A Study of the Transport Properties of Ethylene Carbonate-Free Li Electrolytes

E. R. Logan,1 Erin M. Tonita,1 K. L. Gering,2 Lin Ma,3,* Michael K. G. Bauer,1 Jing Li,1 L. Y. Beaulieu,4 and J. R. Dahn1,3,**

1Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada
2Department of Biological & Chemical Processing, Idaho National Laboratory, Idaho Falls, Idaho 83415-3732, USA
3Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada
4Department of Physics and Physical Oceanography, Memorial University, St. John’s, Newfoundland A1B 3X7, Canada

Recently it has been found that Li-ion cells with organic carbonate-based electrolytes that do not contain ethylene carbonate (EC) can perform exceptionally well at high voltage. This work explores the transport properties of low-EC and EC-free Li electrolytes with lithium hexafluorophosphate (LiPF6) as the conducting salt. Conductivity and viscosity were measured for electrolytes with solvent compositions EC-linear carbonate in a weight ratio of x:(100-x), where linear carbonate = (ethyl methyl carbonate (EMC), dimethyl carbonate (DMC)), and x = {0, 10, 20, 30}. While EC-free electrolytes have lower viscosities, the maximum conductivities of these electrolytes are lower as well. Walden analysis was employed to understand the loss in conductivity as EC is removed from the electrolyte. Electrolyte properties calculated from a theoretical model, the Advanced Electrolyte Model (AEM) show excellent agreement with most of the experimental data. Differential thermal analysis (DTA) was used to investigate the phase diagram of the ternary EC:DMC:LiPF6 solvent system. The addition of both EC and LiPF6 in the ranges studied lowered the liquidus transition temperature of the solution. Li[Ni0.5Mn0.5CoO2][O2]/graphite and single crystal Li[Ni0.5Mn0.5CoO2][O2]/graphite cells containing an EMC-based electrolyte showed good capacity retention and comparably low impedance growth when 5% w/w of fluoroethylene carbonate (FEC) was added.

As the widespread adoption of Li-ion batteries in electric vehicles (EVs) and other larger-scale applications continues, developing cells with larger energy densities, and longer cycle lives and calendar lives becomes crucial. Higher energy density must be achieved without sacrificing long-term stability. Typical non-aqueous Li-ion battery electrolytes composed of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and/or dimethyl carbonate (DMC) may not be suitable in high voltage cells because oxidation of EC at the positive electrode at high voltage can cause significant gas generation and impedance growth.1 EC has traditionally been considered an indispensable component of non-aqueous liquid electrolytes for Li-ion cells. This is due to its high dielectric constant, which is crucial for dissociating Li salts in solution.2 Additionally, EC forms a passivating solid electrolyte interphase (SEI) on graphite negative electrodes, which is necessary for long-term cycling.3 Recently, it has been shown that alternative electrolyte systems that do not contain EC can be used for charge-discharge cycling at high voltage with minimal capacity loss. Electrolytes composed primarily of linear carbonates (e.g. EMC) or aliphatic esters such as ethyl acetate (EA) or methyl propionate (MP) plus ~5% by weight of “enabling” additives such as fluoroethylene carbonate (FEC) are promising electrolyte systems for cells operating at high voltage.1,4-9 Additionally, electrolytes containing relatively low concentrations of EC (< 30% by weight) have been shown to be promising for low-temperature applications.10,11 There have been other novel approaches to EC-free electrolytes that will not be discussed and considered in this paper. For example, Wang et al. recently showed that electrolytes containing high (>3 M) concentrations of lithium bis(fluorosulfonyl) imide (LiFSI) in trimethyl phosphate (TMP) can function well in Li-ion cells.12 Yamada et al. showed that highly concentrated electrolytes containing acetoniitrile as the sole solvent could also function well in Li-ion cells.13 Petiton et al. showed that ethyl acetate could function as the primary solvent in lithium ion cells when high concentrations of LiFSI were used.5 There have also been a number of other studies showing that highly concentrated electrolytes can render uncommon solvents effective in electrolytes for lithium-ion cells. However, this approach suffers from the high cost of the salts required.

Measuring the transport properties of an electrolyte is useful for screening its effectiveness for a given application. Common transport properties such as ionic conductivity and viscosity are relatively easy to measure and can give some indication as to how well a Li-ion cell will perform, especially at high charge/discharge currents. Ionic conductivity has been reported for many carbonate-based electrolytes, including EC, EMC, DMC, diethyl carbonate (DEC), and propylene carbonate (PC), and for many different Li salts.10,14-22 Most of these studies on ionic conductivity have considered electrolytes with relatively high concentrations of EC. However, with the current interest in EC-free electrolytes, it is important to evaluate the transport properties of these low-EC content and EC-free electrolytes. Previous studies have considered the conductivity of lithium hexafluoroarsenate (LiAsF6) electrolytes in low dielectric solvents such as DMC.23,24 Recently, Xiong et al. reported the conductivity of electrolytes containing EMC as the sole solvent for a range of concentrations of lithium hexafluorophosphate (LiPF6).25

The Advanced Electrolyte Model (AEM) is a theoretical model based on a statistical mechanics framework developed by Gering.26-27 It uses molecular-scale solvent-solvent, solvent-ion, and ion-ion interactions to calculate many macroscopic transport properties of electrolytes including, but not limited to: conductivity, viscosity, diffusion coefficients, transference numbers, and activity coefficients. The model can also calculate microscopic properties of electrolyte systems, such as solvated ion sizes, solvation numbers, solvent residence times, and populations of different species such as single ions (SI), ion pairs (IP), and triple ions (TI). The AEM can consider both aqueous and non-aqueous systems, and a number of different solvents and Li salts. The AEM has previously been validated for several aqueous and non-aqueous systems, including electrolyte systems composed of EC, EMC, DMC, and the ester methyl acetate (MA).26-28 Most of the systems that have been validated contained considerable amounts of EC. If the AEM can be validated for low-EC and EC-free electrolytes, it can be used to rapidly optimize these electrolytes for a given application. AEM version 2.17.5 was used for all calculations in this paper.

