

Novel Ternary Composite Electrolytes: Li Ion Conducting Ionic Liquids in Silica Glass

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In this contribution, we report on a novel composite solid electrolyte material, $\text{SiO}_2/[\text{BMIM}]\text{BF}_4/\text{LiTf}$ ($[\text{BMIM}]\text{BF}_4$ = 1-butyl-3-methylimidazolium tetrafluoroborate, LiTf = lithium trifluoromethanesulfonate), prepared via a one-pot sol–gel synthesis route, in which the amorphous SiO_2 glass network provides the mechanical stability and the ionic liquid/Li salt part the high ionic conductivity ($0.5 \times 10^{-2} \text{ S cm}^{-1}$ at 298 K). The mobility of the ionic liquid and Li salt confined within the pores of the fully condensed SiO_2 network is found to increase with the $[\text{BMIM}]\text{BF}_4/\text{LiTf}$ ratio, exhibiting an almost liquidlike mobility, as evidenced by multinuclear solid-state NMR, pulsed-field-gradient solid-state NMR, and impedance spectroscopy.

Introduction

Due to the ever-increasing demand for low-weight Li batteries for mobile electronics, the search for an ideal solid ion conductor for use as solid electrolyte in battery applications is still an important facet of materials science.^{1–4} Apart from desirable properties such as a high chemical resistance, environmental compatibility and low weight, the mechanical stability and ionic conductivity for the transported Li ions in combination with a vanishing electronic contribution constitute the key requirements that have to be met by the ideal lithium ion conducting solid electrolyte. Although recent years have witnessed considerable progress in the search for polymer^{3–5} and crystalline^{6–9} Li ion conducting solid electrolytes, the optimization of the ionic conductivity without compromising too much on the other properties (mechanical strength, environmental compatibility, etc.) still poses a serious challenge. In many cases, the optimization of the mechanical stability or the ionic conductivity entails an unacceptable deterioration of the other. Thus, a cross-linking of a polymer increases the mechanical stability at the cost of a decrease in the ionic conductivity; the addition of plasticizers, on the other hand, amends the amorphicity and hence the ionic conductivity of the polymer, but only at the cost of an impairment of the mechanical stability.

A promising path to overcome this dilemma and consequently toward better performing solid electrolytes may be opened by a complete decoupling of the mechanical and the ion conducting properties. Such a system would comprise an inert solid host material that provides good mechanical stability, in which a second phase (solid or liquid) displaying high ionic conductivity is confined. Possible candidates for the solid host material include stabilized polymers or inorganic glasses; Li salts dissolved in an ionic liquid (IL) may serve as the ion conducting phase. The first reports about the combination of a polymer host with a Li salt/ionic liquid as the conducting phase exhibiting room temperature ionic conductivities $>10^{-4} \text{ S cm}^{-1}$ have appeared in the literature;^{10–13} however, the mechanical performance of these materials still seems to be rather limited. In this respect, composite systems of a silica glass, an ionic liquid, and a Li salt might evolve as an attractive alternative to the established routes. As has been shown by several authors, the system IL/SiO_2 , synthesized via a nonaqueous sol–gel route, forms stable solid membranes.^{14–19} In these solid materials, the ionic liquid exhibits an almost fluidlike dynamic, although being confined within the silica network.^{20,21} Consequently, these systems

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Table 1. Batch Compositions (in relative molar ratios) and Solid-State NMR Parameters for the Samples Investigated in This Work

glass sample	sample compositions				⁷ Li			¹⁹ F		
	TEOS	LiTf	[BMIM]BF ₄	HCOOH	$\delta_{\text{iso}}/\text{ppm}$	ν_Q/kHz	fwhm/Hz	Tf		BF ₄
								$\delta_{\text{iso}}/\text{ppm}$	$\Delta\sigma/\text{ppm}$	$\delta_{\text{iso}}/\text{ppm}$
[BMIM]BF ₄	0	0	1	0	—	—	—	—	—	−149.9
LiTf	0	1	0	0	−1.4	65	4300	−79.3	72	—
ig_0	1	0.5	0	8.8	—	—	—	—	—	—
ig_1	1	0.5	0.5	8.8	−1.1	70	590	−80.0	68	−153.2
ig_2	1	0.5	1	8.8	−1.3	—	154	−79.4	—	−152.0
ig_3	1	0.5	2	8.8	−1.3	—	113	−79.3	—	−151.2
ig_3.2	1	0.5	2	8.8	−1.4	—	126	−79.3	—	−152.2

were advertised as promising materials for electrolytes in fuel cells or dye-sensitized solar cells.^{17,20} However, to the best of our knowledge, no report has been given to date about the performance of SiO₂/IL/Li salt composites as Li ion conductors, although we acknowledge that this possible application has been mentioned by Le Bideau and Vioux.^{16,17,20}

