 25 µm Pt microelectrode as working electrode and a silver wire as reference and counter electrodes. A value of 3.2 V was added to convert potential data to Li/Li$^+$ reference electrode. The XPS measurements were made with a Kratos Axis spectrometer using Al Kα radiation. CasaXPS software was used to process the data and the C 1s peak (284.7 eV) was used as a reference. Cells were opened in the glove box, washed with fresh DMC, mounted on the sample holder and transferred to
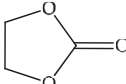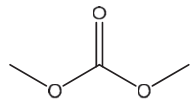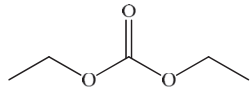
the XPS in an airtight box with minimal exposure to air. All the cells were opened in the discharged state. The Attenuated Total Reflectance Infrared (ATIR) spectra were measured between 4000 cm^{-1} to 500 cm^{-1} for all the solid and liquid samples on a single-bounce diamond crystal using a Nicolet 6700 spectrometer from thermoscientific. The samples were prepared inside the glove box and were transferred to the instrument using an airtight cell that mounts directly on the crystal.

Results and Discussion

Physiochemical properties of electrolyte solutions and battery testing of binary EC:dinitrile electrolyte solutions.— Table I shows the physical properties of dinitrile solvents with $n = 1$ to 8, acetonitrile, linear carbonates (DMC, EMC, DEC) and cyclic carbonates (EC). It clearly demonstrates that dinitriles have superior properties such as wide liquid range, high flash and boiling points that are very important to improve the safety of lithium batteries. It also shows that they have dielectric constant values intermediate between cyclic carbonates and linear carbonates that are enough to sustain high ionic conductivities. Along with these superior properties, dinitrile solvents have sparked interest as alternative solvents for lithium battery electrolyte solutions because of their high electrochemical (anodic) stability. However, solubility of most salts in this type of polar, aprotic solvents is limited due to their moderate dielectric constants and "Gutmann" acceptor numbers (AN) and donor numbers (DN) that results in selective solvation of only some cations and anions. However, salts of lithium, a hard cation, and anions with highly delocalised negative charge that gives low lattice energy and require less solvation can overcome the problem. For example, the lithium salt of the TFSI$^-$ anion, $[(CF_3SO_2)_2N]^-$, was found to dissolve readily in adiponitrile (ADN: $n = 4$) while that of the less basic BF_4^- dissolved sparingly with maximum solubility at 0.25 M and that of the less basic and bulkier PF_6^- was completely insoluble. The solubility trend was found to be true for all the five dinitrile solvents tested with $n = 3$, 4, 5, 6 and 8 but with little variation such as decreased solubility in the more hydrophobic dinitriles with longer chain length, i.e. higher n. Therefore, electrolyte solutions of 1 M LiTFSI in the five dinitrile solvents were prepared and their electrochemical stability was measured using Linear Sweep Voltammetry as shown in Figure 1a. All the electrolyte solutions showed an electrochemical stability window of 7 V in agreement with what was previously reported by this group and Nagahama's group.[10,11,13] These single electrolyte solutions cannot be used directly as a previous study with MCMB /LiCoO$_2$ full cells[10] showed that an electrolyte solution composed of only ADN ($n = 4$) either with LiTFSI alone or with LiBOB as co-salt will only yield limited capacities. This was due to the fact that adiponitrile cannot, due to its reductive decomposition at 0.4 V positive to Li/Li$^+$ redox potential, form a stable SEI unlike both EC and LiBOB which get reduced at more positive potentials at 0.7 V and 1.5 V vs. Li/Li$^+$, respectively, to give excellent passivation of MCMB graphitic electrode. Good capacities with excellent retention were however obtained with an electrolyte solution composed of EC:ADN 1:1 by volume with 1 M LiTFSI and 0.1 M LiBOB as co-salt and SEI/CEI forming additive.[10] This addition of ethylene carbonate (EC) in 1:1 ratio by volume to the dinitrile solution did not affect greatly the electrochemical stability of the electrolyte solutions, as shown in Figure 1b represented by a slightly less electrochemical stability than the electrolyte solutions of the single dinitrile ones reaching 6 V. However, the current collector for the cathode in lithium batteries is aluminum (Al) which is known to become corroded by lithium salts of TFSI$^-$ anion above 4.3 V via the formation of soluble Al(TFSI)$_3$ salt in the electrolyte solution. This phenomenon renders LiTFSI salt unable to form a passivation layer similar to the one formed by LiPF$_6$ or LiBF$_4$ which is composed of Al$_2$O$_3$/AlF$_3$ layer deposited at the Al surface.[16] Since typical voltage limits for cycling LMNO half cells are between 3.5 V and 4.9 V, it precludes the use of LiTFSI in this work.

It was shown by Mun et al. that Li/LMNO half cell with 1 M LiTFSI EC:DEC binary electrolyte solution fails during the first cycle due to Al corrosion[9] and so it was not surprising to observe rapid

Table I. List of physical properties of dinitrile solvents and common carbonate solvents used in lithium electrolytes: ϵ is dielectric constant, η is viscosity, T_m is melting point, T_b is boiling point, T_f is flash temperature, T_{auto} is auto-ignition temperature.

	Structure	ϵ	η(cp)	T_m(°C)	T_b(°C)	T_f(°C)	T_{auto}(°C)
EC		89	2 @ 40°C	35	244	150	465
DMC		3	0.7	3	90	18	458
DEC		3	0.8	−43	127	25	445
Acetonitrile*	CH_3CN	37	0.3	−48	81	2	523
Dinitriles	$CN(CH_2)_nCN$						
	n						
Malononitrile (MAN*)	1	48 @ 30°C	solid	31	220	86	–
Succinonitrile (SCN*)	2	55 @ 55°C	2.7 @ 60°C	54	266	113	–
Glutaronitrile (GLN)	3	37	5.3	−29	287	113	–
Adiponitrile (ADN)	4	30	6.1	1	295	163	550
Pimelonitrile (PMN)	5	28	7.6	−31	175 @ 14 mmHg	112	455
Suberonitrile (SUN)	6	25	8.2	−4	325	110	–
Azelanitrile (AZN*)	7	23	8.7	−18	209 @ 33 mmHg	>110	–
Sebaconitrile (SEN)	8	22	10.7	8	200	>113	–

*Not used in this work but added for comparison

failure of the assembled Li/LMNO half cell with 1 M LiTFSI 0.1 M LiBOB EC:ADN 1:1 binary electrolyte solution. Herein, LiBF$_4$ was chosen an alternative salt to LiTFSI because of its good solubility in the binary EC:ADN 1:1 solution mixture compared to LiPF$_6$, less corrosive behavior toward Al than LiTFSI, and in general its greater SEI forming ability and thermal stability. The electrochemical stability of its binary electrolyte solution on a Pt electrode, not shown here, is comparable to that of the 1 M LiTFSI solution with anodic stability of 0 V and cathodic stability of 7 V vs Li$^+$/Li. Replacement of LiTFSI by LiBF$_4$ comes however with the drawback of a drop in conductivity as measurements show that the conductivity of EC:ADN 1:1 with 1 M LiBF$_4$ and 0.1 M LiBOB electrolyte solution was 0.36 mS cm^{-1}, 2.1 mS cm^{-1}, 7.5 mS cm^{-1} at −20°C, 20°C and 80°C, respectively. This compares to reported values[10] of 0.6 mS cm^{-1}, 3.6 mS cm^{-1} and 12.3 mS cm^{-1} at −20°C, 20°C and 80°C, respectively, for the same electrolyte solutions with 1 M LiTFSI. This is expected due to the generally lower conductivity of electrolyte solutions of LiBF$_4$ due to its lower dissociation constant.[12] Furthermore, the viscosity of the EC:ADN electrolyte solution at 20°C was also slightly higher with 1 M LiBF$_4$ salt (12.5 cP) compared to 1 M LiTFSI (9.2 cP) salt which can be another factor in lowering conductivity. As a comparison, conventional 1 M LiPF$_6$ EC:DEC 3:7 electrolyte solution has a higher conductivity of 7.2 mS cm^{-1} and a lower viscosity of 7.7 cP at 20°C than the two above mentioned electrolyte solutions.[13] Cyclic voltammetry on an Al electrode was carried out to test the corrosion resistance of the LiBF$_4$ based electrolyte solutions. As shown in Figure 2, during the first cycle there is a small increase in the current at 3.1 V due to the oxidation of LiBOB followed by an expected abrupt increase at 4.4 V. However, after the first cycle the electrode was well passivated and the current was very low.

