Li-ion battery packs for electrified vehicles and grid energy storage require high energy density and long lifetime cells.1-3 One approach to increase the energy density of Li-ion cells is to adopt high potential positive electrodes. Layered Li[Ni1-xMnxCo1-x-y]O2 materials have been extensively investigated since they are cheaper alternatives to LCO and since they can function at high potentials.4-9 However, it is a great challenge to cycle high voltage NMC cells (above 4.3V) well. The use of new solvent blends and the introduction of electrolyte additives are two common ways to improve the lifetime of high voltage NMC Li-ion cells.10-22 Ma et al. and Nelson et al. found that a ternary additive combination can greatly improve NMC442/graphite cell performance at high voltage.10,11,23 Xia et al. reported that fluorinated electrolyte and sulfone-based electrolyte also improve high voltage NMC cells.15–17 Compared to EC-containing electrolytes, there is much less literature that reports the physical properties of EC-free electrolytes to optimize the conductivity of EC-free EMC electrolytes at low salt concentrations below 0.4 M. FT-IR results show that the added FEC hinders ion pair formation with competing with EMC to dissociate LiPF6 resulting in increased conductivity in EMC electrolytes. Conductivity measurements show that the conductivity of DMC electrolytes decreases significantly below 0 °C due to the high melting point of DMC. Differential thermal analysis was used to determine the LiPF6-DMC phase diagram which then can be used to explain the conductivity results. The results presented here identify avenues by which EC-free electrolytes can be improved for use in practical Li-ion cells.

**Experimental**

**Conductivity measurements.**—Solution conductivities of the electrolytes were measured using a Mettler Toledo FiveGo conductivity meter. Solutions of LiPF6, (BASF, USA, purity: 99.95%, water content < 20 ppm) were prepared in either EMC (BASF, USA, purity: 99.9%, water content < 20 ppm), FEC:EMC (5:95 w/w) (FEC, BASF, USA, purity: 99%, water content < 20 ppm), FEC:EMC (10:90 w/w), or DMC (BASF, USA, purity:99.9% water content < 20 ppm) in an Ar-filled glove box. Eight mL of each electrolyte was poured into the conductivity meter’s container, sealed and then brought out of the glove box. The conductivity meter’s container, containing the probe, was put into a thermostated bath of ethylene glycol:water solution. Conductivity measurements were taken at 75 minute intervals, at temperatures of -20, -5, 10, 25, 40, and 55 °C.

**FT-IR analysis.**—Measurements were taken on an Agilent Technologies Cary 630 FT-IR, equipped with a diamond attenuated total reflectance (ATR) accessory, in an Ar-filled glove box. The electrolytes analyzed were the same as those used for conductivity measurements in addition to pure EMC, FEC:EMC (5:95), and FEC:EMC (10:90) solvents. 0.1 mL of each solution was placed directly on the ATR crystal. Sixteen scans were taken for each sample, at 2 cm⁻¹ resolution over the frequency range from 600 to 4000 cm⁻¹.

**Differential thermal analysis.**—Differential thermal analysis (DTA) measurements were taken with a custom built cryostat and software setup, using a Model 336 LakeShore temperature controller. The details of the construction of DTA was reported by Day et al.34 The samples measured here were LiFun NMC/graphite pouch cells (402030 size) filled with 0.8 ml of electrolyte (0M–1.5M LiPF6 in EMC and 0M–2.0M LiPF6 in DMC. The cells with EMC electrolytes were cooled from 25 °C to -105 °C at a rate of -2.5 K/min and then heated back up to 25 °C at 2.0 K/min. The cells that contained DMC-based electrolytes were cooled from 25 °C to -45 C at a rate of -1.5 C min⁻¹ and then heated back up to 25 C at 1.0 C min⁻¹.

