On the Study of Electrolyte Solutions for Li-Ion Batteries That Can Work Over a Wide Temperature Range

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Based on previous data and an understanding of possible reactions with electrodes, we selected five electrolyte solutions as promising components for Li-ion batteries that can operate down to $-40°C$, consisting of solutions of $LiPF_6$ or LiTFSI electrolytes in optimized ternary carbonate solvent mixtures and quaternary solvent mixtures containing esters, both with and without vinylene carbonate and LiBOB salt as additives. The main criteria for selecting these solutions were a specific conductivity ≥ 1 mS/cm at $-40°C$ and the ability to work well with a wide variety of electrode materials (for example, transition metal oxides and phospho-olivine cathodes, lithiated titanium oxide and carbon anodes) over a temperature range of -40 to $+60°C$. As a first step in the selection of battery materials for operation at low temperatures, we focused our work on the negative electrodes and tested three types of graphite electrodes with these electrolyte solutions. In general, practical graphite electrodes can work reasonably well only at temperatures above $-20°C$. A limited improvement of their low temperature performance can be achieved by increasing the surface area (i.e., decreasing the particle size) of the active material at the expense of high initial irreversible capacity.
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Electrolyte solutions are key components in electrochemical devices, especially when the electrodes comprise highly reactive materials. The choice of the electrolyte solution is critical for both the performance and the safety of lithium-ion batteries. Relevant families of polar aprotic solvents for Li-ion batteries are ethers, esters, alkyl carbonates, nitriles, and sulfones.[1] Recently, there have also been attempts to introduce ionic liquids as components into electrolyte solutions for Li-ion and metallic lithium batteries.[2] The main solvents relevant for Li-ion batteries and their structural formulae are shown in Fig. 1, and the physical properties that are important in their selection for Li-ion battery electrolytes are summarized in Table I[3-6] for the most commonly used among them.

Figure 2 displays a general picture of the electrochemical windows of the main relevant families of solvents for Li batteries. It is clear that the anodic and cathodic stabilities of solvents are antagonistic properties. Solvents with high anodic stability (e.g., alkyl carbonates) include atoms in a high oxidation state, meaning that their reduction potentials will also be high. The intrinsic electrochemical windows of these solvents can be measured with noble metal (Pt, Au) and glassy carbon electrodes using tetrabutyl ammonium salt solutions (Bu_4NX, the anions X^- being BF_4^-, ClO_4^-, etc.).[7] The reduction of this cation to butene, butane, and tributyl amine occurs at very low potentials, around 0 V vs Li/Li$^+$, and therefore the cathodic reactions of the solvents themselves can be well studied. When the cation in the electrolyte solution is Li$^+$, the thermodynamics of their reduction processes are different from those of Bu_4NX solutions. They can be reduced at higher potentials and, in many cases, the reduction products are insoluble Li salts. These precipitate on the electrodes (lithium metal, lithiated carbon, nonactive metals polarized to low potentials) as surface films (see Fig. 2, lower chart) and usually passivate them. Hence, cyclic voltammograms of noble metal electrodes in most polar aprotic Li salt solutions are characterized by a first cycle irreversible cathodic wave that decays in subsequent cycles.[7]

The first generations of rechargeable lithium batteries (during 1985–1995) included a metallic Li anode and used electrolyte solutions based on cyclic ether solvents.[8-10] The 1990s saw the emergence of the Li-ion battery technology. The replacement of metallic lithium anodes by lithiated graphite and the introduction of 4 V cathode materials ($LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, etc.) required solvents with high anodic stability that do not cointercalate with Li$^+$ ions into graphite, as is the case with ether solvents.[11] Mixtures of

alkyl carbonate solvents in which ethylene carbonate (EC) is a critical component were found to be appropriate for Li-ion batteries.[12,13] The $LiPF_6$ salt was found to be an appropriate Li salt based on a compromise of properties for Li-ion battery technology due to the following reasons. (1) Its solutions with alkyl carbonates have a high room temperature (RT) specific conductivity up to 10 mS/cm. (2) The anodic stability of the PF_6^- anion is very high (>5 V vs Li). (3) Aluminum electrodes become highly passivated in $LiPF_6$ solutions, even at potentials higher than 5 V (vs Li/Li$^+$), probably due to the formation of surface species such as AlF_3 on the aluminum in these solutions.

The apparent metastability of metallic lithium and lithiated graphite electrodes in many polar aprotic solvents is due to the effective passivation phenomena occurring in such systems, as already discussed in details.[12-18]

The highest anodic stability of electrolyte solutions based on alkyl carbonate solvents is achieved in ethylene carbonate–dimethyl carbonate (EC–DMC) mixtures.[19] It is also fortunate that graphite electrodes develop excellent passivation in EC–DMC/ $LiPF_6$ solutions and demonstrate a very good cycle life. However, low temperature performance represents a significant challenge for Li-ion battery electrolyte solutions. Li-ion batteries for automotive transportation applications must function at a wide temperature range. A reasonable, practical low temperature limit for hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) batteries is $-30°C$. However, Li-ion batteries may be required to work even at $-40°C$, especially in military applications. Thereby, when examining low temperature performance of Li-ion batteries components, a reasonable lower limit is $-40°C$. While EC–DMC solutions have a wide electrochemical stability window and good cycle life at room temperature, they cannot operate below $-20°C$. Main reasons for that are the solidification of the EC component in the binary solvent systems and the fact that the solution becomes more ordered at too low temperatures, what worsens the ions separation in solution and the ions' mobility.[20] In order to achieve high ionic conductivity at very low temperatures, the electrolyte solutions must contain three or four solvents. As the electrolyte solutions contain more components, they are less ordered even at the low temperatures and EC can be maintained as a liquid component at low temperatures as well.[13,20-22] However, the electrochemical performance in terms of anodic stability, the high temperature stability, and electrodes' passivation may be negatively affected when the electrolyte solution contains more components in addition to EC, DMC, and $LiPF_6$. The aim of the present work was to select electrolyte solutions for advanced Li-ion batteries that can function over a wide temperature range, from -40 to $+60°C$, and to test the performance of three types of graphite electrodes with these solutions. Preliminary studies