Initial battery testing.— Li/LMNO half cells were assembled using the binary electrolyte solutions of the dinitriles and EC. Voltage-capacity curves of conventional 1 M LiPF$_6$ EC:DEC 3:7 electrolyte solution along with the binary dinitrile electrolyte solution (EC:ADN 1:1) with LiBF$_4$ and LiBOB for the 1st and 10th cycle are shown in Figure 3. The cell with conventional electrolyte solution showed very well-separated plateaus at 4.65 V and 4.7 V corresponding to Ni^{+2}/Ni^{+3} and Ni^{+3}/Ni^{+4} redox couples reactions associated with lithium ion intercalation/de-intercalation with an irreversible capacity of 10 mAh g^{-1} while binary EC:ADN electrolyte solution exhibited a larger difference between the charge and discharge plateaus as well as an irreversible capacity of 90 mAh g^{-1} indicating poor coulombic efficiency. Short, sloped plateaus were also observed at 4–4.3 V corresponding to Mn^{+3}/Mn^{+4} redox couples reactions associated with lithium ion intercalation/de-intercalation. After 10 cycles, the cell with conventional electrolyte solution had little capacity drop while the cell with EC:ADN electrolyte solution still exhibited a large irreversible capacity. The longer-term cycling of the same batteries is shown in Figure 4. While conventional electrolyte solution yielded a stable capacity around 110 mAh g^{-1}, the initial discharge capacity for EC:ADN electrolyte solution was 100 mAh g^{-1} but it rapidly declined to 20 mAh g^{-1} after 50 cycles. Moreover, the efficiency was barely 50% for the first cycles, reaching 65% in the following several cycles and declined to 43% after 50 cycles. To investigate if this poor battery electrolyte solution behavior is related to the high voltage, we tested the EC:ADN binary electrolyte solution with a lower voltage cathode material: LiCoO$_2$ which was cycled between 2.5 V and 4.2 V. As shown in Figure 4, the electrolyte solution worked quite well with LiCoO$_2$ and the cell did not show any sign of deterioration. The initial discharge capacity was 128 mAh g^{-1} and the efficiency was 91%. After 40 cycles, the discharge capacity was 114 mAh g^{-1} indicating a loss of 11% while the efficiency was over 98.7%. Batteries with another cathode material LiMn$_2$O$_4$ with upper voltage of 4.3 V were assembled and cycled with the dinitrile electrolyte solution and led to similar results, not shown here, of high efficiency and low capacity loss. Work done by Isken et al.[12] also showed that 0.9 M LiBF$_4$ EC:ADN 1:1 electrolyte solution can be used with graphite and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ electrodes (4.3 V) with good coulombic efficiency. The degradation thus seems to be caused by the exposure of the electrolyte solution to voltages above 4.3 V and to the highly reactive surface catalytic sites of transition metal cations on LMNO electrode surface.
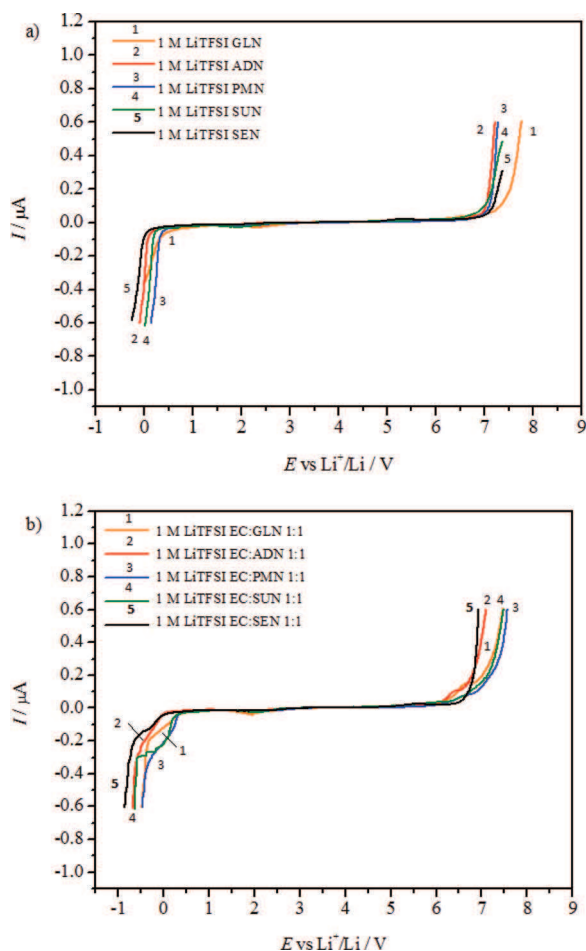
Figure 1. Linear sweep voltammetry scans of a) 1 M LiTFSI Dinitrile; b) 1 M LiTFSI EC:dintrile 1:1 (dinitrile = GLN, ADN, PMN, SUN and SEN) electrolyte solutions using Pt working electrode and Ag wire reference electrode. Scan rate of 10 mV s^{-1}.
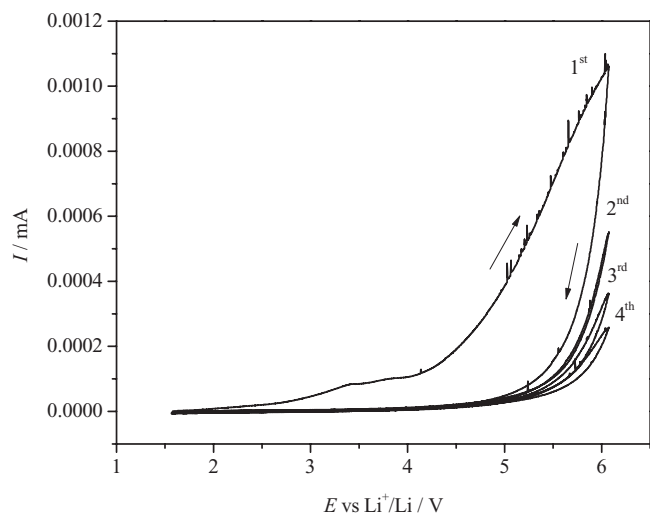

Figure 3. Comparison of the voltage-capacity curve of Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cell using 1 M LiPF$_6$ EC:DEC 3:7 conventional (solid line), 1 M LiBF$_4$ 0.1 M LiBOB in EC:ADN 1:1 binary (dotted line) and EC:DMC:ADN 1:1:2 ternary electrolyte solutions (dashed line), a) first cycle, b) 10th cycle. C/12 rate.