Here we report the first experimental data on a ternary composite in which an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), together with a lithium salt, lithium tetrafluoromethane sulfonate (LiTf), is confined within a SiO₂ glass synthesized via a nonaqueous sol–gel process employing tetraethoxysilane (TEOS) as the source for silicon and formic acid as the solvent.²² The network structure of the silica network and the dynamic state

of the various anions and cations confined within the silica network are analyzed by employing solid-state NMR techniques. The mobility of the Li cations and triflate and tetrafluoroborate anions are found to increase in synchrony with the [BMIM]BF₄/LiTf ratio. For the sample with the highest [BMIM]BF₄/LiTf ratio, an almost liquidlike dynamic behavior is observed already at temperatures below ambient, entailing a very high ionic conductivity of $0.5 \times 10^{-2} \text{ S cm}^{-1}$ at 298 K.

Experimental Section

Synthesis. Lithium trifluoromethanesulfonate (LiTf; Aldrich, 99.995%) was dried at 120 °C in vacuo prior to use. The ion-conducting ionogel-glasses were prepared by employing a

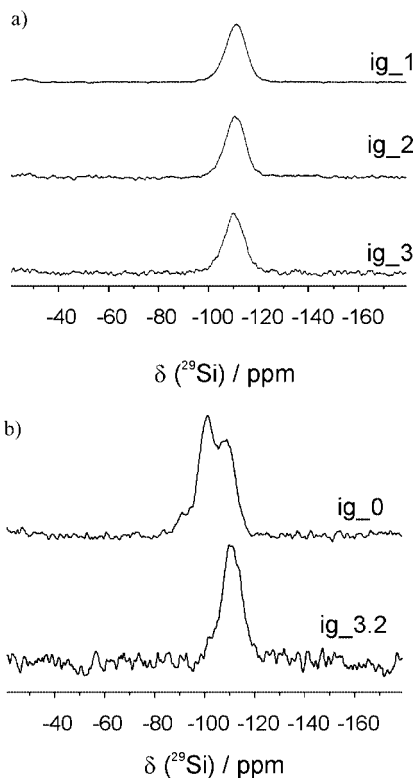


Figure 1. (a) ²⁹Si-MAS NMR spectra for the ionogel-glass samples studied in this work. All spectra were recorded at room temperature. (b) comparison of the ²⁹Si MAS NMR spectra for samples ig_3.2 (SiO₂/LiTf/[BMIM]BF₄ = 1:0.5:2) and the IL-free sample ig_0. Note the exclusive presence of the signal at −110 ppm, indicating a fully condensed network for sample ig_3.2, whereas the appearance of three signals at −91 ppm (Q²), −102 ppm (Q³), and −110 ppm (Q⁴) for the ionic-liquid-free reference sample shows that the gel-to-glass conversion is incomplete in this case. Experimental details: $\nu_{\text{MAS}} = 5 \text{ kHz}$; $\pi/2$ -pulse length, 6 μs ; repetition time, 60 s; spectral width, 25 kHz. An exponential line broadening of 50 Hz was employed to smooth the data.