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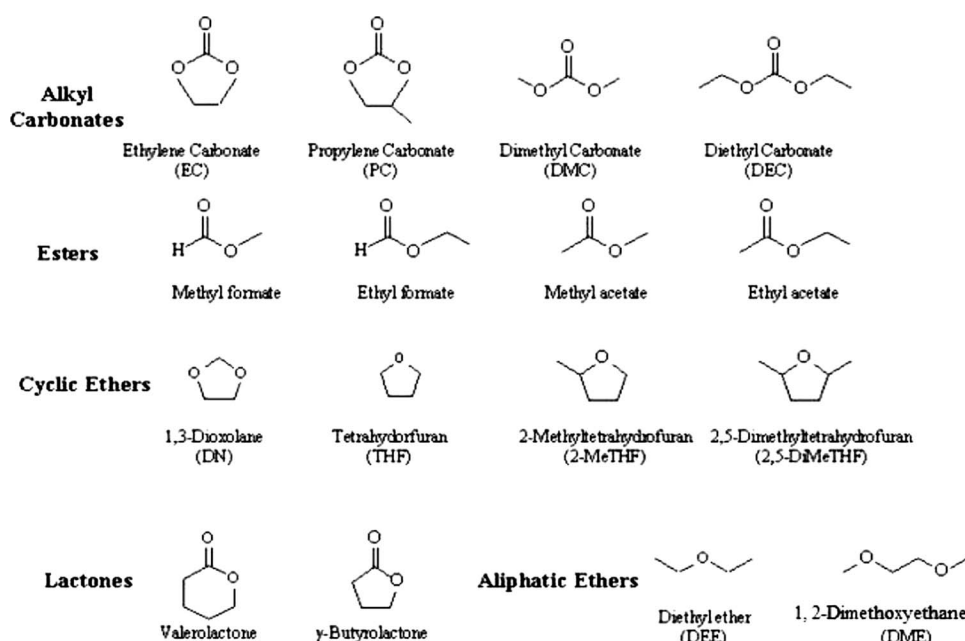** Electrochemical Society Active Member.
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Figure 1. Families of polar aprotic solvents relevant for Li-ion batteries, with examples and chemical structures for each class.

were carried out with $Li_4Ti_5O_{12}$ anodes, $LiFePO_4$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, (NCA) and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ (NMC) cathodes (not reported in detail herein). Despite the extensive work described in the literature on nonaqueous solutions studied at various temperatures, so far, nobody explored so many systems in a very wide temperature domain in a single study, as was carried out in the present work. Therefore, this paper provides a very reliable comparison among different systems and a comprehensive mapping of temperature dependent behavior of electrodes and solutions which are important to the field of Li-ion batteries. It should be noted that the temperature performance of a battery system is very complicated and does not depend on the behavior of a single component (e.g., kinetic limitation at low temperatures may result from interfacial impedance or activation controlled solid state diffusion rather than due to solution conductivity). Moreover, the low temperature performance of a battery system may depend on the history of the battery, namely, on its previous exposure to elevated temperatures. Nevertheless, in order to obtain a realistic picture, it is important to examine first the temperature behavior of individual components. Also, first criteria for the selection of electrolyte solutions for Li ion batteries that have to work in a wide temperature domain are: reasonable conductivity at very low temperatures and good performance of selected (important) electrodes in these solutions at both high and low temperatures. The work described herein was carried out in light of the above understanding.

Experimental

We have used lithium battery grade alkyl carbonate solvents (EC; DMC; ethylmethyl carbonate, EMC; diethyl carbonate, DEC) from Ube, Japan. γ-butyrolactone and ethyl butyrate (EB) were obtained from Aldrich (at the highest purity available for these solvents from this company). $LiPF_6$ was obtained from the Stella Chemifa Corporation (Osaka, Japan), $LiBF_4$ was obtained from the Hashimoto Chemical Corporation (Osaka, Japan), LiTFSI (LiN $(SO_2CF_3)_2$) was obtained from 3M, and LiBOB was obtained from Chemmetal. Vinylene carbonate (VC) was obtained from Ube. All the material used in our research are Li-battery grade (i.e., all possible contaminants at the parts per million (ppm) level). Therefore, all these chemicals could be used as received and the solvent mixtures contained 5–7 ppm of water. Electrolyte solutions were prepared under highly pure argon (99.999%) inside M. Braun glove boxes.

Graphite materials were obtained from Conoco Philips (G5, Ash <100 ppm, carbon content >99.9%), Timcal (Timrex SLP30 Graphite Ac-162, moisture 0.5% maximum, Ash 0.1% maximum carbon content 99.9%), and Kansai (NG15, natural flakes, carbon >99.9%). Typical SEM images are shown in Fig. 3, and their surface area and particle size are listed in Table II. The SEM images were obtained using a scanning electron microscope, model Inspect from FEI. The specific surface area of the graphitic materials was obtained from the N_2 adsorption measurements at its normal boiling

Table I. Physical properties of solvents of interest, relevant for the formulation of electrolyte solutions.[3-6]

| Solvent	Melting point, °C	Boiling point, °C	Viscosity at 25°C, cP	Density at 25°C g/cm³	Relative permittivity εr (25°C)
EMC	−53	110	0.648	1.0063	2.96
DEC	−73.3	126	0.75	0.9690	2.81
DMC	4.6	91	0.589	1.0632	3.11
PC	−48.8	242	2.53	1.2	64.9
EC	36	248	1.93	1.32	95
Acetonitrile	−48.8	81.6	0.341	0.7768	35.9
Sulfolane	28.4	287.3	10.3 (30°C)	1.262 (30°C)	43.3 (30°C)
Gamma butyrolactone (γ-BL)	−43.1	204.8	1.73	1.99	39
EB	−93	120	0.71	0.879	5.19 (20°C)
VC	22	165	N/A	1.54	N/A
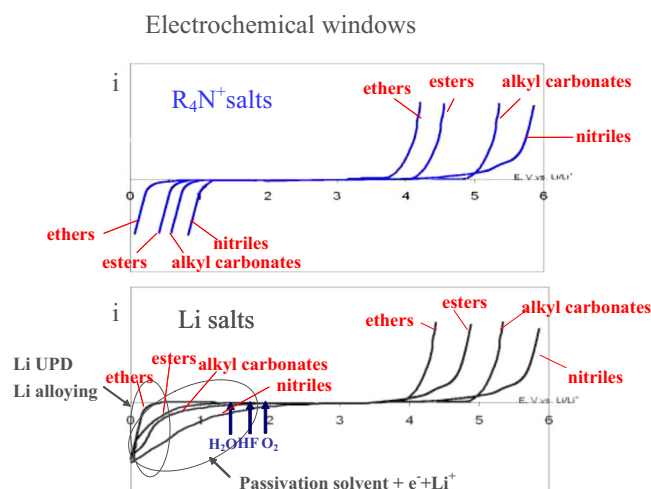
Figure 2. (Color online) Schematic representation of the electrochemical windows for various families of polar aprotic solutions with tetra butyl ammonium and lithium salts shown in the upper and lower panel, respectively (see for instance Ref. 7 as an experimental background).

Table II. BET surface areas and the particle sizes for the graphite materials in the present study.

Supplier	Product ID	BET surface area[a] m^2/g	Particle size, μm	
			Product specification[a]	In-plane size/ thickness[b]
Kansai	NG15	7.9	15	>11/0.4
Conoco Philips	G-5	1.8–3	8–13	~8/0.2
Timcal	SPL-30	8	32	~6/0.15

[a] Company data.
[b] SEM images.

point using equipment from Micromeritics (Gemini 2375 analyzer) and the commonly applied Brunauer–Emmett–Teller (BET) model. It should be noted that it was impossible to predict the relative surface areas of the various graphitic materials used herein from the SEM images. Only the gas adsorption measurements could provide a precise estimation of the surface area of these graphitic materials. $Li_4Ti_5O_{12}$ was obtained from NEI Inc. (USA), $LiFePO_4$ was obtained from Sud Chemie Inc. (Germany), and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ were obtained from Toda, Inc. (Japan).