Physiochemical properties and battery testing of ternary EC:DMC:dinitrile electrolyte solutions.— It was reported that the addition of the liner carbonate solvent DMC to the binary electrolyte, while keeping the overall proportion of ADN the same, i.e. EC:DMC:ADN 1:1:2 by volume, has a positive effect on the capacity retention and coulombic efficiency of LMNO as suggested by Nagahama et al.[13] Although the addition of DMC compromises thermal stability (due to the volatility of DMC), it lowered the viscosity from

Figure 2. Cyclic voltammetry of 1 M LiBF$_4$ 0.1 M LiBOB EC:ADN 1:1 electrolyte solution using Al working electrode and Ag wire reference electrode. Scan rate of 10 mV s^{-1}.
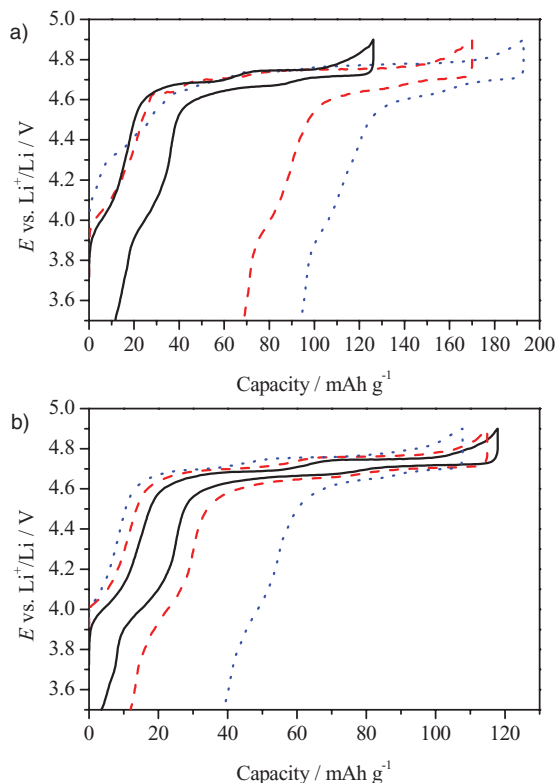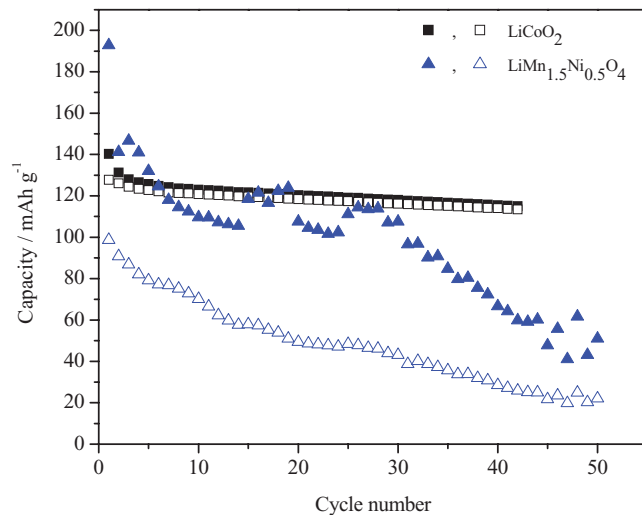

Figure 4. Comparison of the charge (filled symbols) and discharge (unfilled symbols) capacities of Li/LiCoO$_2$ cells and Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cells using 1 M LiBF$_4$ 0.1 M LiBOB EC:ADN 1:1 electrolyte solution. C/12 rate.
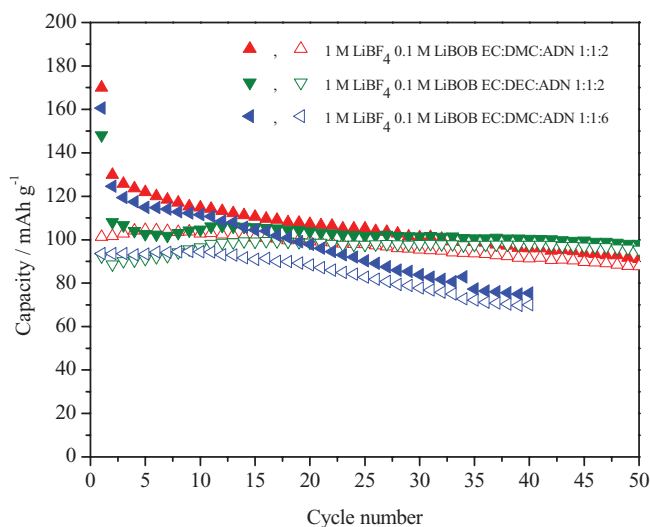
Figure 5. Comparison of the charge (filled symbols) and discharge (unfilled symbols) capacities of Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cells using 1 M LiBF$_4$ 0.1 M LiBOB EC:DEC:ADN 1:1:2 and 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:ADN 1:1:6 electrolyte solutions. C/12 rate.

Figure 6. Linear scan voltammetry of 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:Dinitrile 1:1:2 (dinitrile = GLN, ADN, PMN, SUN and SEN) electrolyte solutions using Pt working electrode and Ag wire reference electrode. Scan rate of 10 mV s^{-1}.

12.5 cP to 8.1 cP while the conductivity remained constant at 2.1 mS cm^{-1}. The decrease in viscosity, which should result in an increase in conductivity of the ternary electrolyte solution is offset by the drop in the dielectric constant. The dielectric constant ($\varepsilon_{DMC} = 3 < \varepsilon_{ADN} = 30 < \varepsilon_{EC} = 89$) of the ternary EC:DMC:ADN and EC:ADN binary mixtures were measured and found to be 35 and 59, respectively. They were also calculated using the simplified mixing rule, assuming little interaction between the three solvents and using volume fractions, and gave very close values to the measured ones at 38 and 60, respectively. This means that there will be less dissociated ions for solvation and more of ion association that results in a drop in conductivity that is counterbalanced by the fact that solvated mobile ions move faster because of lowered viscosity.

Li/LMNO half cell batteries were assembled and tested using the ternary electrolyte solutions. As shown in Figure 5, the initial capacity for an electrolyte solution consisting of 1 M LiBF$_4$ and 0.1 M LiBOB EC:DMC:ADN 1:1:2 was 101 mAh g^{-1}, with an irreversible capacity of 70 mAh g^{-1}. While the efficiency was low in the first cycle (60%), it improved during the next few cycles. The remaining capacity after 50 cycles was 87 mAh g^{-1} representing a loss of 14%. We found that increasing the proportion of dinitrile in the electrolyte solution from a 1:1:2 EC:DMC:ADN ratio to 1:1:6 resulted in a lower capacity, higher capacity loss and lower efficiency. The initial capacity was 94 mAh g^{-1} then dropped to 70 mAh g^{-1} after 40 cycles representing a 25% capacity loss. Furthermore, we found that the coulombic efficiency was lower with a higher dinitrile:carbonate ratio, barely 93% after 40 cycles.

We found that substitution of DMC for another linear carbonate, DEC, which has lower freezing point than DMC, led to good capacities (Figure 5): 92 mAh g^{-1} increasing to 95 mAh g^{-1} after 50 cycles. This can be taken as an indication that a binary electrolyte solution of only cyclic carbonates and dinitriles are not stable at high voltages and that a linear carbonate can successfully stabilize the electrolyte which could be due to the fact that the oxidation product of the linear carbonate possibly catalyzed by highly-energetic inorganic surface species at the surface of LMNO gives a better CEI passivation layer. It is worth mentioning that there is scarce information about the nature of the oxidation product of the carbonate electrolytes, let alone dinitriles, at common and high voltages and their effect on battery performance. Herein, we should not neglect the role of the co-salt LiBOB as an additive which was shown to stabilize LMNO electrode with a con-
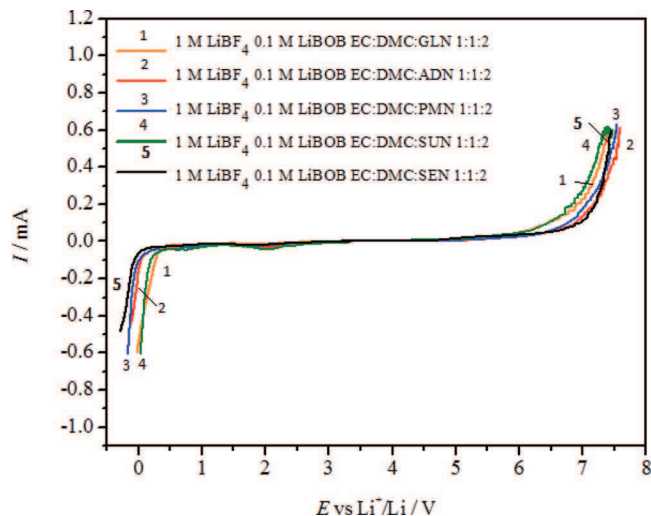
ventional binary electrolyte solution (1.1 M LiPF$_6$ in EC:DEC 1:2) due to its ability to form thinner CEI and decreasing cell impedance.[17]