*Electrochemical Society Student Member.
**Electrochemical Society Fellow.
E-mail: jeff.dahn@dal.ca

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L. Y. Beaulieu,4 and J. R. Dahn

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To support the emphasis on EC-lean and EC-free electrolytes, the AEM theory was adapted to consider low permittivity conditions of linear carbonates and other classes of solvents, where, for example the pure solvent dielectric constant of DMC and EMC fall below 4 at room temperature. Classical theory of ion association is not capable of correct interpretation of such extreme conditions because it views an electrolyte system as a continuum with a static dielectric “constant.” However, the AEM does not assert a dielectric constant for the chosen solvents, but rather determines how the ionic fields and ion pair dipoles influence the solvent permittivity (within a colligative context) in behavior broadly referred to as “dielectric depression”. In short, solvent permittivity decreases in the presence of free ions due to field effects on solvent dipoles and other aspects of molecular entropy. For most systems of modest to high permittivity (say, dielectric constant of 20 or higher), the dielectric depression is readily seen as salt is increased. For example, in Figure 1 for the solvent blend EC:DMC 30:70, dielectric depression occurs more or less continuously for LiPF$_6$ concentrations between 0 and 1 mol/kg. However, for low-permittivity systems, the occurrence of dielectric depression is minor as salt is added, whereafter further salt addition causes permittivity to increase well past the pure solvent value, enabling greater dissociation of salt into free ions. This is due to the presence of ion pairs, which function as dipoles and thereby add to the solution permittivity. Figure 1 shows solution permittivity as a function of LiPF$_6$ concentration for solvent blends ranging from pure DMC to EC:DMC 30:70 (wt. %), as calculated by the AEM. In the EC:DMC 30:70 electrolyte, dielectric depression as salt is added is clearly seen. In the low-dielectric DMC electrolyte, an increase in the solution permittivity is seen as more LiPF$_6$ is added. The AEM calculations that support simultaneous equilibrium state determination of free ions, ion pairs (contact ion pairs (CIP), solvent shared ion pairs (SShIP), solvent separated ion pairs (SSIP)), triple ions (TI), solvent permittivity and solution permittivity are very complex and require several levels of iteration that must converge in concert. To our knowledge, the AEM is the only chemical physics computational tool that provides sufficient theoretical rigor to predict property trends of low-permittivity electrolytes.

In this work, the transport properties of low-EC and EC-free electrolytes for use in high-voltage Li-ion cells are probed. Viscosity and ionic conductivity are measured for LiPF$_6$-based electrolytes containing the binary solvent mixtures EC:EMC and EC:DMC, for a range of EC compositions. Calculations from the AEM are used to further understand the transport properties of these electrolytes. A phase diagram for the EC:DMC:LiPF$_6$ system was constructed using differential thermal analysis (DTA).

**Experimental**

**Electrolyte preparation.**—All electrolyte mixing was done in an Ar-filled glove box. All chemicals used in this work were received from BASF. These included: lithium hexafluorophosphate (LiPF$_6$) (purity 99.94%, water content 14 ppm), ethylene carbonate (EC) (purity 99.95%, water content < 10 ppm), ethyl methyl carbonate (EMC) (purity 99.92%, water content < 6 ppm), dimethyl carbonate (DMC) (purity 99.95%, water content < 20 ppm), and fluoroethylene carbonate (FEC) (purity 99.94%). For conductivity and viscosity measurements, electrolytes containing solvent blends of the form EC:EMC x:(100-x) and EC:DMC x:(100-x) were prepared for x = {0, 10, 20, 30} (wt. %). For each solvent composition, LiPF$_6$ was added in concentrations of 0 molal (mol/kg solvent, denoted m), 0.5 m, 1.0 m, 1.5 m, and 2.0 m. Three different solvent blends were used in the electrolytes for cycling tests: EMC, FEC:EMC 5:95 (wt. %), and EC:EMC 30:70 (wt. %). For all electrolytes used in pock cell cycling, an LiPF$_6$ concentration of 1.0 molar (M) was used.

**Cell filling and cycling.**—The cells used for cycling tests were NMC442/graphite and single crystal NMC532/graphite 402035-size pouch cells. These cells were obtained from LiFun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). Detailed information about electrode materials can be found in Refs. 4,30. Pouch cells were obtained without electrolyte and were vacuum sealed for shipment. Before use in our laboratory, they were cut open and dried at approximately 100°C for 14 hours under vacuum to remove any excess moisture. After drying, cells were moved to an Ar-filled glove box for filling. Cells were filled with 0.9 g of electrolyte and sealed by a vacuum sealer (MSK-115 V, MTI Corp.) to -95.2 kPa gauge for 4 seconds at 165°C. All cells were cycled at 40°C. The NMC442 cells were cycled between 2.8 and 4.4 V at a charge/discharge rate of C/2.5 in constant current-constant voltage (CCCV) mode. The cutoff current for CCCV cycling was C/20. The NMC532 cells were cycled between 3.0 and 4.4 V at a rate of C/2 for both charge and discharge cycles. A cycle at C/20 was done every 50 cycles. The cutoff current for the NMC532 cells was also C/20. All pouch cells were cycled with external clamps to ensure a firm stack pressure of about 25 kPa even if gas was produced during cycling.

**Conductivity measurements.**—Ionic conductivity was measured using a commercial conductivity meter (Hach model 3455) capable of performing four separate conductivity measurements using four separate conductivity probes. Each probe had an integrated PT1000 RTD to monitor the temperature of the electrolyte. Probes were calibrated in air and to a known standard (12.88 mS/cm, Hanna Instruments HI70030C). Approximately 14.5 mL of electrolyte was added to a high-voltage cell. Cells were cycled up to 4.4 V to test the effectiveness of EC-free electrolytes in high-voltage cells.

**Viscosity measurements.**—Viscosity was measured using an Ostwald viscometer (Sibata Scientific Technology, Japan). Two different sized viscometers were used in these experiments, with capillary
Table I. Melting points, boiling points and dynamic viscosities at 25°C (unless otherwise specified) for the carbonate solvents used in this study.

| Name                  | MP (°C) | BP (°C) | Dielectric constant at 25°C | Viscosity at 25°C (cP) | Structure |
|-----------------------|---------|---------|----------------------------|------------------------|-----------|
| Ethylene carbonate (EC) | 36.43   | 248     | 89.78 (40°C)               | 1.93 (40°C)            |           |
| Ethyl methyl carbonate (EMC) | -53     | 110     | 2.958                      | 0.65                   |           |
| Dimethyl carbonate (DMC) | 4.6     | 90      | 3.1075                     | 0.59                   |           |

Diameters of 0.5 mm and 0.75 mm, respectively. The temperature of the electrolyte in the viscometer was controlled by a circulating bath (Thermo Scientific) filled with a water/ethylene glycol mixture. The viscometer was placed inside a triple walled glass Dewar where the mixture was circulated. A resistance temperature detector (RTD) attached to the surface of the viscometer measured the temperature of the electrolyte. Measurement of the viscosity was completed using computer vision (CV) software developed by Beaulieu et al.31 Viscosity measurements were taken for temperatures ranging from 10°C to 40°C with the exception pure DMC, which was measured between 10°C and 50°C. Reproducibility of these measurements is typically within 1%. The raw data were interpolated to temperatures in 5 degree increments using a linear interpolation method in MATLAB. This routine introduces some additional error. Total uncertainty after the interpolation has been applied is taken to be 2%.