**Results and Discussion**

The conductivities of EMC-based electrolytes were measured as a function of the salt concentration and the solution temperature. Figure 1 shows that, in general, the conductivity increases as the salt concentration (below 1.5M) or the temperature increases. This is expected since the concentration or the mobility of free ions (i.e., Li⁺ and PF6⁻)
Figure 1. Conductivity vs molarity of LiPF$_6$ in EMC (a, d), FEC:EMC (5:95 w/w) (b, e) and FEC:EMC (10:90 w/w) (c, f) in the temperature range from -20 to 55 °C.

increases as the salt concentration or temperature increases, respectively. The increase with conductivity with salt concentration is not linear at low molarity as has been found by Doucy et al. for solutions of LiAsF$_6$ in DMC. In addition, even at high salt concentrations, the solution conductivity is relatively low for a Li-ion electrolyte. It is well-known that in non-polar solvents, such as EMC, LiPF$_6$ tends to form ion pairs that do not contribute to ionic conduction in the solution. It is for this reason, in part, that EC, a very polar co-solvent, is commonly used in Li-ion cell electrolytes (the second reason being its tendency to form a passive SEI on graphite electrode surfaces). Therefore, it is desirable to consider how alternative co-solvents like FEC, which have been shown to improve the properties of Li-ion cells with EC-free electrolytes, affect the conductivity of EC-free electrolytes.

Solutions were prepared with 5% or 10% FEC, an SEI-forming additive, a highly polar molecule, and a demonstrated ‘enabler’ for EC-free solutions. Figure 1 shows that the addition of FEC to EMC electrolytes indeed improves the electrolyte conductivity. This matches the expectation that the relative permittivity (dielectric constant) of EMC-based electrolytes increases when FEC is added. Table S1 shows the permittivity of an FEC:EMC mixture as calculated using a simple model described by Prakongpan et al. The permittivity
of the EMC-based electrolytes decreases significantly at low LiPF₆ concentrations, notably below 0.4 M, completely unlike the results for EMC electrolytes with just 5–10 % FEC. This behavior has been observed before in electrolyte solutions prepared with non-polar (low dielectric constant) solvents. Consequently, at low salt concentrations, the low dielectric constant of the solution results in the formation of electrically neutral ion pairs or aggregates.

It is therefore desirable to examine the interactions between the ions and the solvent (or solvents). FT-IR is a good tool that has been applied to investigate solvation behavior and ion pair formation for a wide variety of salts and solvents. Figure 2 and Figure 3 show FT-IR spectra (800–900 and 1600–1900 cm⁻¹) of EMC and mixed FEC:EMC (10:90) electrolyte containing different concentrations of LiPF₆. Figure S1 shows FT-IR spectra of mixed FEC:EMC (5:95) electrolyte containing different concentrations of LiPF₆. The IR-active t₁u absorption of the free, octahedrally symmetric PF₆⁻ anion is observed at 843 cm⁻¹. The formation of contact and/or solvation ion pairs lowers the symmetry of the anion, causing the absorption frequency to shift and split into two bands, approximately centered at 877 and 834 cm⁻¹. EMC has an absorption band at 878 cm⁻¹ that overlaps with this region, complicating any quantitative analysis of the PF₆⁻ ion pair or aggregates, consistent with the behavior in diethyl carbonate (DEC) solvent, as described by Seo et al. Nonetheless, the relative absorbance of the free (843 cm⁻¹) and ion-paired (834 cm⁻¹) PF₆⁻ may be evaluated qualitatively from the spectra shown in Figure 2 and Figure 3. Examination of these peaks reveals that in mixed FEC:EMC electrolytes, there is a lower degree of ion-pairing than is observed in the EMC-based electrolytes. This can be seen from the absorbance of the free (843 cm⁻¹) PF₆⁻ relative to the ion-paired (834 cm⁻¹) PF₆⁻. For a given salt concentration and solution temperature, it is observed that the free PF₆⁻ peak increases as FEC is added. By inhibiting the interaction between Li⁺ cations and PF₆⁻ anions, it is expected that the addition of FEC should increase the concentration of ion carriers in solution. This is indeed consistent with the measured conductivity results, as described above.