Conductivity measurements on the electrolyte solutions were carried out a temperature range of −40 to + 60°C in a programmable refrigeration/oven system from MRC, model LC-40V, using a Metrohm 712 conductometer and a Metrohm AG 9101 conductivity cell. Electrochemical measurements of graphite–Li metal half cells were carried out using an Arbin model BT 2000 computerized multichannel battery cycler. We used coin-type cells with standard 2325 parts from NRC Canada. The composite graphite or lithiated transition metal electrodes included 80% active mass, 10% polyvinylidene di fluoride (PVdF) (Aldrich, Cat. # 182702) binder, and 10% carbon black on a copper foil (Strem Chemical, 99.9% pure)
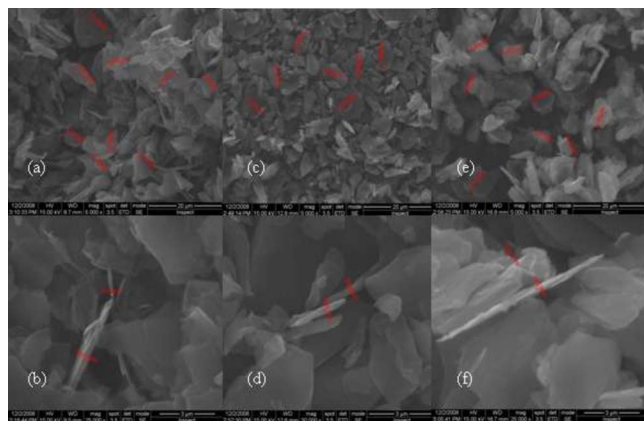
current collector. These electrodes were prepared by spreading a slurry of the above three components in N-methyl-pyrrolidone on the copper foil (doctor blade), followed by pressing and drying in a vacuum oven (100°C, 10^2 mm Hg). The coin-type cells were assembled with disk-shaped composite graphite electrodes, metallic lithium disk counter electrodes, and a porous polypropylene separator (Celgard 3501, 25 μm thickness, 55% porosity) soaked with the selected electrolyte solutions. We used an excess of the electrolyte solution, and before all the experiments the cells were given enough time to allow the complete wetting of the electrode coatings by the electrolyte solution. The cells were further sealed with epoxy resin around their gaskets (on top of the coin cell) in order to ensure a thermetic isolation of the active components from atmospheric contaminants. In a typical set of experiments, measurements were first performed on the cells at 30°C (galvanostatic cycling between 1.5 and 0.01 V potential limits), at a current density corresponding to a C/20 h rate, during several dozens of cycles, after which the temperature was lowered to −40°C in steps of 10°C. At each temperature step, the cells were measured electrochemically after equilibration. The cooling rate was adjusted according to the ease of equilibration: from 30 to − 10°C, the cooling rate was around 0.3°C/min and from −10 to − 40°C, the cooling rate was 1°C/min. The equilibration time at each temperature was about 10 min. After being cycled at −40°C, the electrodes were cycled again at 30°C. The heating rate from −40 to 30°C was around 0.2°C/min, and the equilibration time before measurements at 30°C was 30 min. In separate experiments, cells comprising the same components were measured at 60°C in order to confirm that solutions that are suitable for working at −40°C also work well at elevated temperatures.

Results and Discussion

Selection of electrolyte solutions for operation over a wide temperature range.— In recent years, several groups have investigated and proposed electrolyte solutions for Li-ion batteries that can function at very low temperatures.[13,20-22] The main concern of most of such studies performed to date was the specific conductivity of the electrolyte solutions. It became clear that only multicomponent systems comprising three of four different solvents can reach a reasonably high specific conductivity at very low temperatures. However, when selecting such combinations, one must keep in mind that practical batteries must also function at elevated temperatures (> 40°C). In Li-ion batteries there is no thermodynamic equilibrium between the electrolyte solution and the electrodes. Lithiated graphite anodes, as well as most of the lithiated and delithiated transition metal oxide cathodes, react with most of the relevant electrolyte solutions. These systems can function only because they can reach metastability maintained by unique and highly complicated passivation phenomena. We have found that most types of graphite electrodes develop very stable passivation in EC–DMC-based electrolyte solutions and can be cycled even at a temperature of 80°C (Ref. 23) because of the surface chemistry they develop therein: fast reduction of alkyl carbonates to $ROCO_2Li$, $ROLi$, RLi, and polymeric species at potentials below 1.5 V (vs Li/Li$^+$) forms a solid

Figure 3. (Color online) SEM images of the different types of graphite materials used in our study: NG-15 (a: 20 μm scale) and (b: 3 μm scale); G-5 (c: 20 μm scale) and (d: 3 μm scale); and SLP-30 (e, 20 μm scale) and (f, 3 μm scale). The size and thickness of the particles are indicated in red. The scale bars appears in the bottom right side of each image (20 μm for the upper images and 3 μm for the lower images).

Table III. Selected electrolyte solutions that were proposed in the literature for low temperature operation of Li-ion batteries.

No.	Composition (solvent and salt)	Temperature range, °C	Reference
1	EC:DMC:DEC (1:1:1); LiPF$_6$ 1 M	−40 to +25	22
2	EC:DEC:DMC:MA (or EA, EP, EB) (1:1:1:1); LiPF$_6$ 0.64 M	−60 to +25	6[a]
3	EC:DEC:DMC:PC (3:3:3:1); LiPF$_6$ 0.9 M	To −30	19[b]
4	EC:DEC:DMC:EMC (3:5:4:1); LiPF$_6$ 0.8 M	To −42.5	19[c]
5	PC:EC (0.4:0.6; 0.7:0.3); Et$_4$NBF$_4$, Et$_4$NPF$_4$, LiPF$_6$, LiBF$_4$, LiBOB (0.5 to 2.5) molal	−40 to +60	23[b]
6	PC:EC:EMC (1:1:3); LiPF$_6$ 1 M	−60 to +60	24[b]
7	PC:EC:EMC (1:1:3); LiBOB, LiODFB, LiBF$_4$ 1 M	−50 to +25	25[b]
8	EC:DMC:EMC (15:37:48); LiTFSI 0.7 M to 1.1 M	−40 to +70	20
9	EC:DEC:DMC:GBL (1:1:1:1); LiPF$_6$ 1 M	−60 to +25	21[a]
10	EC:DMC:EMC (1:1:1); LiPF$_6$ 1 M	−40 to +40	26
11	PC:EC:EMC, (1 − x) LiBF$_4$ × LiBOB	−40 to +40	27

EA = ethyl acetate, EP = ethyl propionate, MF = methyl formate, MA = methyl acetate, Et$_4$NBF$_4$ = tetraethylammonium tetrafluoroborate, Et$_4$NPF$_6$ = tetraethylammonium hexafluorophosphate, LiODFB = lithium oxalyldifluoroborate, x = 0, 0.1, 0.5, 1 m (molal).

[a] It appears that lithium salt solutions based on mixtures of alkyl carbonates and esters can provide a good low-temperature ionic conductivity. Note that, based on the experience of the authors of this paper, the performance of graphite electrodes in ester-based solutions is poor.