The behavior of the rest of the dinitrile ternary electrolyte solutions.— In order to investigate the rest of the ternary dinitrile electrolyte solutions and to understand the structure/property relationship, i.e. the role of the alkane chain length (*n*), electrolyte solutions were prepared while keeping the 1:1:2 of EC:DMC:dinitrile ratio constant and replacing adiponitrile by glutaronitrile (GLN), pimelonitrile (PMN), suberonitrile (SUN) and sebaconitrile (SEN) which have *n* = 3, 5, 6 and 8, respectively. Concentrations of LiBF$_4$ and LiBOB salts were kept at 1 M and 0.1 M, respectively. The electrochemical stability of all 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile 1:1:2 electrolyte solutions were similar and reached 6.3 V except for the GLN- and SUN-containing solutions where the oxidation potential was slightly lower at 6 V as shown in Figure 6. A comparison of cyclic voltammetry of the electrolyte solutions measured on an Al electrode shows that the SEN-containing solution had the lowest current during the first cycle as shown in Figure 7 while electrolyte solutions containing ADN and PMN had similar moderate currents and the SUN-containing solution showed the highest current. On subsequent cycles, the currents dropped in all dinitrile electrolyte solutions with the SEN-containing solution exhibiting the best passivating behavior followed by the ones containing PMN, SUN and ADN, respectively. This can be attributed to the longer alkane chain dinitriles that show better passivation behavior than the shorter ones because of the physical coverage of the aliphatic alkane to aluminum surface anchored by the nitrile groups. The longer the chain, the larger the coverage will be that will lead to better passivation and lower corrosion current. This was corroborated by the decrease in the initial rest current, not shown here, (I$_{n=4}$ >I$_{n=3}$ >I$_{n=5}$ > I$_{n=6}$ > I$_{n=8}$) of an Al wire immersed in a 1 M LiTFSI in single dinitrile electrolyte solutions.

Conductivity and viscosity of dinitrile electrolyte solutions.— The conductivity and viscosity of the 1 M LiBF$_4$, 0.1 M LiBOB EC:DMC:dinitrile ternary electrolyte solutions were measured along with those of 1 M LiTFSI in single dinitrile and EC:dinitrile binary solutions for comparison. It can be observed that in the three sets the conductivity decreased while the viscosity increased with the increase in alkane chain length, i.e. *n*. It can also be observed that the ternary electrolyte solutions showed lower conductivities and viscosities than those of the binary electrolyte solutions which in turn showed higher conductivities and lower viscosities than the single ones as
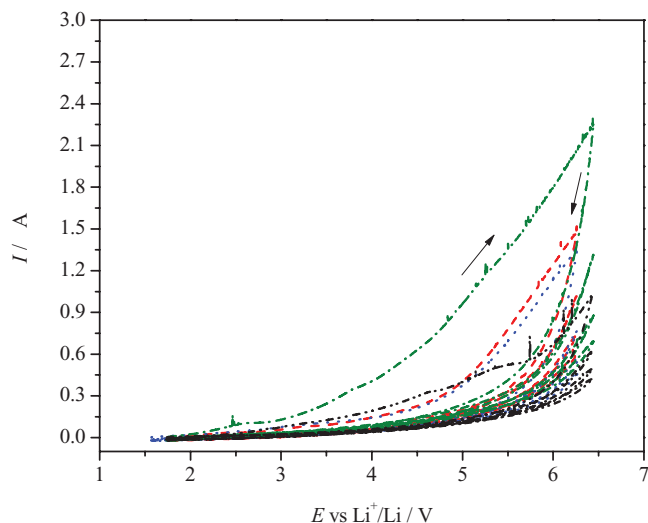
Figure 7. Cyclic voltammetry of 1 M LiBF4 0.1 M LiBOB EC:DMC:dinitrile 1:1:2 electrolyte solutions (dinitrile = ADN (red dashed line); PMN (blue dotted line); SUN (green dash-dotted line) and SEN (black solid line) using Al working electrode and Ag wire reference electrode. Scan rate of 10 mV s^{-1}.

Figure 9. Viscosity of 1 M LiTFSI dinitrile single electrolytes (■), 1 M LiTFSI EC:dinitrile 1:1 binary electrolytes (▲) and 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile 1:1:2 ternary electrolytes (●) at room temperature ($n = 3$ (GLN); $n = 4$ (ADN); $n = 5$ (PMN) $n = 6$ (SUN) and $n = 8$ (SEN).

shown in Figures 8 and 9 respectively. For example, the conductivity at room temperature decreased from 3.60 mS cm^{-1} for the ternary GLN-containing electrolyte solution ($n = 3$) to 1.70 mS cm^{-1} for the ternary SEN-containing electrolyte solution ($n = 8$) while the viscosity increased from 7.8 cP to 9.3 cP, respectively. Also, the conductivity of 1 M LiTFSI in single GLN electrolyte solution was 3.02 mS cm^{-1}, reaching 4.90 mS cm^{-1} in binary 1 M LiTFSI EC:GLN solution and 3.60 mS cm^{-1} in ternary 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC: GLN solution. The lower conductivity of the ternary solutions can be attributed to the lower dissociation of the salt due to the lower dielectric constant of the ternary solution and lower dissociation constant of LiBF$_4$ salt used in place of LiTFSI in binary and single solutions. The decrease in the conductivity for longer alkane chain dinitrile solutions is attributed to a decrease in the number of charge carriers and their mobility. As the aliphatic chain of the dinitrile solvent becomes longer its dielectric constant decreases as shown in Table I, hence less salt dissociation which results in lower conductivity. On the other
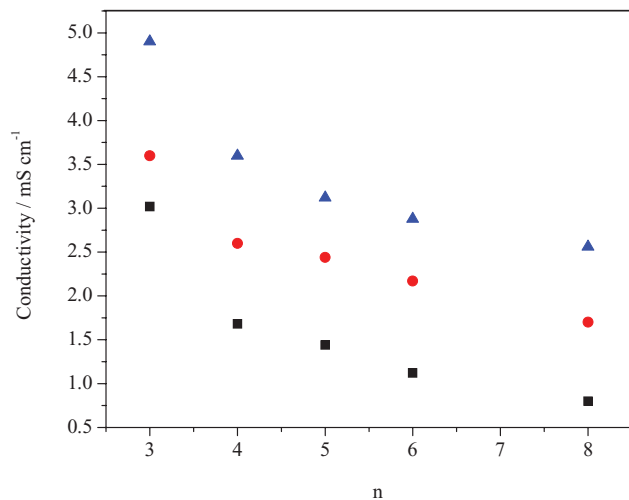
hand, viscosity increases for longer alkane chain dinitrile solutions mostly due to an increase in molecular size that results in a decrease in mobility. Finally, the conductivity of the ternary electrolyte solutions were measured as a function of temperature (−20°C to 80°C), not shown here, and showed a Vogel-Tammann-Fulcher (VTF) behavior with an increase in conductivity as temperature increased except for SEN-containing ternary electrolyte solution which showed a large drop in conductivity at −10°C. This was corroborated by Differential Scanning Calorimetry (DSC) scans, not shown here, measured for all ternary electrolyte solutions between −40 and 90°C. All the solutions except the one containing SEN which had a peak at −10°C showed no thermal events within the tested range indicating good thermal stability and a wide liquid range, a very important property for lithium electrolyte solutions.