**Differential thermal analysis.**—Differential thermal analysis (DTA) was used to do a preliminary investigation of the phase equilibria of the ternary EC:DMC:LiPF6 system. The solvent blends EC:DMC x:(100-x), x = {0, 10, 20, 30} (wt. %) were used, and LiPF6 concentrations 0 m and 1.0 m were considered. On the DTA apparatus, cells were cooled at a rate of 3°C/min to −100°C, and heated at 1°C/min to +25°C. In some cells, an exothermic feature was observed in the DTA spectrum before the solidus transition. In this case, cells were cooled to −100°C, heated to just beyond the exothermic peak, cooled, then heated to 25°C to remove this feature from the spectrum. Cells were filled with 0.75 mL of solution in an Ar-filled glove box using the same filling and sealing procedure as described above. A full description of the Li-ion DTA apparatus can be found in Ref.32. Analysis of the DTA spectra followed the procedure outlined by Ding et al.33

**Results and Discussion**

**Conductivity and viscosity.**—Table I shows basic physical properties for ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) at room temperature (unless otherwise noted), including melting point (MP), boiling point (BP), dielectric constant, dynamic viscosity (η), and chemical structure. Note that the melting point, dielectric constant, and viscosity of EC are all much higher than those of EMC or DMC. EMC and DMC have very similar chemical structures, and correspondingly their physical properties are similar except for the melting point of DMC which is comparatively very high. Figure 2 shows viscosity measured as a function of temperature for EMC and DMC without LiPF6 added. The viscosity of EC shown at 40°C comes from Ref.34. Calculations from the AEM are shown as solid lines.
Figure 4. Viscosity as a function of LiPF$_6$ concentration for electrolytes with solvent blends (a) DMC, (b) EC:DMC 10:90, (c) EC:DMC 20:80, and (d) EC:DMC 30:70 (wt. %) for temperatures between 10°C and 40°C. Calculations from the AEM are shown as solid lines.

Similar trends are observed for electrolytes with solvents of the form EC:DMC x(100-x). Figure 4 shows viscosity as a function of LiPF$_6$ concentration for electrolytes containing solvent blends with (a) x = 0, (b) x = 10, (c) x = 20, and (d) x = 30 for temperatures between 10°C and 40°C. Notice that over both temperature and salt concentration, the viscosities of these electrolytes are universally lower than the corresponding electrolytes containing EMC shown in Figure 3. Since DMC has a lower viscosity than EMC at all temperatures considered (as seen in Figure 2), this is to be expected. As in the EC:EMC case shown in Figure 3, adding EC to DMC-based electrolytes significantly increases the viscosity. At the most extreme conditions of 10°C and 2.0 m LiPF$_6$, viscosity increases by 145% between 0% EC and 30% EC-containing, DMC-based electrolytes. At more moderate conditions such as 1.0 m LiPF$_6$ and 20°C the increase in viscosity is still 69% over the same range of EC. Values for experimental viscosity shown in Figures 3 and 4 are also presented in Tables II–V.

AEM calculations of viscosity for the EC:EMC-based and EC:DMC-based electrolytes are shown as solid lines in Figures 3 and 4. Generally, the agreement of AEM calculations with experiment is quite good; the average deviation from experiment over all solvent compositions, salt concentrations, and temperatures is 10.2%. As seen previously in different electrolyte systems, the AEM’s viscosity predictions can deviate further from experiment at high concentrations of LiPF$_6$, where the deviation can vary somewhat with the chosen system. Here, the deviations of the AEM from experimental measurements for the EC:EMC and EC:DMC systems shown in Figures 3 and 4 are 4.6%, 9.0%, 12.7%, 12.6%, and 12.3% for LiPF$_6$ concentrations of 0 m, 0.5 m, 1.0 m, 1.5 m, and 2.0 m, respectively. One system that deserves particular attention is the case where DMC is the sole solvent. In this case, the agreement with AEM is less than that of EC:DMC systems for all concentrations of LiPF$_6$, with the exception of the salt-free case. For these DMC-only electrolytes, average deviations of the AEM from experiment are 0.8%, 17.9%, 29.5%, 33.4%, and 25.4% for 0 m, 0.5 m, 1.0 m, 1.5 m, and 2.0 m, respectively, over all temperatures. This larger deviation appears to stem from an issue with how the AEM interprets the structure-making interactions between solvated ion associated members formed within mixtures of DMC and LiPF$_6$, which would have plenteous amounts of ion pair and triple ion species. Presumably this artifact is also present in the

| Table II. Viscosity at 10°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF$_6$. |
|---|---|---|---|---|---|---|---|---|
| Solvents | Weight % solvent | LiPF$_6$ concentration (mol/kg) |
| | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
| EC | DMC | 0 | 100 | 0.71 | 1.17 | 2.05 | 3.43 | 5.48 |
| EC | DMC | 10 | 90 | 0.82 | 1.43 | 2.47 | 4.48 | 6.94 |
| EC | DMC | 20 | 80 | 0.96 | 1.69 | 3.01 | 5.20 | 7.64 |
| EC | DMC | 30 | 70 | 1.11 | 2.00 | 3.63 | 7.06 | 13.41 |
| EC | EMC | 0 | 100 | 0.80 | 1.33 | 2.29 | 4.13 | 7.06 |
| EC | EMC | 10 | 90 | 0.92 | 1.66 | 2.94 | 5.13 | 9.14 |
| EC | EMC | 20 | 80 | 1.08 | 1.95 | 3.31 | 6.11 | 12.67 |
| EC | EMC | 30 | 70 | 1.30 | 2.33 | 4.22 | 8.73 | 16.58 |

| Table III. Viscosity at 20°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF$_6$. |
|---|---|---|---|---|---|---|---|---|
| Solvents | Weight % solvent | LiPF$_6$ concentration (mol/kg) |
| | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
| EC | DMC | 0 | 100 | 0.62 | 1.02 | 1.69 | 2.66 | 3.80 |
| EC | DMC | 10 | 90 | 0.72 | 1.20 | 2.01 | 3.41 | 4.85 |
| EC | DMC | 20 | 80 | 0.83 | 1.31 | 2.37 | 3.92 | 5.71 |
| EC | DMC | 30 | 70 | 0.95 | 1.64 | 2.85 | 5.17 | 9.29 |
| EC | EMC | 0 | 100 | 0.70 | 1.12 | 1.82 | 3.25 | 5.25 |
| EC | EMC | 10 | 90 | 0.80 | 1.38 | 2.36 | 4.00 | 7.04 |
| EC | EMC | 20 | 80 | 0.93 | 1.62 | 2.63 | 4.59 | 8.85 |
| EC | EMC | 30 | 70 | 1.11 | 1.91 | 3.31 | 6.25 | 11.40 |
Other DMC-containing electrolytes, however, it becomes much less pronounced due to the increased presence of free ions enabled by the higher permittivity of EC. If the pure DMC electrolytes were removed from the evaluation of the AEM, the average deviation over all parameters becomes only 8.7%. Further efforts are underway to better understand the solvated state of ion associated species and incorporate those improved insights within the AEM.