[b] While PC is a desirable component for good low-temperature conductivity, it is also a well-known destructive solvent for graphite electrodes.

[c] In the same reference, several combinations of the four solvents were suggested and tested.

electrolyte interphase sufficiently quickly on the graphite particles, which prevents exfoliation/cracking due to the massive reduction of the solution species within their bulk.[15,19-21] Note that the development of good passivation on lithiated electrodes depends on a very delicate balance among several surface reactions. Hence, adding more components to an EC–DMC solution may change the surface chemistry and, as a consequence, worsen the passivation and performance of graphite electrodes.

Table III displays a partial list of the ternary and quaternary solvent-based electrolyte solutions that were suggested in recent years as appropriate for use with graphite electrodes, in terms of low temperature performance. (Note the comments associated with this table).[6,20-29] Conductivity data as a function of temperature for selected mixed solvent electrolyte solutions are shown in Fig. 4. It can be seen from Fig. 4 that binary EC–DMC solutions have a conductivity that is too low at temperatures lower than −20°C and that ternary or quaternary solutions that comprise several linear alkyl carbonates have a much better low temperature conductivity. As

Figure 4. (Color online) The temperature dependence of the specific conductivity for 10 electrolyte solutions (indicated by different colors). Conductivity values (in mS/cm) measured at −40°C and at +60°C for each solution are listed, respectively, on the left- and right-hand sides of the graphs. As indicated in the figure, for two solutions the highest temperatures are +50°C and +55°C, and for one solution the lowest temperature is −29°C.

measured in this work (not shown in Fig. 4), LiClO$_4$ solutions have a lower conductivity than LiPF$_6$ or LiTFSI solutions containing similar solvent mixtures. Solutions in which LiBOB is the main component also have a low conductivity at low temperatures, as measured herein. However, it was found that multicomponent solutions with LiPF$_6$ or LiTFSI as the main electrolyte have the best ionic conductivity over a wide temperature range (down to −40°C), as can be seen in Fig. 4. Since the high conductivity of lithium salt solutions at very low temperatures requires the use of components such as esters or DEC, i.e., solvents that are detrimental for the stability of graphite electrodes,[3,24] it is important to include additives that can enhance the passivation of graphite electrodes in electrolyte solutions designed for operation at low temperatures. Moreover, esters and DEC also worsen the anodic stability of electrolyte solutions for Li-ion batteries (relative to the EC–DMC binary solvent mixture) because the ethyl group is a better electron donor than the methyl group in DMC, and the oxidation state of the central carbon in esters is lower compared to that of the central carbon in alkyl carbonates (+3 vs +4). Hence, when selecting additives for the multicomponent solvent solutions, one must also take into account the cathode side and the need for enhancing the anodic stability of these systems.

We have found previously that VC is a bifunctional polymerizable additive, through the double bond and the carbonate groups, that on one hand enhances the passivation and stability of graphite electrodes and on the other hand improves the anodic stability of alkyl carbonate solutions with several types of cathode materials due to the passivation phenomena that are induced by its oxidation.[29] Similarly, several groups have demonstrated that LiBOB is an excellent passivating agent for graphite electrodes in a wide variety of solutions.[30-32] In addition, we have found that nonaqueous LiBOB solutions provide a good passivation for aluminum,[33] which is used as a current collector for cathodes in Li-ion batteries. We have therefore chosen VC and LiBOB as desirable additives for the lithium electrolyte solutions for our present study. We examined the influence of their presence on the specific conductivity of selected multicomponent solutions over a wide temperature range and found that the effect of 1% VC or 0.1 M LiBOB on the temperature dependence conductivity of multicomponent LiPF$_6$ and LiTFSI solutions is negligible and nearly zero at the very low temperatures. Hence, these two additives can indeed be used, in the stated concentrations, without having a significantly detrimental effect on the ionic conductivity of the solutions at low temperatures.

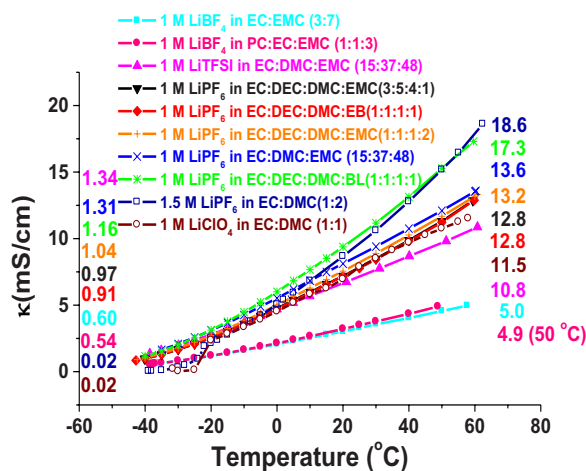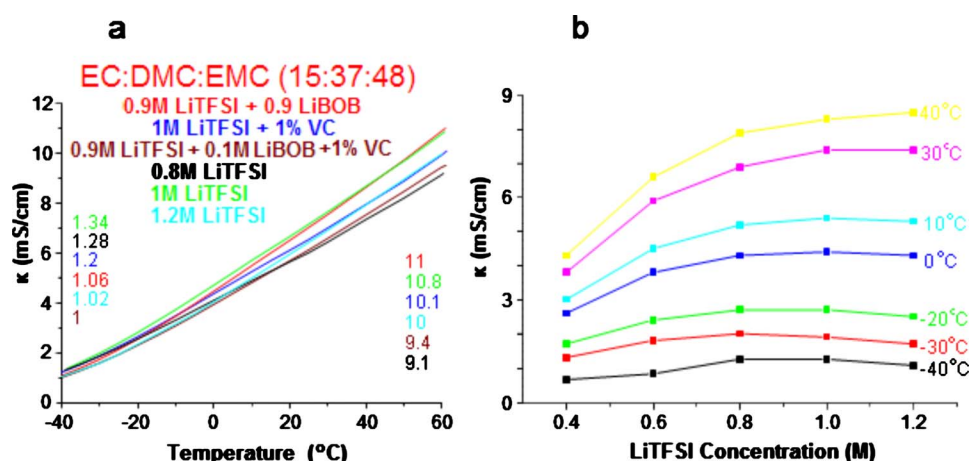From the variety of solutions for which we have measured the

Figure 5. (Color online) (a) Temperature dependence of the conductivity for solutions based on LiTFSI as the main salt and the EC-DMC:EMC (15:48:37) solvent mixture, with and without LiBOB and VC as additives. The numbers on the left- and right-hand sides of the graph represent, respectively, the conductivity at −40°C and +60°C. (b) The dependence of the conductivity of solutions comprising the same ternary solvent mixture, on the molar concentration of LiTFSI in solutions and temperature.

specific conductivity in the framework of this work (see Fig. 4), we have selected solutions for further studies, based on the following two criteria:

1. an ionic conductivity greater than 1 mS/cm at −40°C;
2. expectations for a reasonable performance at elevated temperatures with electrode materials (anodes and cathodes) commonly used in Li-ion batteries.