Attenuated total reflectance infrared spectra of all the electrolyte solutions.— Figure 10a shows the Attenuated Total Reflectance Infrared spectra measured between 4000 cm^{-1} and 500 cm^{-1} for all 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile electrolyte solutions on a single-bounce diamond crystal. The IR spectra looked similar for the whole set with the main peaks shown in their expected frequencies. The fingerprint region of the spectra between 500 cm^{-1} and 1500 cm^{-1} is very populated with peaks from each component of the electrolyte formulation. Clearly, attention was given to the rest of the spectra where three main regions of interest were identified; (I) the stretching frequency of the nitrile triple bond, C≡N, observed in the region 2300–2200 cm^{-1} and originate from the dinitrile solvent; (II) the peak corresponding to the stretching frequency of the carbonyl double bond, C=O, and C–O bond of the carbonate ester group of EC and DMC solvents observed in the region 1900–1600 cm^{-1} and 1200–1450 cm^{-1} respectively; (III) the stretching frequency of the methylene groups, CH$_2$, of the dinitrile and EC and DMC solvents or CH$_3$ groups of DMC solvent in the region 3000–2800 cm^{-1}. The intensity and position of the peaks were similar for all the electrolyte formulations in regions I and II while in III the intensity of the peak increased expectedly as the number of the methylene groups increased in the dinirile solvent. In order to understand spectra in regions I and II of the electrolyte solutions an IR study of the single solvents, the binary and ternary mixtures with no salt, and the singular, binary and ternary electrolyte solutions made with LiTFSI as a salt due to its high solubility and with LiBF$_4$ for the ADN-based electrolyte solutions was conducted and the results are shown in Figures 10b-10d. Table II lists the main stretching frequencies and their assignments

Figure 8. Conductivity of 1 M LiTFSI dinitrile single electrolytes (■), 1 M LiTFSI EC:dinitrile 1:1 binary electrolyte solutions (▲), and 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile 1:1:2 ternary electrolyte solutions (●) at room temperature ($n = 3$ (GLN); $n = 4$ (ADN); $n = 5$ (PMN) $n = 6$ (SUN) and $n = 8$ (SEN).
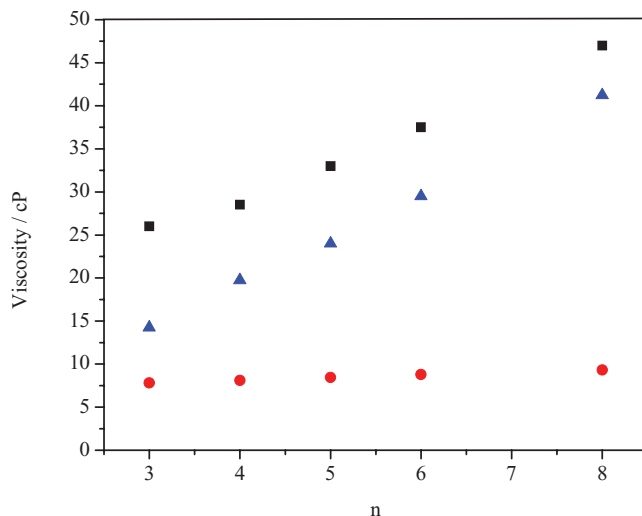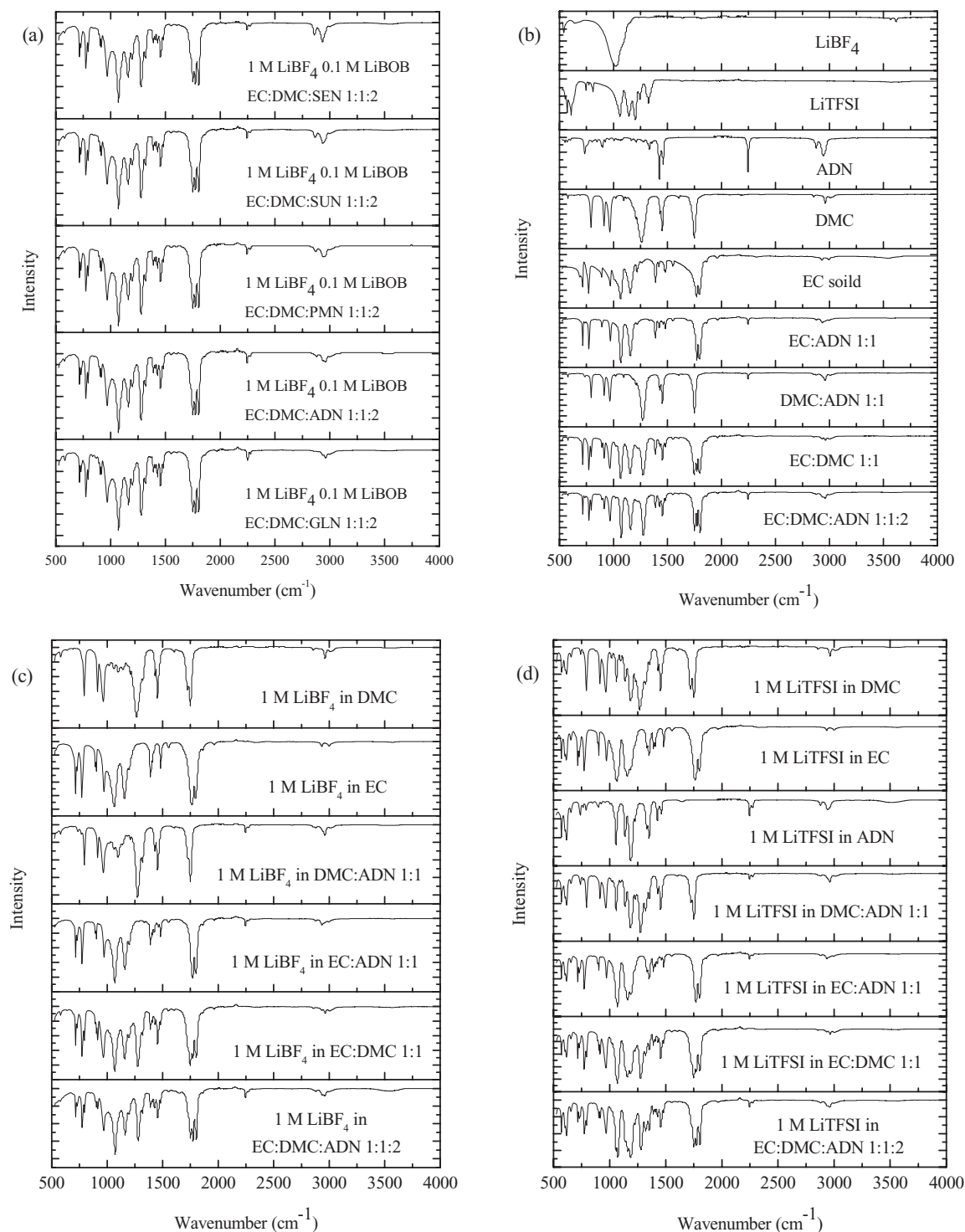
Figure 10. ATR IR scans of a) 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile 1:1:2 ternary electrolyte solutions b) neat solvents and salts, c) LiBF$_4$ in singular, binary and ternary electrolyte solutions, and d) LiTFSI in singular, binary and ternary electrolyte solutions.

for all the studied salts, solvents and electrolyte solutions. The neat solid LiTFSI salt showed no absorption in the region between 1500 and 4000 cm^{-1} while LiBF$_4$, also measured in solid state, showed one broad peak at 1022 cm^{-1} along with other smaller peaks at lower and higher frequencies. Neat ADN showed a sharp single peak at 2246 cm^{-1} corresponding to the stretching mode of C≡N while neat EC, measured in the solid state, showed an asymmetrically split peak at 1795 cm^{-1} and 1770 cm^{-1} corresponding to C=O stretching and overtone of the ring breathing modes, respectively, and two other

peaks at 1350 cm^{-1} and 1150 cm^{-1} corresponding to the stretching mode of C–O bonds. Neat DMC, on the other hand, showed a single sharp peak at 1749 cm^{-1} corresponding to the stretching mode of the carbonyl, C=O, bond and a broad peak at 1260 cm^{-1} corresponding to stretching mode of C–O bonds.[18] The binary and ternary mixtures showed the same peaks as the individual solvents with negligible shift in their positions (≤10 cm^{-1}). However, there was a slight reduction in the intensity of the nitrile peaks in the mixtures that might indicate some degree of dipole-dipole interaction between the solvents.

Table II. List of frequencies of main IR absorptions of all studied electrolytes.

