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^{13}C NMR Spectroscopic, CV, and Conductivity Studies of Propylene Carbonate-Based Electrolytes Containing Various Lithium Salts

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The ion-solvent and ion-ion interactions, oxidative electrochemical stabilities, and ionic mobilities of a series of lithium salt electrolytes with commonly used electrolyte solvents, propylene carbonate (PC) and dimethyl carbonate (DMC), have been studied using ^{13}C nuclear magnetic resonance (NMR) spectroscopy, cyclic voltammetry (CV), and ionic conductivity measurements. The coordinating ability of PC toward lithium salts is significantly higher than that of DMC as shown by the relatively large deshielding of the carbonyl carbon of PC over that of DMC. We have also prepared a novel electrolyte, lithium tetrakis(trifluoromethanesulfonato)gallate [LiGa(OTf)$_4$], and investigated its relative binding to PC by ^{13}C NMR spectroscopy. The latter salt showed significant deshielding of the carbonyl carbon of PC compared to the other salts studied, including the conventional LiPF$_6$. However, its conductivity is not enhanced to the same extent and is comparable to that of LiBF$_4$. The CVs show their relative stabilities toward oxidation around 4.5 V and reduction close to lithium potentials. All electrolytes studied here have good electrochemical stability from 0.1 to 5.0 V *vs.* Li$^+$/Li, and are suitable for applications in lithium-ion cells.
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Lithium-ion batteries developed for commercial and aerospace applications most commonly employ nonaqueous electrolyte solutions consisting of lithium hexafluorophosphate, LiPF$_6$, dissolved in mixtures of cyclic and linear carbonates, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC).[1-10] Although LiPF$_6$-based electrolyte formulations generally provide highly conductive and electrochemically stable solutions, which lead to good cell performance, there is continued interest to identify alternate lithium electrolyte salts that possess greater high temperature resilience and are less expensive.[11-26] In addition to LiPF$_6$, the electrochemical properties of a number of lithium salts have been investigated within the context of nonaqueous lithium-based rechargeable batteries, including lithium perchlorate (LiClO$_4$),[11] lithium tetrafluoroborate (LiBF$_4$),[13,16] lithium hexafluoroarsenate (LiAsF$_6$), lithium triflate (LiOSO$_2$CF$_3$; LiOTf), lithium bis(trifluoromethanesulfonyl)imide [LiN(SO$_2$CF$_3$)$_2$; LiTFSI],[15] lithium bis(pentafluoroethanesulfonyl)imide [LiN(SO$_2$CF$_2$CF$_3$)$_2$; LiBETI], lithium trifluorotris(perfluoroethyl)phosphate [LiPF$_3$(CF$_2$CF$_3$)$_3$],[18] lithium bis(oxalato)borate [LiB(C$_2$O$_4$)$_2$],[19-21] lithium (malonato oxalato)borate [LiB(C$_3$O$_4$)$_2$],[23] lithium tris(trifluoromethanesulfonyl)methide [LiC(SO$_2$CF$_3$)$_3$],[24] as well as, a number of other fluoroalkyl sulfonate and imide salts.[25,26] To date, none of these electrolyte salts have supplanted the widespread use of LiPF$_6$ due to one or more shortcomings preventing their adoption, such as poor safety due to toxicity or explosion, high cost, poor electrochemical stability (including SEI forming characteristics), and/or low conductivity. In the present study, we have investigated a series of electrolyte salts: LiPF$_6$, LiBF$_4$, LiOSO$_2$CF$_3$, LiN(SO$_2$CF$_3$)$_2$, LiN(SO$_2$CF$_2$CF$_3$)$_2$, LiOSO$_2$C$_4$F$_9$, and LiGa(OSO$_2$CF$_3$)$_4$ [lithium tetrakis(trifluoromethanesulfonato)gallate, LiGa(OTf)$_4$], in an attempt to enhance our understanding of their relative coordinating ability with nonaqueous solvents.