Figure 5 shows ionic conductivity as a function of LiPF₆ concentration (molal) for electrolytes with solvent compositions EC:EMCₜ:(100-兮) for (a)兮 = 0, (b)兮 = 10, (c)兮 = 20, and (d)兮 = 30. Experimental data taken at temperatures between 0°C and 40°C are shown as closed circles with the color of each temperature indicated in panel (b). The inset in panel (a) shows conductivity as a function of molar concentration of LiPF₆ for a lower concentration range. This data is reproduced from Ref. 25. Calculations from the AEM are shown as solid lines. As EC is added, the maximum conductivity (denoted σ_max) increases. As well, the LiPF₆ concentration at maximum conductivity (denoted c_max) decreases going from the EC-free electrolyte to 30% EC. The reason for this change in c_max as a function of EC content comes from the change in dielectric constant that is a result of adding or removing EC. Recalling Figure 1, the impact of adding LiPF₆ on the overall dielectric constant of the solution depends on its EC content. Low-EC solutions see an increase in dielectric constant when salt is added, while 30% EC solutions experience dielectric depression on the addition of salt. This will influence the value of c_max. For the EC-free electrolytes, a large amount of LiPF₆ must be added before the dielectric constant of the electrolyte is high enough for significant ion dissociation to occur. As a result, the maximum conductivity occurs at a higher salt concentration. Conversely, for high-EC electrolytes, the dielectric constant is reduced. This, combined with increasing viscosity, causes c_max to be lower when EC is present. At 20°C, σ_max (according to AEM calculations) for the electrolyte with EMC as the sole solvent is 5.2 mS/cm and occurs at approximately 1.75 m. For the electrolyte with the solvent blend EC:EMC 30:70 at the same temperature, σ_max is considerably higher, around 1.18 mS/cm, and occurs at a much lower LiPF₆ concentration of 1.1 m. The temperature of the electrolyte also impacts c_max. The solubility of the solution and the viscosity are both temperature dependent. As temperature increases, for example, the viscosity will decrease and the solubility will increase. This allows for more Li salt to be added to the solution before the increasing viscosity overpowers the addition of more charge carriers. The impact of temperature on c_max will be much less dramatic than the amount of EC added. Similar trends in c_max and σ_max are seen at higher compositions of EC in Ding et al.14

Table IV. Viscosity at 30°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF₆.

| Solvents | Weight % solvent | LiPF₆ concentration (mol/kg) |
|----------|-----------------|------------------------------|
|          | 0               | 0.5             | 1.0              | 1.5              | 2.0              |
| EC       | 0               | 0.55            | 0.88             | 1.31             | 2.16             | 2.99             |
| EC       | 10              | 0.64            | 1.03             | 1.65             | 2.70             | 3.66             |
| EC       | 20              | 0.73            | 1.14             | 1.94             | 3.07             | 4.35             |
| EC       | 30              | 0.83            | 1.38             | 2.30             | 3.63             | 6.61             |
| EC       | 0               | 0.62            | 0.95             | 1.55             | 2.58             | 4.11             |
| EC       | 10              | 0.71            | 1.17             | 1.93             | 3.14             | 5.07             |
| EC       | 20              | 0.82            | 1.36             | 2.20             | 3.60             | 6.53             |
| EC       | 30              | 0.97            | 1.60             | 2.64             | 4.75             | 8.18             |

Table V. Viscosity at 40°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF₆.

| Solvents | Weight % solvent | LiPF₆ concentration (mol/kg) |
|----------|-----------------|------------------------------|
|          | 0               | 0.5             | 1.0              | 1.5              | 2.0              |
| EC       | 0               | 0.50            | 0.76             | 1.24             | 1.80             | 2.56             |
| EC       | 10              | 0.58            | 0.89             | 1.40             | 2.21             | 3.03             |
| EC       | 20              | 0.65            | 0.93             | 1.64             | 2.57             | 3.39             |
| EC       | 30              | 0.73            | 1.18             | 1.92             | 3.21             | 5.10             |
| EC       | 0               | 0.55            | 0.82             | 1.31             | 2.12             | 3.27             |
| EC       | 10              | 0.64            | 1.01             | 1.63             | 2.60             | 4.15             |
| EC       | 20              | 0.73            | 1.17             | 1.83             | 2.93             | 5.00             |
| EC       | 30              | 0.87            | 1.36             | 2.18             | 3.75             | 6.25             |

Figure 5. Ionic conductivity as a function of molal concentration of LiPF₆ for solvent combinations (a) EMC, (b) EC:EMC 10:90, (c) EC:EMC 20:80, and (d) EC:EMC 30:70 (wt. %). Temperatures between 0°C and 40°C are shown, and calculations from the AEM are given as solid lines. The inset Figure in panel (a) shows conductivity as a function of molar concentration of LiPF₆ between 0 and 1.0 mol/L for electrolytes containing EMC as the sole solvent. This data is obtained from Ref. 25. AEM calculations are given as solid lines.
Figure 6. Ionic conductivity as a function of LiPF$_6$ concentration for electrolytes containing solvent mixtures (a) DMC, (b) EC:DMC 10:90, (c) EC:DMC 20:80, and (d) EC:DMC 30:70 (wt. %) for temperatures between 0°C and 40°C. Calculations from the AEM are shown as solid lines.

Figure 6 shows ionic conductivity as a function of LiPF$_6$ concentration for temperatures between 0°C and 40°C for electrolytes composed of the solvent blend EC:DMC x:(100-x) for (a) x = 0, (b) x = 10, (c) x = 20, and (d) x = 30. The conductivities of DMC-containing electrolytes are universally higher than the corresponding EMC-containing electrolytes in Figure 5. Again, this must be due to the slightly lower viscosity of DMC compared to EMC. Similar trends in conductivity are seen between the two classes of electrolytes. As EC is added, $\sigma_{\text{max}}$ increases and $c_{\text{max}}$ decreases for the DMC-containing electrolytes. Comparing to Figure 5, $\sigma_{\text{max}}$ at 20°C for the electrolyte containing DMC as the sole solvent is about 9.0 mS/cm and occurs at 2.0 m LiPF$_6$. For the EC:DMC 30:70 electrolyte, $\sigma_{\text{max}}$ at 20°C is 11.8 mS/cm at a concentration of 1.1 m. For EMC-containing electrolytes (Figure 5), the conductivity almost doubles between 0% EC and 30% EC, while in the DMC case the conductivity only increases by about 30%. Measured ionic conductivity values can also be found in Tables VI–X.