	C≡N in neat solvents	C≡N in LiTFSI electrolyte solution	C≡N in LiBF$_4$ electrolyte solution	C=O in neat solvents	C=O in LiTFSI electrolyte solution	C=O in LiBF$_4$ electrolyte solution	C–O in neat solvents	C–O in LiBF$_4$ electrolyte solution	C–O in LiTFSI electrolyte solution
EC				1795 1770	1799 1761	1795 1762	1389 1155 1155 1196	1391 1405	1391 1406
DMC				1749	1751 1720	1740 1723	1260	1264 1329	
ADN	2246	2246 2273	2246 2270 (weak)						
EC: DMC				1797 1773 1747	1801 1772 1749 1720 (weak)	1800 1773 1748 1722 (weak)	1389 1153 1273	1390 1405 1157 1196 1274 1918	1391 1406
EC: ADN	2246	2246 2264	2246 2269	1796 1772	1799 1770	1780 1771	1389 1156	1390 1406 1159 1197	1391 1406
DMC ADN	2246	2246 2273	2246 2271	1750	1750 1724	1750 1723	1270	1273 1318	
EC: DMC: ADN	2246	2246 2273	2246 2271	1800 1774 1750	1803 1774 1751 1720 (weak)	1801 1774 1750 1723 (weak)	1389 1157 1276	1390 1405 1160 1196 1279 1317	1389 1406

When the salt (LiTFSI or LiBF$_4$) was added to neat ADN, EC and DMC solvents and also to the (1:1) binary solvent mixtures EC:DMC, EC:ADN, DMC:ADN and the (1:1:2) ternary EC:DMC:ADN mixture to make 1 M electrolyte solutions, the following changes to the positions of the peaks and their intensities took place:[1] the sharp peak corresponding to C≡N split asymmetrically in both binary and ternary solutions with the primary "longer" peak remained unchanged at 2246 cm^{-1} while a shoulder "shorter" peak appeared at 2264–2273 cm^{-1}. The unchanged longer peak corresponds to free "uncoordinated" nitrile groups while the new shorter one is an evidence for a strong interaction between Li$^+$ ions and –C≡N: nitrile groups. This has been previously observed in electrolyte systems based on nitrile containing liquids, e.g. acetonitrile, or solid polymer electrolytes, e.g. Poly(acrylonitrile) and was interpreted as an evidence for a strong interaction between the lone pair or to lesser extent the π electrons of the nitrile group with the Li$^+$ ions leading to coordinated species with a coordination number of 3-4.[19] The C=O peak of EC showed no change in position; appearing at 1799 cm^{-1} and the longer peak at 1761 cm^{-1} in single electrolyte solutions and with a slight shift in the binary and ternary electrolyte solutions. In DMC, the C=O peak split with a shoulder peak appearing at a lower wavenumber at 1720 cm^{-1} while the longer peak showed a slight shift at 1751 cm^{-1} in single, binary and ternary electrolytes.[3] The C–O peak of EC at 1389 cm^{-1} split with the shoulder peak appearing at higher wavenumber at 1406 cm^{-1} while the effect on the other peak could not be identified due to the interference from peaks of the LiTFSI salt in single, binary and ternary electrolytes. In the case of DMC, the C–O peak also split with a shoulder peak appearing at higher wavenumber at 1320 cm^{-1} in single electrolyte solutions while in binary and ternary electrolyte solutions that contained EC the splitting was weaker and the shoulder peak can hardly be detected. In the case of LiBF$_4$ electrolyte solutions, similar behavior was observed with slight change in frequency and peak intensities but in this case it was easier to observe the effect of salt addition on the second C–O peak of EC. The peak split with a shoulder peak appearing at higher wavenumber at 1196 cm^{-1} while the original peak remained unchanged at 1155 cm^{-1} in single, binary and ternary electrolyte solutions.

The ability of a solvent to solvate ions depends on its dielectric constant and to a greater extent on its acceptor/donor number. As mentioned earlier in the text, the dielectric constant of the ternary electrolyte solution is moderate in value and therefore there will be great deal of dissociation of the lithium salt into Li$^+$ cation and TFSI$^-$, BF$_4^-$, and BOB$^-$ anions. The fact that in ternary electrolyte solutions the peak of the carbonyl group of EC remained unchanged upon salt addition while it split weakly in DMC and that the peaks of the nitrile group in ADN and the C–O bonds in EC and DMC split suggests that EC and DMC molecules coordinate Li cation through the ring oxygen while DMC also coordinates weakly through the carbonyl group and ADN through the nitrile group. There is also the possibility, however, that coordination through the carbonyl group of EC does in fact occur, but this is not manifested as a carbonyl peak position change. This hypothesis will be tested in future work via theoretical calculations to determine the proper correlation between the changes in peak frequencies/intensities and coordination mechanisms. It is believed that in ternary solutions of linear and cyclic carbonates such as EC:DMC:DEC, EC binds stronger to Li cation than the other solvents due to its higher donor number (DN) and does that with a coordination number of 4.[20] The replacement of one of linear carbonates with a dinitrile slightly changes the solvation dynamics as nitrile solvents in general have slightly lower DN than carbonates (DN for EC is 16.4 while the value for ADN is not reported but the closest can be found is for acetonitrile at 14.1 or propionitrile at 16.1). There is little information about mixed-solvent electrolyte solutions composed of carbonates and nitriles and the closest electrolyte system is polymer gels of carbonate solvent/lithium salt/poly(acrylonitrile). In this electrolyte system, it was also shown that Li$^+$ interact stronger with the carbonyl group of the carbonate solvent than with the nitrile group of the polymer.[21] In this work the IR results show that there is a strong interaction between Li$^+$ ions and the nitrile groups of ADN, the C–O bonds of EC and DMC and weak interaction with the carbonyl group
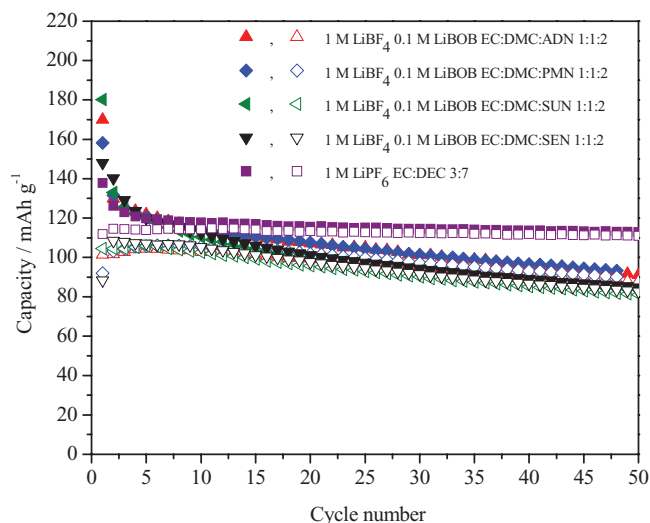
Figure 11. Comparison of the charge (filled symbols) and discharge (unfilled symbols) capacity of Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cells using 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile (ADN, PMN, SUN and SEN) ternary electrolyte solutions with 1 M LiPF$_6$ EC:DEC 3:7 conventional electrolyte solution. C/12 rate.

Figure 12. Rate capability of Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cells using 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:dinitrile (ADN, △ red; PMN, ◇ blue; SUN, ▽ green; and SEN, ◁ black) ternary electrolyte solutions and 1 M LiPF$_6$ EC:DEC 3:7 conventional electrolyte solution.

of DMC. The significance of this is that the solvated species determine the chemistry at the interface. In most electrolytes where EC is present the EC-solvated lithium ions dominate the interface precluding other solvated lithium ions. In this work, the dinitriles have moderate dielectric constant and donor number slightly lower than carbonates so there is more chance for dinitrile-solvated lithium to be present at the interface and participate in the SEI/CEI formation or be involved in de-solvation/intercalation or de-intercalation/salvation of lithium ions within the LMNO electrode.