Due to ion-ion and ion-solvent interactions, the conductivity of lithium-based nonaqueous electrolytes is dependent upon the nature of the solvents and type of lithium electrolyte salt employed.[27] In general, the higher the dielectric constant and coordinating ability of the solvent to lithium ions, the higher the resulting conductivity of the electrolyte. Desirable solvents possessing these attributes are often plagued by high viscosity, such as with PC and EC, so that low viscosity cosolvents are required to increase conductivity, especially at low temperatures. The lithium ion coordinating ability of solvents is dependent on their polarity, dielectric constant (or permittivity), and electron donating ability (the Lewis basicity). The relative strengths of various Lewis bases are often expressed by Gutmann's donor numbers, which are derived from the enthalpy of complexation of the solvents with a strong Lewis acid, SbCl$_5$.[28]

Nuclear magnetic resonance (NMR) techniques have been useful in probing the characteristics of the solvent coordination spheres surrounding solvated ions and degree of ion pairing. Matsubara and co-workers have performed ^{13}C NMR spectroscopy studies and have elucidated the coordination of the lithium ions to the carbonyl groups of the carbonate-based solvents.[29] They have estimated an average coordination number of four for the lithium ions in the mixed solvents which included esters, carbonates, and amides. Coordination of Li$^+$ ions in solvents such as PC and EC is achieved through the carbonyl groups, as reflected in the enhanced deshielding of the carbonyl carbons in the ^{13}C NMR spectra. By using gradient field NMR and conductivity studies it was shown that 1 M LiBF$_4$ is dissociated to an extent of 30% in PC solutions.[30] It was also shown that about 1.8 PC molecules are coordinated to each of the Li$^+$ ions at relatively high concentrations.[30]

It has been recently shown that the fluorine-19 chemical shifts, δ^{19}F, of the LiBF$_4$ solutions are correlated with the dielectric constants and dipole moments of the solvents.[31] As the polarities of the solvents, as indicated by their ε and μ (D) values, are increased the δ^{19}F of LiBF$_4$ are shifted to relatively lower fields. Thus, the δ^{19}F of LiBF$_4$ in PC (-151.8) is 0.49 ppm more deshielded than that of the corresponding solution in DMC (δ^{19}F $= -156.1$).

Salt dissociation and subsequent ion segregation are also dependent on the Lewis acidic nature of the anions. We have envisioned that the lithium salts derived from stronger conjugate acids should be relatively more dissociated in the carbonate solvents, as compared to those derived from the weaker conjugate acids. Thus, the

degree of ion-pairing (contact ion pairs *vs.* solvent-separated ion pairs) should be directly related to the strengths of the corresponding conjugate acids. Further, lowering the ion-pairing should improve the ion-conductivity of the salt. Here we report the results of ionic conductivity, cyclic voltammetry (CV), and ^{13}C NMR spectroscopic study of carbonate-based electrolytes involving a wide range of lithium salts, with differing Lewis acidities.

Experimental

Battery grade PC and DMC were obtained from Mitsubishi Chemicals, Inc. (less than 30 ppm water content), and used as received. All manipulations of the solvents and the electrolyte solutions were performed in an inert atmosphere dry box under argon. The ^{13}C NMR spectra were recorded for neat samples of the salt solutions on a Bruker 500 MHz instrument at 125 MHz, using internal acetone-d_6 capillary. The chemical shifts are referenced with respect to the carbonyl carbon of acetone-d_6 (δ^{13}C 206). The specific conductivities of the electrolyte solutions prepared were measured over the temperature range of -50 to $30°$C using a conductivity cell, which consists of two platinized platinum electrodes immobilized in a glass apparatus and separated by a fixed distance. The cell constant of the conductivity cell was determined using a standard 0.1 M KCl solution. A Tenney environmental chamber was used to maintain the desired temperature within $+1°$C for the cells. LiGa(OTf)$_4$ was prepared by the reaction of Ga(OTf)$_3$ with LiOTf (1:1 mol ratio) in anhydrous acetonitrile. Evaporation of the solvent gave LiGa(OTf)$_4$ as a colorless crystalline solid.