These expectations emerged from our previous studies of passivation phenomena of Li, graphite, and LiMO$_2$ (M = Co, Ni, Mn) electrodes.[7,9,10,12,15,16,18,19,34,35] For instance, the passivation of Li or Li–graphite electrodes in ester solvents and DEC are much worse than that in EC-DMC, propylene carbonate (PC) or EMC solutions. In turn, graphite electrodes are not stable in solutions containing too high concentration of PC. Also, the anodic stability of EC and DMC seems to be the highest among the alkyl carbonate solvents and higher compared to that of ester solvents. Thereby, it was logical to use EC–DMC as the basic system to which a third component or two more solvent components were added. A most desirable third component is EMC because of its similarity to DMC (provided that a sufficiently high conductivity could be achieved at low temperatures).

Another factor that determines the conductivity is the concentration of the main electrolyte in the solution. We expect a parabolic type of behavior of the conductivity versus electrolyte concentration.[36] The solution conductivity increases initially monotonically with the electrolyte concentration. However, beyond a certain concentration, strong ionic interactions in the solution will slow down the dynamics of ion transport, and hence the conductivity will decrease at high electrolyte concentrations. We have attempted to optimize the concentration of the main electrolyte in the electrolyte solutions from the present study, and Fig. 5 provides a typical example of these optimization efforts related to LiTFSI solutions in EC–DMC–EMC mixtures that contain VC and LiBOB, as indicated in the figure. In fact, the optimal concentration of salt for maximizing the solutions' conductivity depends on the temperature, and apparently it would make sense to have different optimal electrolyte concentration at low and high temperatures. However, the theme of this work was to select solutions that work well at a wide range of temperatures (−40 to 60°C), thereby a single salt concentration was used herein. For both LiTFSI and LiPF$_6$ solutions, the optimized electrolyte concentration for a wide range of temperatures is approximately 1 M (see Fig. 5b). We have therefore selected ten solutions, each having a total electrolyte concentration of 1 M, for investigating the behavior of the Li-ion battery anode and cathode materials over a wide range of temperatures. Table IV lists the components and the optimized concentrations, together with specific conductivity values at four temperatures (−40, −30, −20, and 30°C) for the ten electrolyte solutions. These solutions can be used in

Li-ion batteries that must function over a very wide temperature range (−40 to + 60°C) and should be compatible with a large variety of electrodes materials.

The electrochemical stability windows of the selected electrolyte solutions.— An obvious and critical stage in the investigation of electrolyte solutions for any electrochemical application is the study of their potential windows. General aspects of the electrochemical stability windows of polar aprotic systems and their measurements were described in the Introduction. We chose platinum electrodes for this study. Lithium ions undergo pronounced under-potential deposition (UPD), and alloying processes with platinum start at potentials smaller than 0.8 V vs Li/Li$^+$.[35] In the presence of Li$^+$ ions, the onset of the reduction of trace oxygen and water on Pt and Au electrodes in alkyl carbonate/ester solutions is around 2 and 1.5 V (vs Li/Li$^+$), respectively. Solvent reduction occurs below 1.5 V.[36] All of these reduction processes form passivating surface films.[15] Figure 6 displays repeated cyclic voltammograms measured with Pt electrodes in the selected electrolyte solutions. Note that all these experiments were performed with an excess of solution, so the ratio between the electrode surface area and the solution volume was several orders of magnitude larger than that encountered in practical battery systems or even in laboratory coin-type cells. Therefore, the effect of any contaminants that may exist in solutions at ppm levels can be very influential on the measurements of the electrochemical window that we report on here. The voltammetric responses of Pt electrodes in the selected solutions differ significantly from each other. When the electrolyte is LiPF$_6$, the first cycle voltammograms are characterized by a very pronounced irreversible cathode wave whose peak is located near 1.8 V (vs Li/Li$^+$). This peak corresponds to the reduction of trace HF, PF$_5$ and PF$_3$O, which are always unavoidably present in LiPF$_6$ solutions. This assignment is based on our measurements of LiPF$_6$ solutions with different HF or trace water contaminations; potentiodynamic behavior (e.g., by cyclic voltammetry) always demonstrated as pronounced dependence of the cathodic wave around 1.8 V on the contamination level. For solvent mixture containing only alkyl carbonates, passivation of the electrodes is reached within the first voltammetric cycle, after which an electrochemical window around 5 V is obtained. When the LiPF$_6$ solutions also contain an ester component (Ethyl butyrate (EB) or Gama butyrolactone (GBL) in the present study), full passivation of the electrodes is achieved during three consecutive cycles. As expected, the presence of ester components in the solution interferes with the formation of effective passivating surface films that may be formed by the reduction of alkyl carbonates in the presence of Li$^+$ ions on the electrodes. However, after electrode passivation is reached, the electrochemical window of all LiPF$_6$ solutions is around 5 V. The ester component does not appear to increase the anodic reactions of the multicomponents solutions that we have examined. As can be seen in the charts of Fig. 6, the electrochemical

Table IV. Compositions of the 10 selected lithium electrolyte solutions in the present study and their specific ionic conductivities at several temperatures.

Electrolyte solution		Conductivity at 30°C, mS/cm	Conductivity at −20°C, mS/cm	Conductivity at −30°C, mS/cm	Conductivity at −40°C, mS/cm
Salt	Solvent				
1 M LiPF$_6$	EC:DMC:EMC 1:25:32	8.5	2.9	2	1.2
1 M LiTFSI	EC:DMC:EMC 1:25:32	7	2.6	1.9	1.2
0.9 M LiTFSI + 0.1 M LiBOB	EC:DMC:EMC 15:37:48	6.6	2.3	1.6	1
1 M LiPF$_6$	EC:DEC:DMC:BL 1:1:1:1	10	2.85	1.8	1.1
1 M LiPF$_6$	EC:DEC:DMC:EB 1:1:1:1	8.6	2.6	1.7	1
1 M LiPF$_6$ + 1% VC	EC:DMC:EMC 15:37:48	8.5	2.9	2.0	1.2
1 M LiTFSI + 1% VC	EC:DMC:EMC 15:37:48	7.0	2.6	1.9	1.2
1 M LiPF$_6$ + 1% VC	EC:DEC:DMC:GBL 1:1:1:1	10.0	2.9	1.8	1.1
1 M LiPF$_6$ + 1% VC	EC:DEC:DMC:EB 1:1:1:1	8.6	2.6	1.7	1.0
0.9 M LiTFSI + 0.1 M LiBOB + 1% VC	EC:DMC:EMC 15:37:48	6.6	2.3	1.6	1.0

window of LiTFSI solutions is smaller than that of LiPF$_6$ solutions. This may be attributed to a lower anodic stability of the TFSI anion compared to that of PF$_6^-$. Also, we found that in LiPF$_6$ solutions, there is a passivation of all electrodes at high enough potentials, including inert ones such as Pt, due to adsorption of fluoride anions, what mitigate possible electro-oxidation of the solvents at high posi-

tive potentials (this requires further work for a solid proof). However, since there is no HF or PF$_5$ contamination and the main relevant contaminant may be trace water (up to 20 ppm), the typical voltammetric behavior of platinum electrodes immersed in solutions of lithium salt in polar aprotic solvents is well reflected, including Li UPD processes below 0.8 V, stripping peaks (of the Li deposited by the UPD process) around 1.1 V, peaks related to the reduction of trace water, and adsorption–desorption of hydrogen (1.5–2 V).[34,35] When the solution contains LiBOB, its electrochemical window is even smaller, since the BOB anion is oxidized around 4.5 V. It should, however, be noted that BOB oxidation leads to passivation phenomena. Therefore, Al electrodes can be effectively passivated in LiBOB solutions, even at potentials >5 V and at elevated temperatures.