The electrolytes containing only linear carbonate solvents EMC or DMC (Figures 5a and 6a) show extremely low conductivities when [LiPF$_6$] ≤ 0.5 m. The electrolytes containing EC do not show this behavior. The non-linear increase in conductivity can be seen more closely in the inset in Figure 5a. This has been shown to be due to the low dielectric constant of EMC and DMC (see Table I). LiPF$_6$ cannot dissociate into its constituent ions readily in the low dielectric environment of EMC or DMC, and instead remains as neutral ion pairs (IP) that do not contribute to the conductivity of the solution. At higher concentrations of salt, the presence of ion pair dipoles causes an increase in permittivity of the solution enough to promote the existence of charged single ions (SI) and triple ions (TI), and as a result the conductivity increases. Higher concentrations of Li salt have also been shown to lead to lower impedance growth, and altered compositions of the SEI layer on both the cathode and the anode for cells with electrolytes composed of EC:DMC 30:70 and different additives. For cells containing only EMC in the electrolyte, a slight increase in cell impedance is seen when salt concentration is increased. Additionally, the increased cost of using higher salt concentrations must be considered in potential industrial applications. When EC is present in the electrolyte, the Li salt is able to dissociate at lower concentrations. This has long been known, but with the increased interest in EC-free electrolytes, it is important to revisit the problems of low dielectric solvents such as EMC and DMC and ensure that they are addressed in any potential commercial EC-free electrolytes. The modest decrease in viscosity that is seen from removing EC in Figures 3 and 4 does not make up for the conductivity “lost” by removing the high-dielectric solvent. For applications where high conductivity is absolutely necessary such as for high power cells, it may be necessary to operate cells with EC-free electrolytes at higher concentrations of salt, up to 1.5 m or even 2.0 m. Additionally, even when extremely

| Table VI. Ionic conductivity at 0°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF$_6$. |
| Solvents | Weight % solvent | LiPF$_6$ concentration (mol/kg) |
|----------|-----------------|-------------------------------|
|          | 0.5             | 1.0             | 1.5             | 2.0             |
| EC       | DMC             | 0               | 100             |                |
| EC       | DMC             | 10              | 90              |                |
| EC       | DMC             | 20              | 80              |                |
| EC       | DMC             | 30              | 70              |                |
| EC       | EMC             | 0               | 100             |                |
| EC       | EMC             | 10              | 90              |                |
| EC       | EMC             | 20              | 80              |                |
| EC       | EMC             | 30              | 70              |                |

| Table VII. Ionic conductivity at 10°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF$_6$. |
| Solvents | Weight % solvent | LiPF$_6$ concentration (mol/kg) |
|----------|-----------------|-------------------------------|
|          | 0.5             | 1.0             | 1.5             | 2.0             |
| EC       | DMC             | 0               | 100             |                |
| EC       | DMC             | 10              | 90              |                |
| EC       | DMC             | 20              | 80              |                |
| EC       | DMC             | 30              | 70              |                |
| EC       | EMC             | 0               | 100             |                |
| EC       | EMC             | 10              | 90              |                |
| EC       | EMC             | 20              | 80              |                |
| EC       | EMC             | 30              | 70              |                |
high conductivity is not necessary, a higher salt concentration will ensure that a catastrophic drop in conductivity will not occur from either salt consumption or concentration gradients that form during cycling.

Conductivity calculations from the AEM are shown in Figures 5 and 6 as solid lines. The AEM is able to capture the trends in conductivity for low-EC and EC-free electrolytes. The average disagreement between AEM and experiment over all temperatures, salt concentrations, and solvent compositions is 11.1%. Unlike with the viscosity results, the AEM’s conductivity calculations do not deviate further from experiment at high LiPF6 concentration. The average deviations from experiment at 0.5 m, 1.0 m, 1.5 m, and 2.0 m are 18.5%, 9.1%, 4.8%, and 9.3%, respectively. In most cases the location of the conductivity maxima are well predicted. The largest deviation from experiment is seen for the case of 0.5 m LiPF6 in DMC, so a big contribution to the overall disagreement comes from situations with low salt content and low dielectric solvents. For low permittivity systems under conditions of low salt concentration there is a profound change in the permittivity landscape as the salt concentration is increased, and subtle changes in solution permittivity can make a relatively large change in free ion populations (starting from practically zero) and in the small values of conductivity. These trends are captured by the AEM, which can further be used to diagnose behavior of ion association in low-permittivity electrolytes.

Walden plots.—In previous publications, it has been shown that a simple model for conductivity can be derived assuming that the drag force on migrating ions in the electrolyte obeys Stokes’ law. The resulting expression for conductivity is

$$\sigma = \sum z_i^2 \frac{F e c_i}{6\pi \eta r_i},$$  \[1\]

where $c_i$, $z_i$, and $r_i$ denote the concentration, charge, and Stokes radius of ionic species $i$, respectively, and $\eta$ is the dynamic viscosity of the electrolyte. $F$ and $e$ are Faraday’s constant and the elementary charge, respectively. The Stokes radius represents the effective solvated radius of ionic species $i$ under faradaic transport conditions. Assuming that a 1:1-salt is used (e.g. LiPF6), Equation 1 can be simplified somewhat

$$\sigma = \frac{F e c_\pm}{6\pi \eta} \left( \frac{1}{r_+} + \frac{1}{r_-} \right)$$  \[2\]

Here, $r_+$ and $r_-$ represent the Stokes radii of the Li$^+$ and PF6$^-$ ions, respectively. Both $r_+$ and $r_-$ will be close in magnitude, but not equal (see Figure 9, explained below). The new variable $c_\pm$ is the concentration of positive or negative ions in the solution, taking advantage of the fact that the concentrations of positive and negative ions should be the same, not accounting for higher order charged structures such as triple ions or ionic clusters. Simplifying the expression for conductivity

Table VIII. Ionic conductivity at 20°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF6.

| Solvents | Weight % solvent | LiPF6 concentration (mol/kg) |
|----------|-----------------|-------------------------------|
|          | 1 | 2 | 1 | 2 | 0.5 | 1.0 | 1.5 | 2.0 |
| EC DMC  | 0 | 100 | 2.53 | 7.17 | 8.78 | 9.20 |
| EC DMC  | 10 | 90 | 5.90 | 9.24 | 10.21 | 9.15 |
| EC DMC  | 20 | 80 | 8.22 | 10.80 | 10.46 | 8.98 |
| EC DMC  | 30 | 70 | 9.38 | 11.14 | 10.60 | 9.38 |
| EC EMC  | 0 | 100 | 1.42 | 4.00 | 4.90 | 4.96 |
| EC EMC  | 10 | 90 | 3.59 | 5.89 | 6.55 | 5.90 |
| EC EMC  | 20 | 80 | 4.94 | 7.22 | 7.54 | 5.83 |
| EC EMC  | 30 | 70 | 6.84 | 7.94 | 7.10 | 6.17 |

Table IX. Ionic conductivity at 30°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF6.

| Solvents | Weight % solvent | LiPF6 concentration (mol/kg) |
|----------|-----------------|-------------------------------|
|          | 1 | 2 | 1 | 2 | 0.5 | 1.0 | 1.5 | 2.0 |
| EC DMC  | 0 | 100 | 2.70 | 7.92 | 10.15 | 10.71 |
| EC DMC  | 10 | 90 | 6.71 | 10.53 | 12.00 | 11.20 |
| EC DMC  | 20 | 80 | 9.03 | 12.09 | 12.37 | 10.93 |
| EC DMC  | 30 | 70 | 10.89 | 13.25 | 12.90 | 11.80 |
| EC EMC  | 0 | 100 | 1.52 | 4.45 | 5.58 | 5.72 |
| EC EMC  | 10 | 90 | 3.59 | 5.89 | 6.55 | 5.90 |
| EC EMC  | 20 | 80 | 4.94 | 7.22 | 7.54 | 5.83 |
| EC EMC  | 30 | 70 | 6.84 | 7.94 | 7.10 | 6.17 |