Results and Discussion

The most commonly used solvents for liquid or gel-polymer lithium-ion batteries are binary or ternary mixtures of EC, PC, DMC, DEC, and EMC. We have chosen a 1:1 solvent mixture (v/v %) of PC and DMC in our current ^{13}C NMR and ionic-conductivity studies of the electrolyte solutions. We have selected a number of commonly used lithium salts for our studies, including: (a) lithium triflate (LiOSO$_2$CF$_3$ or LiOTf), (b) lithium hexafluoro-phosphate (LiPF$_6$), (c) lithium bis(pentafluoroethanesulfonyl)imide [LiN(SO$_2$CF$_2$CF$_3$)$_2$, or LiBETI] (d) lithium bis(trifluoromethane-sulfonyl)imide [LiN(SO$_2$CF$_3$)$_2$ or LiTFSI], (e) lithium tetrafluoroborate (LiBF$_4$), and (f) lithium nonafluorobutanesulfonate (LiOSO$_2$C$_4$F$_9$). In addition, we have also prepared lithium tetrakis(trifluoromethanesulfonato)gallate [LiGa(OSO$_2$CF$_3$)$_4$ or LiGa(OTf)$_4$], by reaction of LiOTf with gallium triflate [Ga(OSO$_2$CF$_3$)$_3$ or Ga(OTf)$_3$].[32] The conjugate acid of LiGa(OTf)$_4$, HGa(OTf)$_4$ is expected to be a stronger acid than its boron analogue, HB(OTf)$_4$, which can be used in the generation of superelectrophilic species.[33] Thus LiGa(OTf)$_4$ salt is derived from one of the strongest superacids. Lithium triflate, similarly is derived from triflic acid, a superacid (H$_0$ = -14). LiBETI and LiTFSI are also derived from the corresponding sulfonic acids which have similar acidities as that of triflic acid. The conjugate acids of LiBF$_4$ and LiPF$_6$-HBF$_4$ and HPF$_6$-are expected to be strong superacids. Unfortunately, due to their complicated equilibria, their acidities could not be measured in nonaqueous systems.

^{13}C *NMR spectroscopic results.*—The ion-pairing effect of the lithium salts is expected to correlate with the acidity of their corresponding conjugate acids. Thus, the weaker the basicity of the anion the less the ion-pairing of the lithium salt. The basicity of the anion in turn depends on its polarizability and the delocalization of the charge. Based on earlier work, it should be possible to measure the relative ion-pairing (*i.e.*, contact ion pairs *vs.* solvent separated ion pairs) of the salts in the electrolytic media by using ^{13}C NMR spectroscopy.[29,34-37] The dielectric constant and dipole moment of PC (62.9 and 4.98, respectively) are significantly higher than that of DMC (3.17 and 1.06, respectively),[29] indicating that the lithium ions preferentially complex with PC over DMC. In addition, PC (donor number = 15.1) is anticipated to be a slightly stronger Lewis base

Table I. ^{13}C NMR Deshielding values ($\Delta\delta^{13}$C) of the carbonyl group of PC for various lithium salt supporting electrolytes.

Lithium salt in (0.1 M in PC/DMC (1:1 v/v))	($\Delta\delta^{13}$C)^a
LiGa(OTf)$_4$	0.29
LiOTf	0.13
LiPF$_6$	0.12
	0.68^b
LiN(SO$_2$CF$_2$CF$_3$)$_2$	0.12
LiN(SO$_2$CF$_3$)$_2$	0.12
LiBF$_4$	0.12
LiOSO$_2$C$_4$F$_9$	0.11

^{a} $\Delta\delta^{13}$C = [δ^{13}C PC/**1** – Li$^+$ – δ^{13}C PC].
^{b} 1.0 M in PC/DMC 1:1 v/v.

compared with linear aliphatic carbonates, such as DMC. We have indeed observed that in this binary solvent mixture, the δ^{13}C of the DMC carbonyl group is relatively unaffected (maximum shift up to 0.02 ppm for all the lithium salts studied), whereas the carbonyl carbon of PC is significantly deshielded (0.11 to 0.68 ppm; Table I and Fig. 1). We have also observed that the $\Delta\delta^{13}$C of the carbonyl carbon of PC is dependent on the concentration of the lithium salts. Thus, a 0.1 M solution of LiPF$_6$ showed a downfield shift of the carbonyl carbon ($\Delta\delta^{13}$C) by 0.12 ppm whereas in the presence of 1 M LiPF$_6$, the corresponding $\Delta\delta^{13}$C is 0.68. These results are in accordance with those of Matsubara and co-workers[29] and indicate