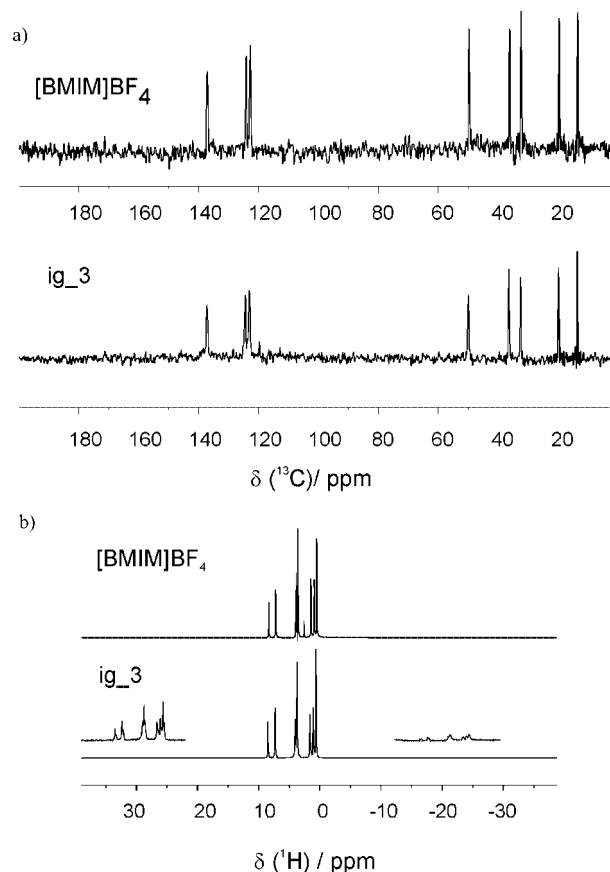


Figure 2. ¹³C (a) and ¹H MAS NMR spectra (b) for the pristine ionic liquid [BMIM]BF₄ (top) and the ionogel-glass ig_3 (bottom). The insets show the spinning sidebands in a magnified ($\times 40$) view. Experimental details: $\nu_{\text{MAS}} = 10 \text{ kHz}$; $\pi/2$ -pulse length, 3–4 μs (¹³C), 7.25 μs (¹H); repetition time, 60 s (¹³C), 5–15 s (¹H). An exponential line broadening of 15 Hz (¹³C) and 1 Hz (¹H) was used to smooth the data.

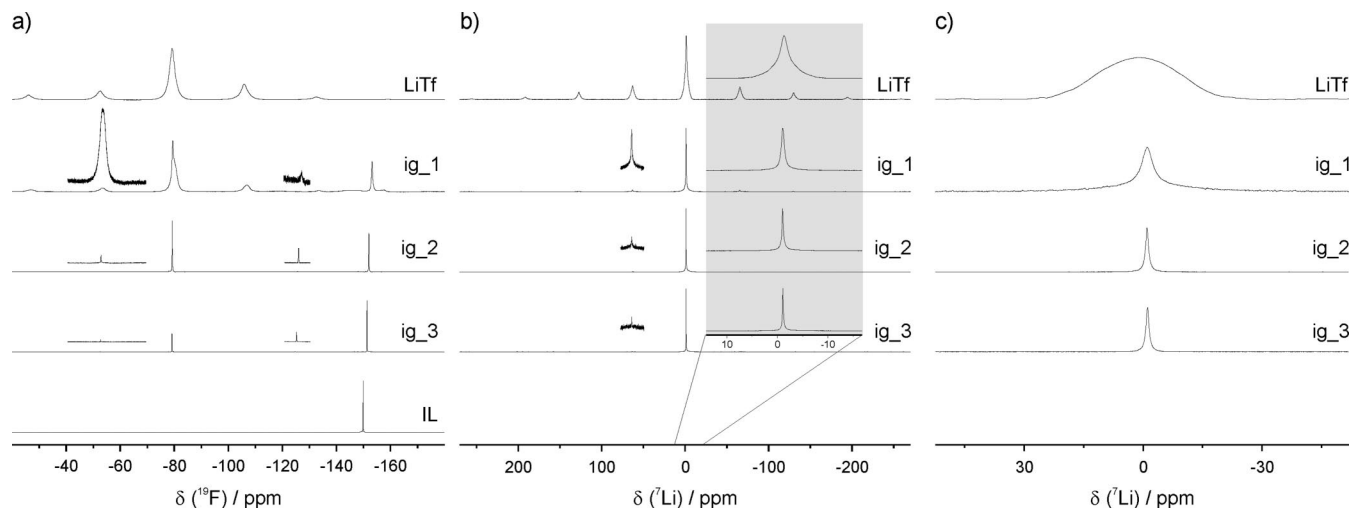


Figure 3. ^{19}F -MAS (a), ^7Li -MAS (b), and static ^7Li spin echo NMR (c) spectra for the studied iongel-glasses. The spectra for pristine LiTf are incorporated for comparison. An expanded view of some spinning sidebands (y-scale $\times 20$) is shown in the insets. Experimental details: $\nu_{\text{MAS}} = 10$ kHz; $\pi/2$ -pulse lengths = $2\ \mu\text{s}$ (^{19}F), $5\ \mu\text{s}$ (^7Li); repetition time, 2–15 s (^{19}F), 5–90 s (^7Li). An exponential line broadening of 1 Hz (^{19}F), 5 Hz (^7Li -MAS), and 25 Hz (^7Li static) was used to smooth the data.