Table X. Ionic conductivity at 30°C for EC:EMC and EC:DMC-based electrolytes for different concentrations of LiPF6.

| Solvents | Weight % solvent | LiPF6 concentration (mol/kg) |
|----------|-----------------|-------------------------------|
|          | 1 | 2 | 1 | 2 | 0.5 | 1.0 | 1.5 | 2.0 |
| EC DMC  | 0 | 100 | 2.85 | 8.59 | 10.90 | 11.95 |
| EC DMC  | 10 | 90 | 6.71 | 10.53 | 12.00 | 11.20 |
| EC DMC  | 20 | 80 | 9.03 | 12.09 | 12.37 | 10.93 |
| EC DMC  | 30 | 70 | 10.89 | 13.25 | 12.90 | 11.80 |
| EC EMC  | 0 | 100 | 1.61 | 4.86 | 6.18 | 6.36 |
| EC EMC  | 10 | 90 | 3.59 | 5.89 | 6.55 | 5.90 |
| EC EMC  | 20 | 80 | 4.94 | 7.22 | 7.54 | 5.83 |
| EC EMC  | 30 | 70 | 6.84 | 7.94 | 7.10 | 6.17 |
Equation 2 becomes
\[ \sigma = \frac{F e c}{3 \pi \eta R} \]  \[ \text{[3]} \]
which is the harmonic mean of the Stokes radii of the cation and anion. Equation 2 becomes

\[ \sigma = \frac{F e c}{3 \pi \eta R} \]  \[ \text{[3]} \]

Now, dividing both sides of Equation 3 by the molar concentration of salt added, \( c \) (not to be confused with \( \epsilon_{\infty} \)),

\[ \frac{\sigma}{c} = \frac{F e c \epsilon_{\infty}}{3 \pi \eta R} \]  \[ \text{[4]} \]

\[ \Lambda \eta = \frac{K f}{R} \]  \[ \text{[5]} \]

In Equation 5, \( K = \frac{\epsilon_{\infty}}{2} \) is a constant, \( \Lambda \) is the molar conductivity, and \( f = c \epsilon_{\infty}/c \) is defined to be the molar ratio of ionic species to salt species. For a fully dissociated electrolyte, \( f = 1 \), again not taking triple ions or other larger charged structures into account. Taking the logarithm of Equation 5, an expression is obtained that resembles the empirical Walden Rule

\[ \log \Lambda = \log \frac{K f}{R} + \log 1/\eta. \]  \[ \text{[6]} \]

Walden plots have been used extensively to evaluate the ionicity (i.e., the degree of dissociation) of ionic liquids.\textsuperscript{37–43} Less frequently, Walden analysis has been applied to non-aqueous electrolytes.\textsuperscript{44,45} Figure 7 shows log \( \Lambda \) versus log \( 1/\eta \) for electrolytes previously presented in Figures 3–6. LiPF\(_6\) concentrations of 0.5 m, 1.0 m, and 2.0 m are shown, all at 20 °C. Solid lines are drawn between data points of related solvent composition for a given LiPF\(_6\) concentration. Different symbol types specify unique solvent compositions. The dashed line is a linear fit to all points with 30% EC by weight in the solvent mixture.

Figure 7. Walden plot for the different electrolyte systems considered in this work for different concentrations of LiPF\(_6\). All data shown are at 20 °C. Solid lines are used to connect electrolytes of related composition. Different solvent mixtures are specified by plotting symbol. The dashed line is a linear fit to all points with 30% EC by weight (open and closed rhombi symbols). In a previous work it was shown that electrolytes with solvent systems composed of 30% EC and different ratios of EMC, DMC, and methyl acetate (MA) had roughly the same ionicity and Stokes' radius independent of LiPF\(_6\) concentration and temperature.\textsuperscript{28} Therefore, the dashed line in Figure 7 specifies a region in the Walden plot of constant ionicity and Stokes radius. Deviations from this line are indicative of a variation of one or both quantities. As EC is removed from the electrolyte, the points move further away from the line of constant ionicity. This move is most dramatic at lower concentrations of LiPF\(_6\) (0.5 m), where the molar conductivity drops by almost an order of magnitude between the 30% EC and EC-free electrolytes. Referring to Equation 6, this drop represents a quantity of conductivity that is “lost” by changing the ratio of solvents involved. Under circumstances where the ionicity and Stokes radius of the electrolyte are stable over different solvent compositions, a decrease in viscosity (or increase in fluidity \( \phi \), where \( \phi = \eta^{-1} \)) should correspond to an increase in molar conductivity. However, as has been discussed regarding Figures 5 and 6, replacing EC with low-dielectric solvents leads to significantly more ion pairing, which in turn dramatically lowers the conductivity due to the resulting lower populations of ionic species, even though the viscosity is decreased (Figures 3 and 4). Electrolytes with low dielectric constants fall well below the expected conductivity due to the increase in ion association, and possibly also a change in Stokes' radius. The Walden plot explicitly illustrates how the composition of EC in the electrolyte impacts the resultant conductivity of the electrolyte, and can act as a guide to explain the lower conductivity in low-EC electrolytes.

Figures 8 shows Walden plots using data calculated from the AEM for (a) EC:EMC-based and (b) EC:DMC-based electrolytes. The “ideal” KCl line with a slope of 1 and a y-intercept of 0 is shown in both (a) and (b) as a solid line for reference. Traditionally, this line has been used in Walden plots to specify a region on the plot where the salt is fully dissociated. \textsuperscript{39,42,53} For electrolytes containing high concentrations of EC in the solvent blend (>20% by wt), the Walden rule is obeyed. These electrolytes have a slope of approximately 1 for a range of LiPF\(_6\) concentrations between 0 and 3 m. As the fraction of EC is decreased, the data from the AEM begin to deviate from the Walden rule at low concentrations of salt. As well, for all concentrations of LiPF\(_6\), as the fraction of EC is lowered, the data start to shift downwards, suggesting an overall lower ionicity in electrolytes with lower EC contents. For electrolytes containing solely EMC or
DMC ($x = 0$), the conductivity is extremely low at very low concentrations of salt (refer to Figs. 5a and 6a), which corresponds to a sharp deviation from ideal Walden behavior. As discussed above, this deviation can be attributed to a high degree of ion pairing at low LiPF$_6$ concentrations in low-dielectric solvents. As more LiPF$_6$ is added, the relative solution permittivity of the electrolyte increases sufficiently for more salt species to dissociate, and the Walden rule is again obeyed. These observations from the AEM agree with what has been seen experimentally in Figure 7.