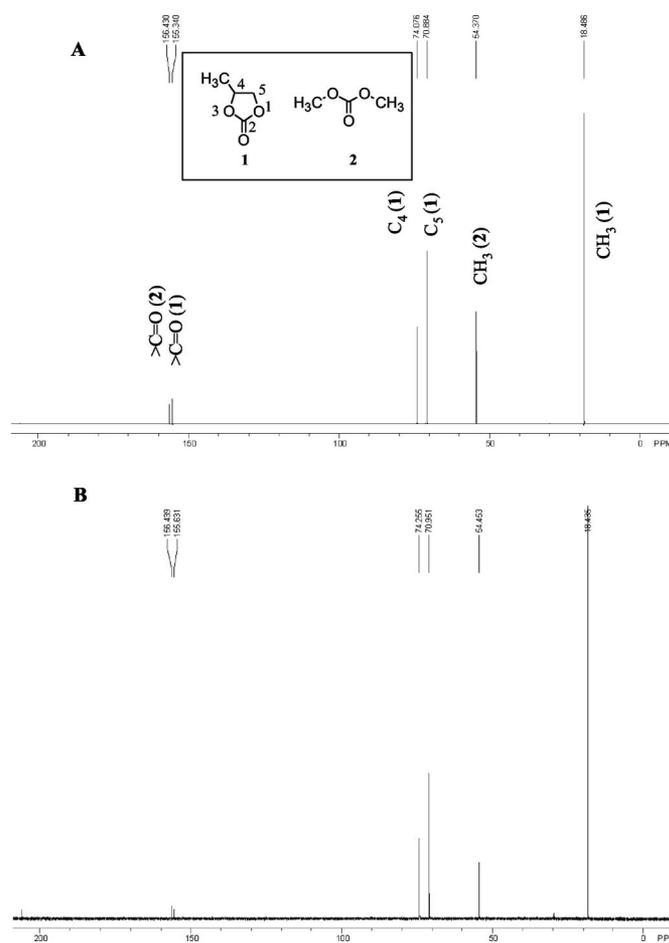**Figure 1.** ^{13}C NMR spectra of solutions of PC and DMC (1:1 v/v) in (A) the absence of added salt and (B) in the presence of 0.1 M LiGa(OTf)$_4$.

that rapid equilibration of lithium ions occurs between complexed and uncomplexed salts. The relatively small chemical shift differences observed in this study are as a result of low concentration of the lithium salts. The complexation of the lithium cation to the carbonyl oxygen was also demonstrated for PEO-based gel polymer

1-Li⁺
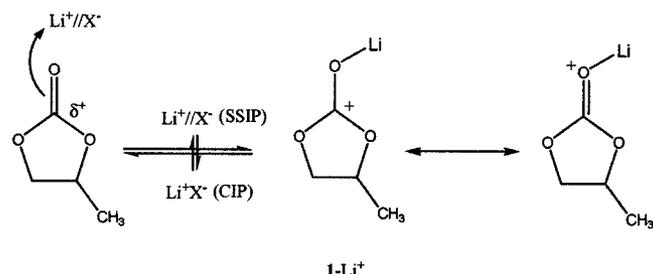
Scheme 1.

electrolytes (see Scheme 1).[36,37]

We have examined the ^{13}C NMR spectra of the PC/DMC solutions in the presence of the following lithium salts: $LiGa(OTf)_4$, LiOTf, $LiPF_6$, $LiN(SO_2CF_2CF_3)_2$, $LiN(SO_2CF_3)_2$, $LiBF_4$, and $LiOSO_2C_4F_9$. In the case of $LiGa(OTf)_4$, the carbonyl group of PC showed significantly deshielded absorption ($\Delta\delta^{13}C = 0.3$; Fig. 1). All of the other salts showed relatively smaller deshielded absorptions for the carbonyl group of PC ($\Delta\delta^{13}C = 0.1$; Table I). Unfortunately, due to the relatively small downfield shift for these salts, their relative ion-pairing effects could not be distinguished by ^{13}C NMR. However, the downfield shift of $LiGa(OTf)_4$ is distinctly higher than those of the others. These results show that the degree of ion-pairing in $LiGa(OTf)_4$ is relatively smaller as compared to the other salts which have similar ion-pair characteristics. This observation is also in accord with the expected superior superacidity of the corresponding conjugate acid $HGa(OTf)_4$.