The C=O bond of the carbonate functional group has a very strong IR absorption in the carbonyl region (1650–1850 cm⁻¹). The carbonyl shift depends on the local environment and is typically shifted to a higher wavenumber upon coordination to the Li⁺ cation. The uncoordinated C=O stretching frequencies for EMC and FEC occurs at 1745 cm⁻¹ and 1835 cm⁻¹, respectively, while the stretching frequencies for a C=O group coordinated to Li⁺ appear at 1710 cm⁻¹ and 1810 cm⁻¹, respectively. As the FEC concentration is increased, the ratio between uncoordinated and coordinated C=O groups belonging to EMC decreases while the ratio between uncoordinated and coordinated C=O groups belonging to FEC increases. This result may be interpreted that FEC competes with EMC to associate with the Li⁺ cations in solution, as may be expected from the significantly larger dipole moment of the FEC molecule. The significance of this result is that FEC can indeed serve as both an SEI-forming additive and as a polar co-solvent, even at very low concentrations. DTA can be used to examine the state of the electrolyte in a cell and generate phase diagrams of electrolyte systems as well. Here, this method was used to examine the phase transition behavior of
Figure 3. FT-IR (800–900 and 1600–1900 cm\(^{-1}\)) spectra of LiPF\(_6\):FEC:EMC (10:90) electrolytes of various molarities and of pure EMC. Dashed lines indicating the 834, 843, 1710, 1745, 1810 and 1845 cm\(^{-1}\) positions have been inserted into the Figures to guide readers.

Figure 4. DTA curves for various molarities (0, 0.25, 0.6, 0.8, 1.3 and 1.5M) of LiPF\(_6\) in EMC electrolyte.

Emeraldine and DMC electrolytes with various salt concentrations. The phase diagram can, among other things, show the liquidus point of the solution, which marks a sharp decrease in electrolyte conductivity. Thus, the method can be used to determine the lowest temperature that a cell can be expected to function properly.

Figure 4 shows the DTA traces for NMC/graphite cells containing LiPF\(_6\):EMC electrolytes with various LiPF\(_6\) concentrations. This figure shows that the freezing point of the electrolyte decreases as salt concentration increases. This data can then be used to construct a phase diagram showing the relationship between the melting points and the salt compositions of the LiPF\(_6\):EMC system. The phase diagrams are created by plotting the onset of the solidus feature and peak of the liquidus features, as shown by Ding et al.\(^{32}\) In the case of the LiPF\(_6\):EMC system, the solidus and liquidus features are very close in temperature, which makes the eutectic point and the other finer points of the phase diagram very difficult to discern. This issue could perhaps be overcome with lower heating rates, which would give more precise measurements, but these rates might be experimentally impractical for testing a large number of samples.

Other solvents, such as DMC, freeze at higher temperatures than EMC (4°C vs. -53°C, respectively, for the pure compounds). The LiPF\(_6\):DMC system also has a greater temperature difference between the solidus and liquidus features, which allows for more clarity in
The pouch cells for DTA were filled with electrolyte and measured immediately. The pouch cells for DTA did not undergo a formation procedure, that is, they were never charged. This figure more clearly shows the liquidus (higher temperature) and solidus (lower temperature) features present in DTA signals. Using the same liquidus/solidus convention as described by Ding et al., this diagram can be used to construct the phase diagram shown in Figure 6.

The DTA curve for a particular electrolyte can help explain the conductivity vs. temperature curve for the same electrolyte. These data can then be used to determine relationship between conductivity and phase change. Figure 7 shows the DTA trace and conductivity vs. temperature behavior of 1M LiPF₆ in DMC can be understood. The solid DMC crystals then increase the molarity of the remaining liquid, while also significantly reducing the mobility of the rest of the DMC. As the presence of DMC in a solvent mixture will increase the freezing point, cells that are to be used for low temperature applications should not have DMC in large quantities, in order to optimize low temperature performance.

Conclusions

In this report, EC-free electrolytes were studied by conductivity measurements, FT-IR and DTA. The results show that LiPF₆:EMC electrolytes have low conductivity compared to conventional EC:EMC electrolytes due to the formation of non-conducting ion pairs and/or aggregates. The addition of additive quantities (5–10%) of FEC significantly improve EMC electrolyte conductivity especially at low salt concentrations. The phase diagram of the LiPF₆:DMC system has been determined for the first time. Anomalies in the conductivity versus temperature behavior of 1M LiPF₆ in DMC can be understood based on the determined phase diagram. The results suggest that a large portion of DMC should not be used in electrolytes when cell performance at low temperature is important.

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