In conclusion, it can be stated that the multicomponents solutions based on LiPF$_6$ electrolytes have, after electrode passivation by cathodic reactions, an electrochemical window of about 5 V, while similar LiTFSI solutions have a smaller electrochemical window (4.5 V). Therefore, the multicomponent solutions with LiPF$_6$ electrolytes suggested herein may be suitable for high voltage cathodes (up to 5 V).

The behavior of graphite electrodes in the five selected electrolyte solutions.— In order to investigate the behavior of graphite electrodes we chose three types of graphitic materials differing in morphology and surface area (see Fig. 3 and Table II). Figure 7 displays the results of a typical experiment in which electrodes comprising SLP-30 graphite as the active mass were cycled in one of the selected solutions, EC–DMC–EMC 1 M LiTFSI + 1% VC (denoted as solution B). It shows the capacity upon discharge (delithiation) and charge (lithiation) versus cycle number at different temperatures and the current density corresponding to a C/20 h rate. The cells were allowed to adjust to each new temperature at open circuit voltage (OCV) in the discharged (delithiated) state. In a successful experiment, a difference between the charge (lithiation) and discharge (delithiation) capacities is observed only during the first cycle, after which the charge and discharge capacities were the same throughout the entire experiment. In addition, at the end of the experiment, when the temperature is returned again to 30°C, the measured capacity should be the same as the capacity measured initially at 30°C from the second cycle onward.
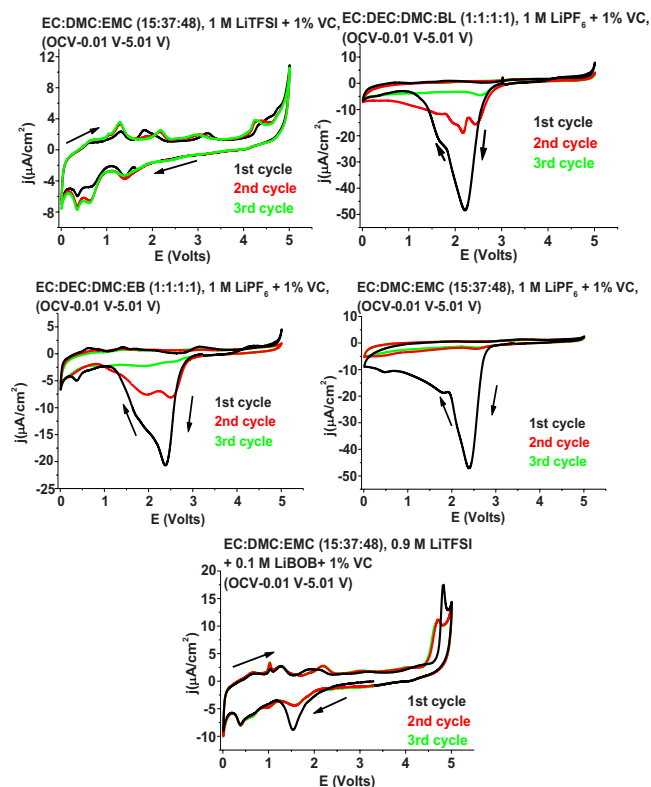

Figure 6. (Color online) The first three consecutive voltammograms measured with Pt electrodes in five selected electrolyte solutions; +30°C temperature, 20 mV/sec potential scan rate.
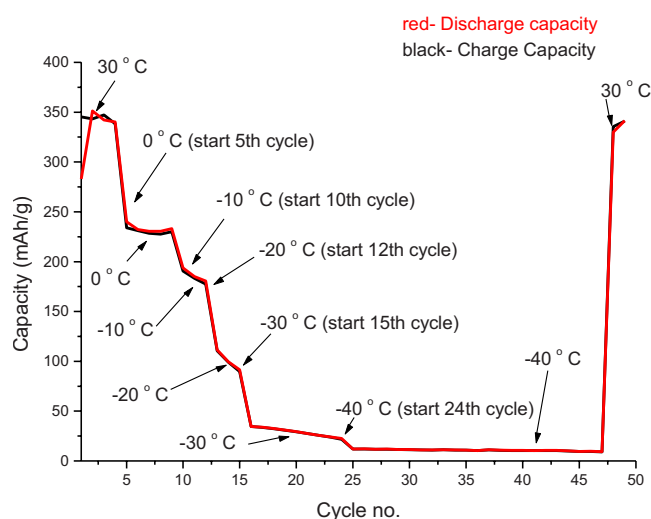
Figure 7. (Color online) A typical graph of capacity vs cycle number at various temperatures for SLP-30 graphite electrodes in a EC:DMC:EMC (15:37:48) 1 M LiTFSI + 1% VC solution. The cells were cycled between the potential limits of 1.5 and 0.01 V at a current density corresponding to a C/20 h rate.

The initial irreversible capacity represents a very important parameter for graphite electrodes. This irreversible capacity should be relevant only during the first cycle for well-designed systems, and the stable capacity of graphitic materials at room temperature and above ($> 25°$C) should be approximately 350 mA h/g (i.e., no less than 94% of the theoretical capacity of 372 mA h/g), as was indeed obtained in all the experiments reported on herein. The irreversible capacity represents the capacity change during the first cycle, $\Delta Q_1 = Q_{1\ charge} - Q_{1\ discharge}$ (the difference between the charge and discharge capacities measured during the first cycle), expressed as a percentage of the stable reversible capacity $Q_{2\ discharge}$ (the capacity measured during the second cycle discharge), i.e., $100\ [Q_{1\ charge} - Q_{1\ discharge}]/Q_{2\ discharge}$.

Table V lists representative irreversible capacities obtained at 30°C with the three types of graphite electrodes in the selected electrolyte solutions, together with the capacities obtained using a 1 M LiPF$_6$ solution in the binary solvent EC–DMC as benchmarks. The specific surface area of the graphite particles is also listed here. The following trends become apparent from an examination of the data presented herein:

1. The irreversible capacity measured with the graphite electrodes used herein is higher than what is usually measured in prac-

tical cells. We attribute it to a higher solution/electrode's active mass ratio used in the present study, which leads to a pronounced effect of unavoidable contaminants such as trace water and HF (reduced irreversibly at low potentials).

2. As expected, electrodes comprising the G-5 graphite, which has the lowest surface area, have the lowest irreversible capacity.

3. The irreversible capacity measured with electrodes comprising SLP-30 graphite was higher than that measured with the electrodes comprising NG-15 graphite, even though both the materials have similar specific surface areas. This result correlates with the small particle size of the SLP-30 graphite, as obtained from SEM imaging (see Table II).