Ionic conductivity results.—The ionic conductivities of these electrolytes were measured over a range of temperatures, as shown in Fig. 2 and summarized in Table II. When the results were compared at ambient temperature, the following trend was observed in decreasing specific conductivity: $LiPF_6$ > $LiN(SO_2CF_2CF_3)_2$ > $LiN(SO_2CF_3)_2$ > $LiGa(OTf)_4$ > LiOTf > $LiBF_4$ > $LiOSO_2C_4F_9$. At lower temperatures, this same trend is maintained, most likely due to the fact that viscosity effects contributed by the anion are minimized due to the low salt concentration (0.10 M). These results are in good agreement with the findings reported by other groups, in that the $LiPF_6$-based electrolyte yields the most highly conducting solution.[38] The ionic conductivity of the electrolyte containing $LiGa(OTf)_4$ is somewhat lower than the $LiPF_6$-based solution. However, it is comparable with those of the other salts, such as LiOTf and $LiBF_4$. Although higher conductivity
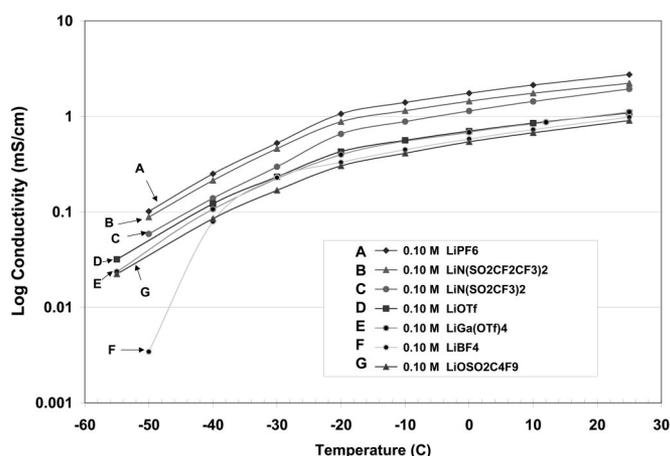

Figure 2. Ionic conductivity of various electrolytes dissolved in solutions of PC + DMC (1:1 v/v%): (A) $LiPF_6$, (B) $LiN(SO_2CF_2CF_3)_2$, (C) $LiN(SO_2CF_3)_2$, (D) LiOTf, (E) $LiGa(OTf)_4$, (F) $LiBF_4$, and (G) $LiOSO_2C_4F_9$.

might be expected for the $LiGa(OTf)_4$ electrolyte based on its decreased ion pairing effect, as determined from the ^{13}C NMR data, there may be other factors that determine ionic mobility, *e.g.*, viscosity of the medium, size of the mobile ions of both charges, and their solvated sheaths. In fact, the mobility of the coordinated anions contributes significantly to the overall conductivity, as is supported by the fact that generally low lithium ion transference numbers have been measured in liquid organic electrolytes.[39] Thus, the conductivity results obtained (Table II) reflect not only the dissociative properties of the electrolyte salt, but also the mobility of the coordinated anion in solution.

CV results.—CV measurements have been performed, using Pt working electrodes, to determine the oxidative and reductive stability of the solutions containing the various electrolyte salts described. Others have also investigated the relative stability of electrolyte solutions containing different salts, usually with the intention of establishing "breakdown" voltages.[40,41] It has been shown that Pt is a desirable electrode to perform these studies, due to the fact that there are no interfering reactions involving Pt, the electrolyte reactions are fairly facile, and the results generally display proper diffusion controlled kinetic behavior in solutions.[42] CV measurements were made in the potential range down to 0.1 V *vs.* Li, (Fig. 3), to assess the cathodic stability of the electrolyte formulations at reducing potentials, *i.e.*, potentials corresponding to lithium intercalation into carbon anodes. Traditionally, more work has been focused in investigating the anodic stability of anions and solvents in contrast to establishing the cathodic stability of formulations, due to the contention that the electrolyte salt stability close to lithium potentials is most often governed by the reduction of the cation, with no

Table II. Ionic-conductivities (mS/cm) of 0.10 M PC/DMC-LiX electrolytes.