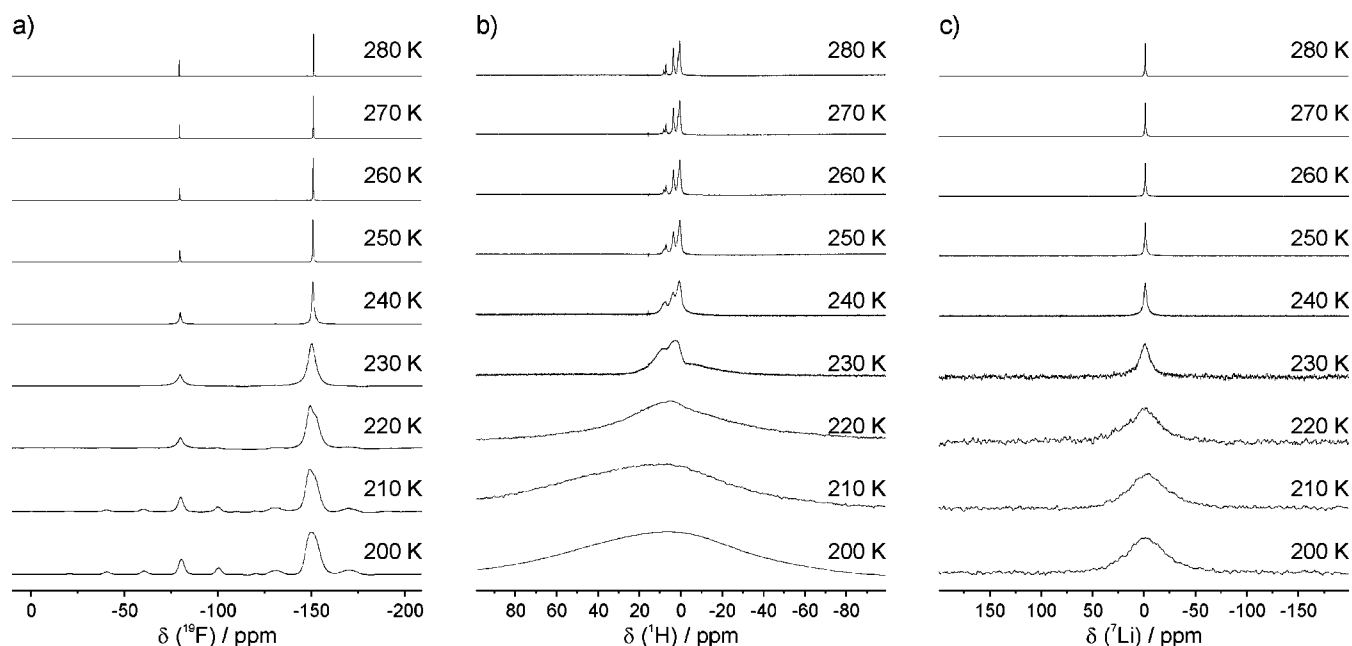


Figure 4. ^{19}F MAS (a), static ^1H (b), and static ^7Li spin echo NMR spectra (c) for iongel-glass ig_3 for the indicated temperatures. $\nu_{\text{MAS}} = 10$ kHz; $\pi/2$ -pulse lengths = $4.25\ \mu\text{s}$ (^{19}F), $10\ \mu\text{s}$ (^1H), $3.5\ \mu\text{s}$ (^7Li); repetition time: 5–20 s (^{19}F), 30–60 s (^1H), 15 s (^7Li). Exponential line broadening of 10 Hz (^{19}F), 1 Hz (^1H), 5 Hz (^7Li) was used to smooth the data.

nonaqueous sol–gel route.²² 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄, Aldrich) was used as the ionic liquid. In a typical synthesis procedure, 1 g of LiTf was dissolved in 4 mL of formic acid (HCOOH). To this, 2.7 mL of tetraethoxysilane (TEOS, Aldrich) was added (see Table 1 for the resulting molar ratios); the resulting mixture was stirred at room temperature for 10 min, during which a clear solution was formed. Upon addition of [BMIM]BF₄, gelation occurred within less than 1 min. Without the addition of the ionic liquid, the gelation took about 1 h. The clear and transparent gels were subsequently dried at 50 °C overnight and then stored at 110 °C for several weeks, resulting in transparent glass monoliths.

NMR Experiments. NMR measurements were carried out on a BRUKER DSX 400 spectrometer with resonance frequencies of 100.6, 155.5, 376.6, and 400.13 MHz for ^{13}C , ^7Li , ^{19}F , and ^1H , respectively, and on a Tecmag Apollo spectrometer operating at 7.04 T for ^{29}Si (59.6 MHz). Spectra are referenced to 1 M aqueous LiCl for ^7Li NMR, CFCl₃ for ^{19}F NMR, adamantane [$\delta(\text{CH}_2) = 38.5$ ppm] for ^{13}C , and tetramethylsilane for ^{29}Si and ^1H . For the PFG NMR measurements, a commercial probe (Bruker Diff 30) was employed, which allows magnetic field gradients of up to 12 T/m. The self-diffusion coefficients were determined using the stimulated echo (PGSTE) technique.^{23,24} The spectral width was set to 100 kHz (^1H , ^{13}C) and 150 kHz (^7Li , ^{19}F). More experimental details for the individual experiments are given in the figure captions.