4. The highest irreversible capacity was obtained for all three graphite electrodes with a LiTFSI solution that also contained Li-BOB. The LiBOB salt is an excellent passivating agent for graphite because it reacts on its surface at relatively high potentials and the reaction products precipitate onto the graphite particles. The higher irreversible capacity is thus a reflection of the initial surface reactions of LiBOB.

5. In general, the differences in the irreversible capacity values obtained with the ten different solutions are not large, which means that adding a third alkyl carbonate component or a fourth ester component to an alkyl carbonate mixtures does not significantly affect the surface reactions on graphite. The irreversible capacity of graphite electrodes obtained in the multicomponent solutions is comparable with that obtained in binary EC–DMC solutions. This may indicate that the surface chemistry of graphite in all of these systems is dominated by the reduction of EC, which is the most cathodically reactive component in all of them. It should be noted that the values of the irreversible capacity obtained in this work are all too high for practical Li-ion battery systems, in which the tolerable irreversible capacity should be less than 10%. Nevertheless, the relative irreversible capacity values obtained herein are significant and appear to reflect the difference in the morphology of the graphite particles.

Figure 8 compares the representative capacities of the three types of graphite electrodes in five of the selected solutions as a function of temperature, and Fig. 9 compares the capacity of the same graphite electrodes measured at different temperatures in each of the remaining five electrolyte solutions. The results can be summarized as follows:

1. In general, graphite electrodes have a very low capacity at temperatures below −20°C in carbonate-based electrolyte solutions. Hence, Li-ion batteries comprising graphite electrodes and most (if not all) of relevant electrolyte solutions may not be practical for operation at very low temperatures.

2. The graphitic material with the highest surface area, SLP-30, which has the highest irreversible capacity, also provides the highest capacity at very low temperatures. An increase in the surface area of

Table V. Irreversible capacity (charge loss) for graphite from various sources, measured at room temperature (30°C) during the first charge in ternary and quaternary solvents mixed with LiPF$_6$ and LiTFSI salts. The effect of VC and LiBOB as additives is also shown. Data obtained with LiPF$_6$ solutions in the binary solvent mixture EC:DMC (electrolyte solutions K and L) are included as benchmarks. Electrolyte solutions IDs: (A) EC:DMC:EMC (1:25:32) 1 M LiPF$_6$; (B) EC:DMC:EMC (1:25:32) 1 M LiTFSI; (C) EC:DMC:EMC (17:37:48); 0.9 M LiTFSI + 0.1 M LiBOB; (D) EC:DEC:DMC:BL (1:1:1:1) 1 M LiPF$_6$; (E) EC:DEC:DMC:EB (1:1:1:1) 1 M LiPF$_6$; (F) EC:DMC:EMC 1 M LiPF$_6$ + 1% VC; (G) EC:DMC:EMC (17:38:45) 1 M LiTFSI + 1% VC; (H) EC:DMC:EMC (17:38:45) 0.9 M LiTFSI + 0.1 M LiBOB + 1% VC; (I) EC:DEC:DMC:EB (1:1:1:1) 1 M LiPF$_6$ + 1% VC; (J) EC:DEC:DMC:BL (1:1:1:1) 1 M LiPF$_6$ + 1% VC; (K) EC:DMC(1:1) 1 M LiPF$_6$; (L) EC:DMC(1:2) 1.5 M LiPF$_6$.

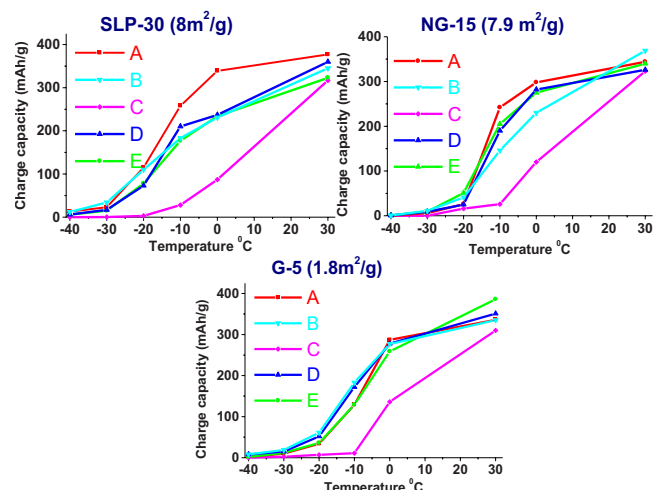| Graphite type | BET SSA m^2/g | First cycle irreversible capacity, % | | | | | | | | | | | |
		Electrolyte solution											
		A	B	C	D	E	F	G	H	I	J	K	L
NG-15	7.9	20	21	26	20	21	20	21	26	21	20	12	17
G-5	1.8–3	18	20	25	16	16	18	20	25	16	16	20	—
SLP-30	8	26	28	32	26	26	26	28	32	26	26	27	—

Figure 8. (Color online) Charge capacity of the three types of graphite electrodes used in various electrolyte solutions at several temperatures ranging from −40°C to + 30°C. The reversible capacity measured at 60°C is comparable to that measured at 30°C. The cells were cycled between the potential limits of 1.5 and 0.01 V at a current density corresponding to a C/20 h rate. Electrolyte solutions IDs: (A) EC:DMC:EMC (1:25:32) 1 M LiPF$_6$; (B) EC:DMC:EMC (1:25:32) 1 M LiTFSI; (C) EC:DMC:EMC (17:37:48); 0.9 M LiTFSI + 0.1 M LiBOB; (D) EC:DEC:DMC:BL (1:1:1:1) 1 M LiPF$_6$; (E) EC:DEC:DMC:EB (1:1:1:1) 1 M LiPF$_6$.
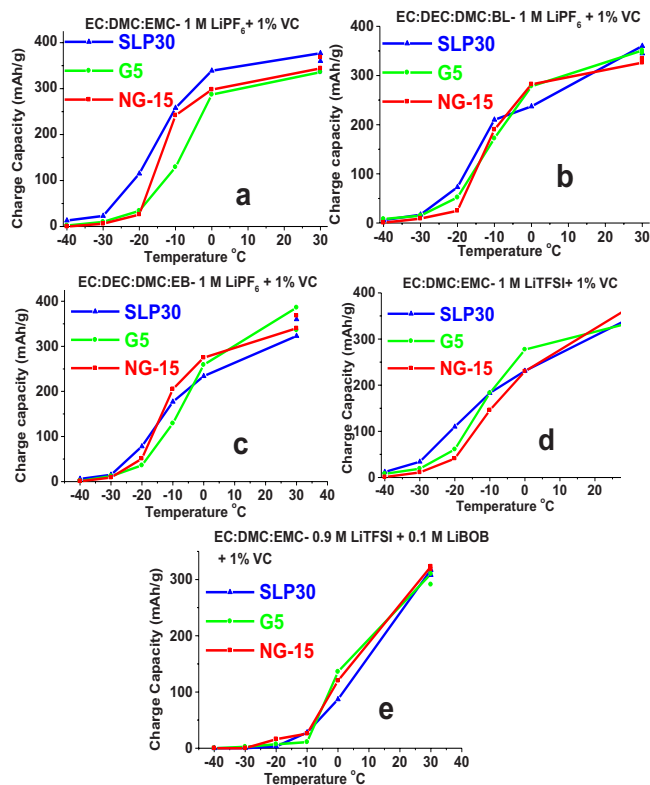