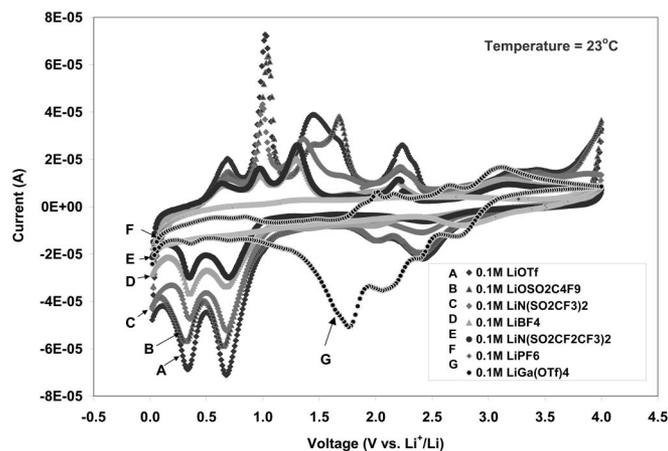| Temperature (°C)	$LiPF_6$	$LiN(SO_2CF_2CF_3)_2$	$LiN(SO_2CF_3)_2$	$LiGa(OTf)_4$	LiOTf	$LiBF_4$	$LiOSO_2C_4F_9$
25	2.73	2.22	1.93	1.11	1.09	0.98	0.90
10	2.13	1.75	1.43	0.87	0.85	0.73	0.67
0	1.75	1.44	1.14	0.68	0.70	0.58	0.54
−10	1.40	1.14	0.88		0.56	0.45	0.41
−20	1.06	0.88	0.65	0.40	0.43	0.33	0.30
−30	0.52	0.46	0.30		0.23	0.23	0.17
−40	0.25	0.21	0.14	0.11	0.12	0.08	0.08
−50	0.10	0.09	0.06	0.02	0.03	0.00	0.02

Figure 3. CV measurements, performed over a voltage range of 0.10 to 4.00 V, of various electrolytes dissolved in solutions of PC + DMC (1:1 v/v%) including: (A) LiOTf, (B) $LiOSO_2C_4F_9$, (C) $LiN(SO_2CF_3)_2$, (D) $LiBF_4$, (E) $LiN(SO_2CF_2CF_3)_2$, (F) $LiPF_6$, and (G) $LiGa(OTf)_4$.

Figure 4. CV measurements, performed over a voltage range of 1.0 to 5.0 V, of various electrolytes dissolved in solutions of PC + DMC (1:1 v/v%), including: (A) LiOTf, (B) $LiOSO_2C_4F_9$, (C) $LiN(SO_2CF_3)_2$, (D) $LiBF_4$, (E) $LiN(SO_2CF_2CF_3)_2$, (F) $LiPF_6$, and (G) $LiGa(OTf)_4$.

contribution from anion.[43] The observation of distinct differences in the cathodic stability of the formulations (Fig. 3) suggests that decomposition of the solvent species is occurring, which is influenced by the coordinative properties of the electrolyte salt. The reductive currents observed with the electrolytes investigated (data compared on the fifth scan using a 10 mV/s scan rate) displayed the following trend in decreasing stability (higher current) with respect to salt type: $LiPF_6 \geqslant LiGa(OTf)_4 > LiN(SO_2CF_2CF_3)_2 > LiBF_4 > LiN(SO_2CF_3)_2 > LiOSO_2C_4F_9 > LiOTf$ (Fig. 3). Definitive assignment of decomposition reactions to particular peaks observed in the voltammograms is difficult and complicated by the fact that they are not only determined by thermodynamic factors, but also by kinetic factors including the electrode surface, scan rate, and concentration of the species in solution.[43] Ideally, the conclusions drawn from CV studies should be complemented by other analytical characterization techniques. For example, voltammetry studies have been performed by Aurbach and co-workers in conjunction with other techniques (including infrared spectroscopy and X-ray photoelectron spectroscopy) on $LiClO_4$ in propylene carbonate using Au noble metal electrodes and have led to the following peak assignments of the irreversible processes: solvent oxidation was ascribed to peaks arising >3.5 V (*vs.* Li/Li+), trace oxygen reduction at ~2.0 V (*vs.* Li/Li+), trace water reduction in the range of 1.5 to 2.5 V (*vs.* Li/Li+), and solvent and/or salt reduction at potentials below 1.5 V (*vs.* Li/Li+).[44,45] Given these assignments, it is likely that the electrolyte solution containing the $LiGa(OTf)_4$ salt contains trace amounts of water and dissolved oxygen, corresponding to the cathodic peaks at ~1.7 V and ~2.2 (*vs.* Li/Li+), respectively. Despite these peaks arising out of trace contamination from water, the $LiGa(OTf)_4$ salt interestingly exhibits low reduction currents, lower than most of the salts examined here, at potentials below 1 V *vs.* Li/Li+ implying that the SEI formed here provides better kinetic stability to the (graphitic) anodes.