From Equation 6, the drop in molar conductivity as EC is removed can be attributed either to a lower ionicity or an increased solvated ion size, or both. Without further information about the system, it is not possible to distinguish between a change in Stokes radius or a change in ionicity, according to Equation 6. As seen in Figures 5 and 6, and discussed above, low-EC electrolytes will experience a significant amount of ion pairing, especially at low concentrations of LiPF$_6$. However, it remains to be seen how much impact the solvated ion sizes will have on the resultant conductivity of these electrolytes. The AEM provides calculations of solvated diameters for both the cations and anions in the electrolyte solution. Figure 9 shows the solvated diameters of Li$^+$ and PF$_6^-$ as a function of EC concentration in an electrolyte containing the solvents EC and DMC, as calculated by the AEM. LiPF$_6$ concentrations of 0.5 m, 1.0 m and 2.0 m are shown. The solvated diameters of both ions decrease as more salt is added. This is due to increased competition for solvent molecules when more salt is present. However, for a given concentration of LiPF$_6$, the solvated diameters are relatively unchanged as a function of EC content. This observation is explained as follows: if the molecular volumes of different solvents are about the same and they have the same core moieties (e.g., carbonates), then the effective solvated diameter around lithium will be similar, but also may differ due to solvent configuration to an ion. The high surface charge density of the small lithium ion helps drive this general outcome. Lastly, based on the development in Eqs. 1–6 we would expect that placement of data on a Walden plot will depend somewhat on the solvated ion sizes. Although the size attributes in Fig. 9 do not show significant change over EC content and modest decrease over salt concentration, it is the extent of ion solvation past the bare ion baseline that partially contributes to the offset of the data from the ideal KCl line. Note that for aqueous KCl the constituent K$^+$ and Cl$^-$ are sparingly solvated such that their effective transport diameters are close to the bare ion values.

Figures 10 shows AEM results for single ion (SI), ion pair (IP), and triple ion (TI) populations at 20°C (given as a mole fraction) as a function of EC content in electrolytes containing EC and DMC. The SI populations shown are the sum of individual Li$^+$ and PF$_6^-$ populations. LiPF$_6$ concentrations of (a) 0.5 m, (b) 1.0 m, and (c) 2.0 m are shown.

The electrolyte with a solvent mixture of EC and DMC. The SI populations presented here are the sum of individual Li$^+$ and PF$_6^-$ populations. Overall, populations of triple ions are very low, making up no more than 2% of the total population of salt over all conditions considered. The AEM predicts a large percentage of ion pairs for electrolytes with low concentrations of EC. In the most extreme case, at 0.5 m LiPF$_6$ and 0% EC, the mole fraction of ion pairs in the electrolyte is 0.902. The population of ion pairs becomes insignificant as EC is added. The AEM calculations in Figures 9 and 10 suggest that ion association is the primary reason for the drop in conductivity in low EC electrolytes seen in Figures 7 and 8. The change in the Stokes radii of the ions in solution has little or no impact on the conductivity as a function of EC content.

**EC:DMC:LiPF$_6$ phase diagram.**—Considerable progress has been made toward understanding the phase diagrams of electrolyte solutions containing Li salts such as LiFSI, Li bis(trifluoromethyl)sulfone)imide (LiTFSI), Li bis(perfluoroethanesulfonyl)imide (LiBETI), Li perchlorate (LiClO$_4$), Li tetrafluoroborate (LiBF$_4$), Li difluoro(oxalato)borate (LiDFOB), and Li bis(perfluoroethanesulfonyl)imide (LiBETI). These salts have been studied in solvents such as acetonitrile (AN) and dimethoxyethane.
Figure 11. Differential thermal analysis (DTA) spectra for electrolytes containing solvent mixtures EC:DMC x:(100-x) (wt. %) with LiPF₆ concentrations (a) 0 m and (b) 1.0 m. The spectra are shifted for clarity. For the three component system in panel (b), three distinct features are identified in the spectrum and are labelled for the EC:DMC 20:80 case.

Figure 12. Phase diagrams for the EC:DMC:LiPF₆ system for (a) 0 m LiPF₆, and (b) 1.0 m LiPF₆. Results for the salt-free system are compared to differential scanning calorimetry (DSC) results reproduced from Ref. 33. In panel (b) the three parts of the phase diagram reflect the three distinct features identified in Figure 11.

However, the liquid-solid equilibria of LiPF₆ in carbonate solvents have not been considered in such detail. Recently, Xiong et al. determined the phase diagram of the DMC:LiPF₆ system using differential thermal analysis (DTA). Here, differential DTA was used to investigate the phase behavior of the ternary EC:DMC:LiPF₆ system. The phase equilibria of the salt-free system has been well-studied by Ding et al., and Ding et al. showed results for LiPF₆-containing solutions for a single composition of EC:EMC. Okumura and Horiba demonstrated melting point depression when LiPF₆ is added to the single solvent systems EC, EMC, and DMC, but two-solvent systems such as EC:DMC were not considered. Figure 11 shows the raw DTA spectra for EC:DMC solutions with (a) 0 m, and (b) 1.0 m LiPF₆ added. Converted to a weight percent, the 1.0 m electrolytes in panel (b) correspond to 15.2% LiPF₆. The curves in Figure 11a are typical of a binary eutectic system. The pure DMC curve shows a single peak corresponding to the melting point of DMC. As EC is added, a second feature emerges. For the EC:DMC 10:90 and 20:80 samples, solid DMC exists alongside liquid between the solidus and liquidus peaks. The composition EC:DMC 30:70 is close to the eutectic point of the system, so only a single feature is observed. The ternary system in Figure 11b is much less simple. For solvent compositions away from the binary eutectic point (i.e. EC:DMC 10:90 and EC:DMC 20:80), a third feature emerges between the solidus and liquidus peaks. These three features are labeled for the EC:DMC 20:80 + 1 m LiPF₆ DTA spectrum in Figure 11b. At this time it is unclear what this third feature represents, but it could involve the presence of solid solvates. A more complete study of the EC:DMC:LiPF₆ system is underway, which should help to elucidate the physical meaning of this feature.