Li/LMNO battery performance and rate capability of ternary electrolyte solutions.— Li/LMNO half cells were assembled and tested in EC:DMC:dinitrile ternary electrolytes and the results are shown in Figure 11. The capacities obtained were quite similar regardless of the dinitrile chain length (*n*). The highest initial capacity was obtained by SEN-containing electrolyte solution (*n* = 8), with an initial discharge capacity of 108 mAh g^{-1} that also gave the highest capacity loss after 50 cycles (23% loss) reaching 83 mAh g^{-1}. PMN (*n* = 5) and ADN (*n* = 4) -containing electrolyte solutions yielded essentially the same initial capacities; 103 mA h-g^{-1} and 101 mAh g^{-1}, respectively, reaching 90 mAh g^{-1} and 87 mAh g^{-1} after 50 cycles. This translates into a capacity loss of 14% and 13% for ADN- and PMN-containing electrolyte solutions, respectively. The SUN-containing electrolyte solution yielded an initial capacity of 104 mAh g^{-1} reaching 81 mAh g^{-1} after 50 cycles with a loss of 22%, similar to that of SEN-containing solution. The battery results reflect the superior physical and chemical properties of the shorter alkane dinitriles over the longer ones. In general, the capacities of the ternary electrolyte solutions are still lower than the binary conventional electrolyte solution of EC:DMC that can be explained, in part, by the fact that the dinitrile-solvated lithium ions can be present at the interface along with the EC-solvated and to lesser extent DMC-solvated lithium ions. The dinitriles are more resistant to oxidation than the carbonates and therefore in the ternary electrolyte solutions the higher portion of dinitriles are competing for sites at the interface and precluding more solvated carbonates from decomposing and form an effective CEI. Upon subsequent cycling other factors become more important such as de-solvation, and diffusion in bulk, across the interface and within the cathode material. This is corroborated by Xing et al.[22] who have shown theoretically that lithium ion solvated with cyclic carbonates such as EC and PC could reach the cathode easier than those of the linear carbonates, e.g. DMC, DEC, EMC, and hence are more prone to oxidative decomposition. This indicates that during the first few cycles DMC-solvated lithium
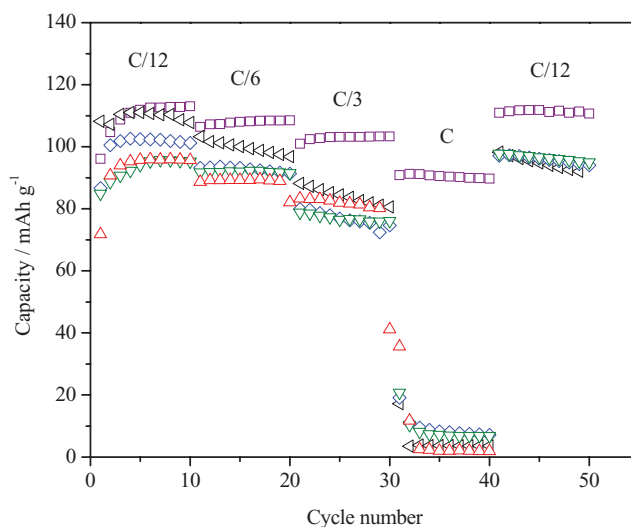
ions have difficulty reaching the interface, a behavior exacerbated by the presence of dinitriles.

The rate capabilities of the same batteries were evaluated by performing 10 cycles at each C-rate: C/12, C/6, C/3, C and finally 10 recovery cycles at C/12. All the ternary electrolyte solutions behaved in a similar manner, as shown in Figure 12. The SEN-containing electrolyte solution achieved an initial higher capacity (110 mAh g^{-1}) compared to the rest of the dinitriles: 100 mAh g^{-1} for PMN and 95 mAh g^{-1} for ADN and SUN-containing solutions. The cells kept a reasonable capacity up to C/3 (80 mAh g^{-1}) but faded greatly at C rate (10 mAh g^{-1}). A capacity of 98 mAh g^{-1} was obtained during the recovery cycles regardless of the type of electrolyte solution. The lower conductivity of the electrolyte solution and possibly lower transport numbers compared to conventional binary carbonate (EC:DMC) electrolyte solution could be responsible for this lower rate capability behavior.

X-ray photoelectron spectroscopy of LMNO electrodes after battery cycling.— In an effort to shed some light on the CEI formed at the surface of the LMNO electrode during the cycling of the binary EC:ADN and ternary EC:DMC:ADN electrolyte solutions of 1 M LiBF$_4$ and 0.1 M LiBOB, batteries were opened after 50 cycles and the electrode was examined by XPS. The cell with the binary solution showed visual signs of electrolyte solution deterioration; the separator and Li disk were covered with a black paste while the cell with the ternary solution did not show any abnormality. Previous work on the LMNO/electrolyte interface[2,4,23] with conventional carbonate electrolyte solution showed that the organic species present at the surface were polyethers and carbonates originating from the ring opening of EC while inorganic species were LiF, Li$_x$BF$_y$ and Li$_x$BF$_y$O$_z$ from the decomposition of the salt (when LiBF$_4$ is used.)[4] In addition to those species, we expect in our case contributions from the decomposition products of dinitriles and LiBOB. The O 1s, C 1s and N 1s spectra for cells cycled with both electrolytes were shown in Figure 13a,b. Surprisingly, given the number of possible O-containing species the O 1s peak could be fitted with only one peak at 532 eV in case of the ternary solution (Figure 13a) originating from carbonates[24] while with the binary solution there were two additional peaks at 531 eV and 529 eV. The C 1s contained several peaks (Figure 13b); the carbon peak at 284 eV, and peaks at 288 eV and 289 eV that can be assigned to –ROCO$_2$ species agreeing with O 1s peaks at 531–532 eV.[4,24] A peak at 286.3 eV was assigned to the –CN group, along with the N 1s peak at 399.5 eV[25] but it was hard to specifically assign this peak
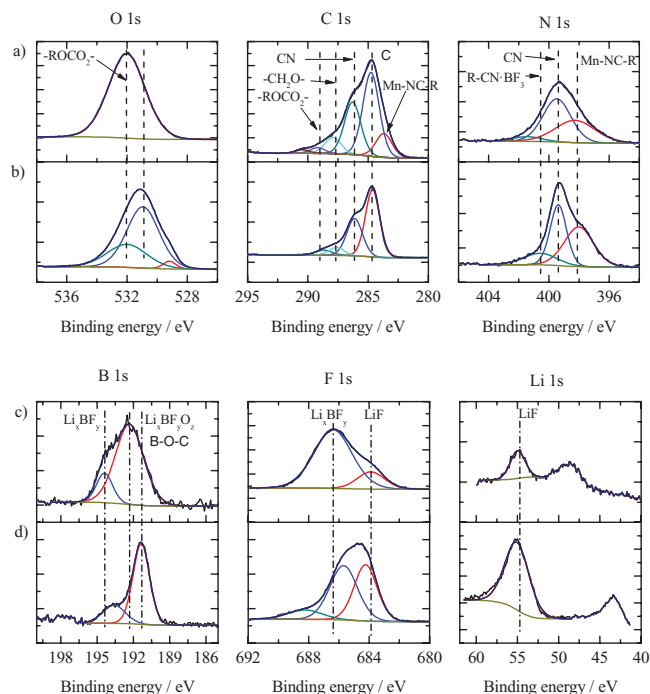
Figure 13. O 1s, C 1s and N 1s spectra of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ electrode opened after 50 cycles using a) 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:ADN 1:1:2 ternary electrolyte solution and b) 1 M LiBF$_4$ 0.1 M LiBOB EC:ADN 1:1 binary electrolyte solution c) 1 M LiBF$_4$ 0.1 M LiBOB EC:DMC:ADN 1:1:2 ternary electrolyte solution and d) 1 M LiBF$_4$ 0.1 M LiBOB EC:ADN 1:1 binary electrolyte solution.

since it can also be indicative of (CH$_2$O)$_n$ or C–H species that could be present at the surface. The N 1s peak at 398 eV (Figure 13) was tentatively assigned to a Mn-NC-R complex[26] that was formed when dinitriles were in contact with the electrode. A N 1s third peak at 401 eV could be assigned to R-CN·BF$_3$ complex,[27] BF$_3$ being formed during the decomposition of LiBF$_4$: LiBF$_4 \rightarrow$ LiF + BF$_3$.