In addition to assessing the stability of the electrolytes with respect to reducing potentials, the electrolyte solutions were measured in the potential range of 1.0 to 5.0 V *vs.* Li+/Li to determine the anodic stability at oxidative potentials (Fig. 4). The oxidative currents observed with the electrolytes investigated displayed the following trend in decreasing stability (higher current) with respect to salt type: $LiN(SO_2CF_2CF_3)_2 \geqslant LiGa(OTf)_4 > LiBF_4 > LiN(SO_2CF_3)_2 > LiPF_6 > LiOSO_2C_4F_9 > LiOTf$ (Fig. 4). These results are generally in good agreement with studies performed by Ue and co-workers, in which the oxidation potentials of several anions in PC have been measured using a glassy carbon (GC) electrode (with the exception of the imides which were deter-
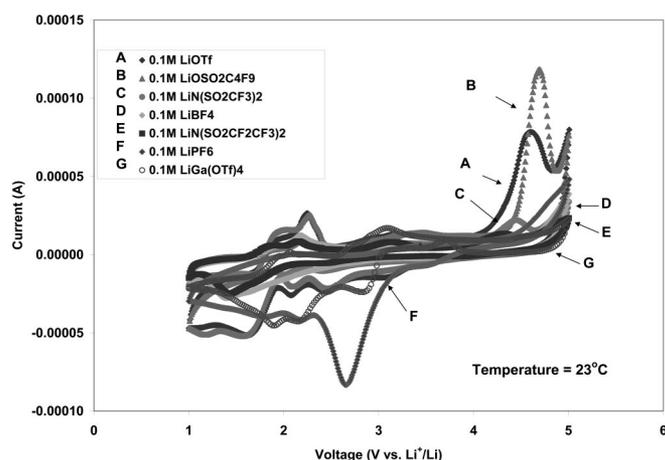
mined to be less stable).[46] Based upon linear sweep voltammetry and *ab initio* molecular orbital and density functional theories, Ue and co-workers have concluded the inorganic fluorine-containing anions are more resistant against oxidation than their organic counterparts.[47] Although the results we have obtained are generally in good agreement with Ue's findings, the discrepancy regarding the imide anion ranking in stability may arise from the fact that these measurements were performed on different working electrodes (platinum instead of GC) and a definitive breakdown voltage assignment was difficult due to faster scan rates adopted here. Similar to the scans at reductive potentials, it is difficult to assign peaks observed definitively to particular reactions/processes, with the exception of the peak at ~2.6 V *vs.* Li+ observed in the case of the $LiPF_6$-based electrolyte that has been ascribed to water present in this electrolyte sample. Presumably, due to poor kinetics of water reduction in the $LiGa(OTf)_4$ salt solutions, there is a shift in its potential to higher values, as the potential is retraced from high positive values, compared to previous scans at low potentials. As shown for solutions of various electrolyte salts in EC + DEC and EC + DMC,[48] it is probable that the onset potentials for these solutions start at potentials significantly lower than 4.0 V *vs.* Li/Li+, corresponding to some measurable current. However, it is not until reaching potentials greater than 4.0 V *vs.* Li/Li+ that significant solvent oxidation occurs, leading to the likely formation of primarily CO_2, $CH_3OCO_2CH_2OCO_2CH_3$, $CH_3OCO_2CH_2CH_2OCO_2CH_3$, and propylene oxide, which in turn can react to form other products.[48,49]

Note that even though solvent oxidation begins at potentials lower than 4 V *vs.* Li on Pt electrodes, it may be hindered noticeably on the metal oxide cathode, as evidenced by successful operation of a Li-ion cell with high voltage metal oxide cathode in these solution formulations. Accordingly, the $LiGa(OTf)_4$ salt is expected to be kinetically stable against high voltage cathodes in Li-ion batteries.

Conclusions

We have investigated the conductivity and ^{13}C NMR characteristics of a number of carbonate-based electrolytes, involving a variety of lithium salts: PC/DMC-LiX. It was shown by ^{13}C NMR spectroscopy that the PC/DMC-$LiGa(OTf)_4$ exhibits decreased ion-pairing behavior as compared to the other salts. In contrast, the ion pairing effect of the other lithium salts is similar. The conductivity of $LiGa(OTf)_4$ unexpectedly is smaller than that of $LiPF_6$ and of comparable value to that of $LiBF_4$. Further studies on the effect of

the counteranions on the conductivity and redox potentials of liquid and polymer electrolytes are currently in progress in our laboratory.

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