Figure 9. (Color online) Plots of capacity as a function of temperature for three different graphite materials (SLP-30, NG-15 and G-5, as indicated on each panel) in five electrolyte solutions: (a) EC:DMC:EMC (17:38:45) 1 M LiPF$_6$ + 1% VC; (b) EC:DEC:EMC:DMC:BL (1:1:1:1) 1 M LiPF$_6$ + 1% VC; (c) EC:DEC:DMC:EB (1:1:1:1) 1 M LiPF$_6$ + 1% VC; (d) EC:DMC:EMC (17:38:45) 1 M LiPF$_6$ + 1% VC; and (e) EC:DMC:EMC (17:38:45) 0.9 M LiTFSI + 0.1 M LiBOB + 1% VC. The reversible capacity measured at 60°C is comparable to that measured at 30°C.

the graphite particles compensates for the slowing down of the Li+ cation intercalation kinetics at low temperatures, resulting in a higher capacity.

3. The composition of the solutions has a strong influence on the temperature dependence of the capacity. This is related to the quality of the passivation of the graphite electrodes in the various solutions and to the transport properties of the passivating surface films that cover the graphite particles. Lithium cation desolvation, lithium cation migration through the surface films, and the interfacial charge transfer between the solution and the surface films, as well as between the surface films and the graphite material, all affect the overall lithium insertion–deinsertion kinetics into graphite.

The low temperature capacity of all graphite electrodes is lowest with the solution containing 0.1 M LiBOB. It is known that the BOB⁻ anion reacts on the graphite electrodes, and its reduction products have a pronounced influence on the surface films that are formed. The data from the present studies suggest that the surface species formed by LiBOB reduction are poor Li-ion conductors at low temperatures. The low temperature behavior of the graphite electrodes in the other four solutions is basically similar, and it is not possible to discern clear and consistent differences in the behavior of the three graphite electrodes in these solutions. These graphite electrodes were studied in the five electrolyte solutions at 60°C in half cells (vs Li CE). In the ternary solutions, EC–DMC and EMC containing VC or LiBOB as additives with either LiPF$_6$ or LiTFSI electrolyte (1 M), we could demonstrate a reversible and stable capacity around 350 mA h/g. When the cells were first measured at RT and then the temperature was raised to 60°C, the irreversible capacity measured in the first cycle at the elevated temperature was only a few percent of the reversible one. During a couple of cycles at the elevated temperature, the cycling efficiency reached nearly 100%. We found that both VC and LiBOB can be considered as a desirable additives for graphite electrodes that enhance their stable passivation and lead to a good performance in terms of the capacity retention upon prolonged cycling at 60°C.

Based on the present studies, it can be stated that graphite electrodes behave reasonably well over the temperature range of −10 to + 60°C in mixed solvent solutions of both LiPF$_6$ and

LiTFSI as the main electrolytes that contain EC and DMC as critical components and VC or LiBOB as a surface reactive additive (1% and 0.1 M, respectively). Once these electrolyte solutions contain EC, DMC, and VC, additional alkyl carbonate components such as EMC or ester components (which enable good ionic conductivity at very low temperatures) do not interfere in any significant fashion with the stable cycling behavior of graphite electrodes. However, it is clear that no graphite electrodes can be used as anodes in Li-ion batteries with an electrolyte solution having carbonates as major solvent components, operating at temperatures lower than −20°C.

On the behavior of other electrodes in the five selected electrolyte solutions (a brief discussion).— A detailed discussion on the behavior of electrodes other than graphite in the selected electrolyte solutions described herein is beyond the scope of this paper and will be presented later.[37] The most important point to be discussed herein is the performance of selected electrode materials at the extreme temperatures dealt with in this work, namely, −40 and 60°C. The layered cathodes that we measured, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$, cannot function well at −40°C in any of the five selected electrolyte solutions. Less than 10% (< 25 mA h/g) of their usual RT capacities could be obtained at the very low temperature at relatively slow rates (C/20). Both electrodes function very well and fully reversibly in EC–DMC–EMC/LiPF$_6$ solutions. When the salt is LiTFSI, the performance of NCA and NMC cathodes at 60°C in the alkyl carbonate solutions is poor due to the fact that the Al current collector used cannot reach effective passivation at potentials >4 V (vs Li) at elevated temperatures in these solutions. The Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$ electrodes demonstrated a prom-

ising performance at −40°C as more than 70% (> 100 mA h/g) of their usual RT capacities could be obtained at the very low temperature at C/20 rates in LiPF$_6$ and LiTFSI solutions of the ternary EC–DMC–EMC solvents mixtures used herein. Both electrodes function well (good capacity retention upon cycling) with these electrolyte solutions at 60°C. Hence, an important conclusion from this work is that Li-ion batteries comprising the electrodes couple Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$ and conventional electrolyte solutions containing LiPF$_6$ and EC/DMC/EMC mixtures can work well within a wide temperature range of −40 to 60°C.

Conclusions

Binary solutions based on EC–DMC LiPF$_6$, in which most of the lithium insertion electrodes (both anodes and cathodes) behave well at room temperature and at elevated temperatures (up to 60°C), cannot be used at temperatures lower than −20°C due to their drastic drop in conductivity. A reasonable high–low temperature conductivity (1−1.3 mS/cm at −40°C) can be obtained with solutions of LiPF$_6$ or LiTFSI in ternary carbonate solvent mixtures that contain, in addition to EC and DMC, a third alkyl carbonate solvent such as EMC or with quaternary solutions that contain an additional ester component (EB, GBL) besides a ternary mixture of carbonate solvents. VC is a desirable additive in all of these solutions due to its surface reactions on both negative and positive electrodes, which improves the passivation of the electrodes at elevated temperatures. Graphite electrodes behave well at elevated temperatures in all the previously described multicomponent, carbonate solvent-based solutions. However, at temperatures lower than −20°C, the kinetics of graphite electrodes is slow, and therefore they can no longer be considered practical. Therefore, binary solutions based on the EC–DMC binary are adequate for Li-ion batteries with graphite anodes. The operation of Li-ion batteries at temperatures lower −20°C requires the use of anode materials other than graphite in conjunction with electrolyte solutions in carbonate solvents. The next stages of the study address electrode materials (negative and positive) with which Li-ion batteries can be operated at very low temperatures (down to −40°C), using the ternary and quaternary solvent solutions from the present study. We found that Li-ion batteries comprising the electrodes couple Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$ and conventional electrolyte solutions containing LiPF$_6$ and EC/DMC/EMC mixtures can work well within a wide temperature range of −40 to 60°C, resulting in an impressive discharge and charging capacities at the very low temperatures and a very good capacity retention during prolonged cycling at the elevated temperatures.

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