Figure 12 shows partial phase diagrams for the ternary EC:DMC:LiPF₆ system for (a) 0 m LiPF₆, and (b) 1.0 m LiPF₆, plotted as a function of the weight percent of EC in the solution. In Figure 12a, results from Ref. 33 are also given for comparison. The three sections of the phase diagram in Figure 12b correspond to the three features of the DTA spectrum as labelled in Figure 11b. The phase diagram for the salt free system in Figure 12a agrees well with the results of Ding et al. The solidus line occurs slightly lower in the phase diagram in this work, but the melting point of pure DMC and the EC:DMC eutectic point as determined here agree quite well with the data from Ref. 33. In both the salt-free and 1.0 m LiPF₆ cases, the addition of EC depresses the liquidus point. In both cases the liquidus point drops by nearly 10°C between solvent compositions with 0% EC and 30% EC. The addition of LiPF₆ to the system further depresses the liquidus line in the phase diagram at compositions with low-EC content. This agrees with the results of Okumura and Horiba for single solvent systems. For solutions close to the binary eutectic for the EC:DMC system (&lt;30% EC), the difference in the liquidus point between Figures 12a and 12b is minimal. It should be of interest to obtain phase diagrams for a wider range of LiPF₆ concentrations. During operation of a Li-ion cell, high currents can cause gradients in the Li salt concentration in the cell, which will lead to local variations in the phase behavior of the electrolyte. The high melting point of DMC is particularly worrying. For all combinations studied here, the liquidus line of the phase diagram is above -10°C. Even for the salt-containing solutions, solid precipitates will exist at temperatures below this point. Today, many commercial cells use electrolyte formulations with high concentrations of DMC. Commercial cells opened in this lab have been found to have electrolytes with solvent compositions containing up to 80% DMC. Ambient temperatures of -10°C or below are extremely common in the winter months in many locations around the world. Operation of Li-ion batteries in EVs or other larger-scale applications may become difficult in these climates when high-DMC cells are used. One solution may be to add a ternary or even quaternary solvent to the electrolyte. It has been shown in previous studies that electrolytes containing ternary or quaternary mixtures of carbonates can operate well at low temperature.
cells, respectively. Figures 13c and 13d show voltage hysteresis versus cycle number for NMC442/graphite, and single crystal NMC532/graphite cells. The NMC442 cells were charged between 2.8 and 4.4 V at a rate of C/2.5 for both charge and discharge. The NMC 532 cells were cycled between 4 and 4.4 V at a rate of C/2. Both types of cells had a cycle at C/20 every 50 cycles. Different electrolyte solvent compositions are shown. For all the cells the electrolyte contains 1 M LiPF6. Two identical cells were made for each unique electrolyte and electrode combination. In panels (b) and (d), only every 10th cycle is displayed.

electrolytes in the future development of Li-ion cells, especially for automotive or grid-scale energy storage applications.

Charge-discharge cycling data.—Ma et al. found that adding up to 5% of an enabling compound to EC-free electrolytes significantly improves high voltage cycling of Li-ion cells.4 These enabling compounds form passivating solid electrolyte interphase (SEI) layers on the surface of the graphite negative electrode. Since EC has good SEI-forming properties as well, its suitability as an enabler was tested in a previous work.1 However, it was found that it did not perform nearly as well as other enabler candidates.1,4 One of the best enablers for EC-free electrolytes was found to be fluoroethylene carbonate (FEC). Figures 13a and 13b show normalized capacity as a function of cycle number for NMC442/graphite, and single crystal NMC532/graphite cells, respectively. Figures 13c and 13d show voltage hysteresis versus cycle number for NMC442/graphite, and NMC532/graphite cells, respectively. The NMC442 cells were charged/discharged at a rate of C/2.5, and the NMC532 cells were charged and discharged at C/2. Three different solvent formulations were considered: EC:EMC 30:70 (wt. %), FEC:EMC 5:95 (wt. %), and pure EMC. Each electrolyte containing 1 M LiPF6. No additional electrolyte additives were used in these cells. Two cells were made for each electrolyte composition to test for reproducibility. Figures 13b and 13d only show NMC532 cells with the FEC:EMC 5:95 electrolyte. The cycles with higher normalized capacity and lower voltage hysteresis correspond to the C/20 cycles, as labeled in Figure 13. In Figure 13a, the capacity fade is comparable for cells with electrolytes containing EC:EMC 30:70 and EMC. For these cells, about 10% of their original capacity is lost after less than 100 cycles. This is reproducible for the pair of cells for each type. The cells containing the electrolyte with FEC:EMC 5:95 perform much better at high voltage. Very little capacity fade is seen after over 500 cycles. In Figure 13c, cells containing solvents EC:EMC 30:70 and EMC show much higher impedance growth than the cells with FEC:EMC 5:95. For the NMC532 cells, almost 85% of the original capacity is retained after 3000 cycles, as seen in Figure 13b. There is some impedance growth in these cells, however it is comparable to the NMC442 cells after just 500 cycles. EC-free electrolytes can cycle extremely well at high voltage, and the addition of FEC or other film-forming enablers is crucial for long-term operation of cells with EC-free electrolytes. The impact of FEC on the transport properties of EC-free electrolytes was not studied here. However, Reference 51 gives a good evaluation of the conductivity of FEC:EMC 5:95 and FEC:EMC 10:90 electrolytes. Due to FEC’s high dielectric constant, it gives a boost to the electrolyte’s conductivity much like EC, but without the adverse effects on cycling performance at high voltage.

Conclusions

The transport properties of low-EC and EC-free carbonate-based Li electrolytes were considered. Ionic conductivity and viscosity were measured for electrolytes containing solvent blends EC:EMC x:(100-x) and EC:DMC x:(100-x) (wt. %) with a range of LiPF6 concentrations. Electrolytes with lower EC contents had lower viscosities, as expected. As well, low-EC electrolytes had lower maximum conductivities, with the maximum occurring at higher LiPF6 concentrations. Extremely low conductivity seen at low LiPF6 concentration is due to significant ion pairing. Calculations from the Advanced Electrolyte Model (AEM) agree well with experimental data, with challenging cases noted in viscosity predictions for electrolytes with DMC or EMC as the sole solvent. Walden plots prove to be useful tools to describe the lower conductivity due to ion pairing in low-dielectric electrolytes. AEM results confirmed that the contribution of solvated ion size to the change in conductivity in low-EC electrolytes is minimal.

The phase behavior of electrolytes composed of the solvents EC and DMC was presented. A phase diagram was constructed for systems containing LiPF6, which has been largely absent from the literature. The liquidus transition for high DMC systems containing salt is lower than the corresponding salt-free system, but it is still high enough to cause concern for low temperature applications. More work needs to be done to fully understand the ternary EC:DMC:LiPF6 phase diagram.

Cycling data for NMC442/graphite and single crystal NMC532/graphite cells charged to 4.4 V showed that cells containing FEC:EMC 5:95 electrolytes can cycle well at high voltage, with very little capacity fade after many cycles. The best performing electrolyte containing 5% of the film-forming enabler fluoroethylene carbonate (FEC). NMC442 Cells containing EMC:FEC 95:5 showed less capacity fade and lower impedance growth over ~500 cycles than cells containing EC and cells without the enabler. NMC532 cells retained 85% of their original capacity after 3000 cycles, with comparable impedance growth to the NMC442 cells. The cycling data suggests that linear carbonates such as EMC and DMC have higher oxidative stability than cyclic carbonates EC or PC. However, it is presently not known why the linear carbonates are more stable at high voltage. More work should be done to elucidate the reason for the high-voltage stability of linear carbonates.

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