The B 1s, F 1s and Li 1s spectra are shown in Figure 13c,d. The B 1s peak at 194.4 eV and F 1s peak at 686 eV were assigned to Li$_x$BF$_y$ originating from LiBF$_4$.[4] A B 1s peak at lower binding energy (192 eV) was dominant in the ternary solution and was assigned to Li$_x$BF$_y$O$_z$ from the reaction of BF$_3$ with traces of water.[4] In the binary solution, the predominant B 1s peak was slightly lower at 191 eV and was assigned to LiBOB.[28] LiF (F 1s 684 eV and Li 1s 55 eV) can also be observed in both electrolyte solutions but clearly making up a higher proportion in the binary solution. This can be seen in the F 1s spectra where the 684 eV peak had almost the same height of the Li$_x$BF$_y$ peak in the binary solution while it was much lower in intensity in the ternary solution. Furthermore, a quantification of F, O, N, C, B and Li revealed that Li makes up 31 wt% of the composition at the surface in the binary solution and only 3.6 wt% in the ternary solution. The proportions of other elements were similar in both electrolytes except for C in the ternary solution where the proportion of F, O, N, C and B are 12.6%, 18.6%, 7.9%, 53.9% and 3.3%, respectively, while they were 7%, 20%, 5.3%, 32.9%, and 3.6%, respectively, in the binary solution. An explanation of the rapid deterioration of the capacity in the binary solution with LMNO electrode could reside in the decomposition of the LiBF$_4$ salt to LiF which was prevented in the presence of DMC in the ternary solution. This is most likely due to the high-voltage cycling necessary for the LMNO since this electrolyte solution does not behave this way with electrodes such as LiCoO$_2$ or LiMn$_2$O$_4$ cycled below 4.3 V.

To combine the results from IR, XPS and charge-discharge battery cycling, it can be concluded that dinitriles, due to their moderate DN and dielectric constant, when placed in a ternary electrolyte so-

lution with ethylene carbonate and dimethyl carbonate can compete and solvate lithium ions. The solvated ions play a great role at the interface and their selective decomposition control the nature of the passivation layer and hence the electrode performance in the battery. The formation of a passivation layer, CEI, at the surface of LMNO seems to be enhanced by the presence of DMC along with EC and a dinitrile solvent that can protect both the solvents and LiBF$_4$ salt from undergoing uncontrolled oxidative decomposition. Although the reversible capacities of the ternary electrolytes were slightly lower than those of a conventional electrolyte, this work should still be seen as a first step in the direction of introducing dinitrile solvents into lithium electrolyte formulations for high voltage lithium batteries and more work is needed not only to improve the ternary electrolyte solution formulation but also the single and binary solutions with the use of SEI and CEI forming additives.

Conclusions

The possibility of using dinitrile-based electrolyte solutions in high-voltage lithium batteries has been successfully demonstrated. It was shown that dinitriles with chain lengths of $n = 4$-8 used alone or mixed with a second solvent EC could not sustain Li/LMNO batteries (poor capacities with low coulombic efficiencies) except when DMC was used as a third solvent and LiBF$_4$ as salt and LiBOB as co-salt. This was investigated by the examination of cycled cells by XPS and is attributed to the ability of DMC to sacrificially protect from the oxidative decomposition of the LiBF$_4$ salt at high voltage. We have investigated the conductivity of the dinitrile solutions as a function of concentration, added solvent and salt, and have shown that the shorter alkane dinitriles have much higher values than the longer ones due to higher viscosities and lower dielectric constant of the latter. The electrochemical stability window of all the electrolyte solutions was found to be very high ranging between 6 to 7 volts. An IR study of the electrolyte solutions showed a strong interaction between the lithium ion and the functional groups of the three solvents. Battery cycling of the ternary electrolyte solutions shows that there is a slight correlation between the reversible capacities and the chain length of the aliphatic dinitrile solvent after 50 cycles. The shorter alkane dinitriles such as adiponitrile and pimelonitrile give higher capacities than the longer alkane dinitriles such as sebaconitrile and suberonitrile that show similar capacity fade.

References

1. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, and J. R. Dahn, *Journal of The Electrochemical Society*, **144**, 205 (1997).
2. R. Dedryvere, D. Foix, S. Franger, S. Patoux, L. Daniel, and D. Gonbeau, *The Journal of Physical Chemistry C*, **114**, 10999 (2010).
3. H. Duncan, Y. Abu-Lebdeh, and I. J. Davidson, *Journal of The Electrochemical Society*, **157**, A528 (2010).
4. H. Duncan, D. Duguay, Y. Abu-Lebdeh, and I. J. Davidson, *Journal of The Electrochemical Society*, **158**, A537 (2011).
5. L. Yang, B. Ravdel, and B. L. Lucht, *Electrochemical and Solid-State Letters*, **13**, A95 (2010).
6. K. Xu and C. A. Angell, *Journal of The Electrochemical Society*, **145**, L70 (1998).
7. X.-G. Sun and C. A. Angell, *Electrochemistry Communications*, **7**, 261 (2005).
8. A. Abouimrane, I. Belharouak, and K. Amine, *Electrochemistry Communications*, **11**, 1073 (2009).
9. J. Mun, T. Yim, K. Park, J. H. Ryu, Y. G. Kim, and S. M. Oh, *Journal of The Electrochemical Society*, **158**, A453 (2011).
10. Y. Abu-Lebdeh and I. Davidson, *Journal of The Electrochemical Society*, **156**, A60 (2009).
11. Y. Abu-Lebdeh and I. Davidson, *Journal of Power Sources*, **189**, 576 (2009).
12. P. Isken, C. Dippel, R. Schmitz, R. W. Schmitz, M. Kunze, S. Passerini, M. Winter, and A. Lex-Balducci, *Electrochimica Acta*, **56**, 7530 (2011).
13. M. Nagahama, N. Hasegawa, and S. Okada, *Journal of The Electrochemical Society*, **157**, A748 (2010).

14. A. J. Gmitter, I. Plitz, and G. G. Amatucci, *Journal of The Electrochemical Society*, **159**, A370 (2012).
15. H. Deng, I. Belharouak, Y.-K. Sun, and K. Amine, *Journal of Materials Chemistry*, **19**, 4510 (2009).
16. S.-T. Myung, Y. Hitoshi, and Y.-K. Sun, *Journal of Materials Chemistry*, **21**, 9891 (2011).
17. S. Dalavi, M. Xu, B. Knight, and B. L. Lucht, *Electrochemical and Solid-State Letters*, **15**, A28 (2011).
18. J. Wang, Y. Wu, X. Xuan, and H. Wang, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **58**, 2097 (2002).
19. Y. S. COHEN and D. AURBACH, in *Lithium-Ion Batteries*, p. 70 (2004).
20. L. Yang, A. Xiao, and B. L. Lucht, *Journal of Molecular Liquids*, **154**, 131 (2010).
21. A. Manuel Stephan, *European Polymer Journal*, **42**, 21 (2006).
22. L. Xing, W. Li, C. Wang, F. Gu, M. Xu, C. Tan, and J. Yi, *The Journal of Physical Chemistry B*, **113**, 16596 (2009).
23. A. Guerfi, M. Dontigny, Y. Kobayashi, A. Vijh, and K. Zaghib, *Journal of Solid State Electrochemistry*, **13**, 1003 (2009).
24. T. Eriksson, A. M. Andersson, A. G. Bishop, C. Gejke, T. r. Gustafsson, and J. O. Thomas, *Journal of The Electrochemical Society*, **149**, A69 (2002).
25. G. Deniau, G. Lecayon, P. Viel, G. Hennico, and J. Delhalle, *Langmuir*, **8**, 267 (1992).
26. T. Nakayama, K. Inamura, Y. Inoue, S. Ikeda, and K. Kishi, *Surface Science*, **179**, 47 (1987).
27. J. L. Magalhães, L. M. Moreira, U. P. Rodrigues-Filho, M. J. Giz, M. A. Pereira-da-Silva, R. Landers, R. C. G. Vinhas, and P. A. P. Nascente, *Surface and Interface Analysis*, **33**, 293 (2002).
28. L. Yang, T. Markmaitree, and B. L. Lucht, *Journal of Power Sources*, **196**, 2251 (2011).