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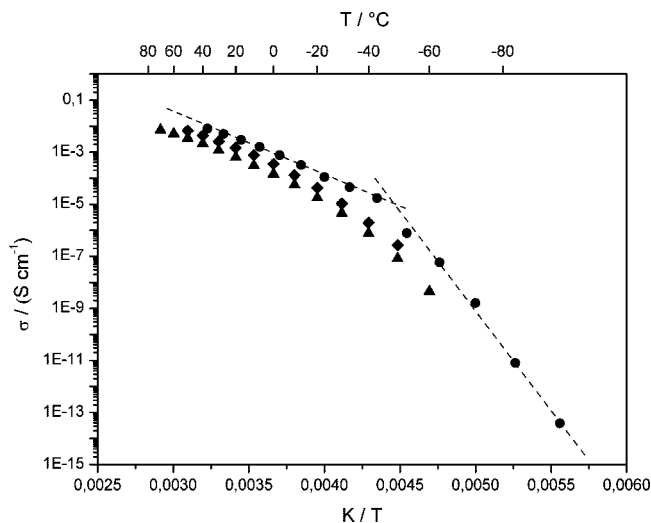


Figure 5. Ionic conductivity as a function of the inverse temperature for ionogel-glasses *ig_2* (triangles), *ig_3* (circles), and *ig_3.2* (squares). For *ig_3*, an Arrhenius type of temperature dependence is observed at high ($T > 240$ K) and low ($T < 220$ K) temperatures with activation energies of 44 and 150 kJ mol⁻¹, respectively.

Impedance Data. Impedance data were acquired using a Novocontrol Alpha analyzer, which was connected to a BDS 1200 sample cell (Novocontrol). The sample material itself was prepared in a home-built sample chamber (stainless steel) to protect the sample from moisture. Data were collected in the frequency range from 10 mHz to 3 MHz with an ac voltage of 20 mV. Experiments were performed in the temperature range 180–320 K in steps of 10 K, employing stainless steel electrodes.

Results and Discussion

The compositions of the ionogel-glasses studied in this work are compiled in Table 1. Annealing of the ionogel-glasses at 383 K for several days results in transparent and colorless glass monoliths. In the ²⁹Si-MAS NMR spectra for the SiO₂/[BMIM]BF₄/LiTf ionogel-glasses (cf. Figure 1a) only a single resonance at -110 ppm can be identified, whereas in an ionic liquid-free reference sample SiO₂/LiTf, three different signals at -91, -101, and -111 ppm are discernible (cf. Figure 1b). The signals can be assigned to Q² (-91 ppm), Q³ (-101 ppm), and Q⁴ units (-110 ppm), employing the well-established Qⁿ notation, in which Qⁿ denotes a SiO₄ group connected to *n* further SiO₄ tetrahedra. Thus, it seems that the addition of the ionic liquid considerably accelerates the condensation reactions, entailing a fully condensed glass network (i.e., complete gel-to-glass conversion) for the annealed samples, whereas for the IL-free samples, processed under identical conditions, the gel-to-glass conversion proves to be quite incomplete, producing a loose silicate network with a high residual amount of terminal Si-OH and Si-OC₂H₅ groups, in accord with the observations by Karout and Pierre.²⁵ In the ¹H and ¹³C MAS NMR spectra for sample *ig_3*, which are collected in Figure 2 together with the corresponding spectra of pristine [BMIM]BF₄, no signals related to formic acid or ethanol can be identified, supporting the view of a fully condensed, solvent-free silica host confining the [BMIM]BF₄/LiTf mixture.

The dynamics of the ionic liquid and the Li salt within the pore system of the confining rigid silica network was analyzed by employing solid-state ¹⁹F and ⁷Li NMR techniques. The corresponding spectra are compiled in Figure 3 the spectra for pristine LiTf and for pristine [BMIM]BF₄ are incorporated for reference. The ¹⁹F-MAS and ⁷Li MAS NMR spectra for pristine LiTf (cf. Figure 3a,b) bear the typical characteristics for immobile triflate anions and Li cations with the observed numerous spinning sidebands indicating nonaveraged chemical shift anisotropy [¹⁹F: $\delta_{\text{iso}} = -79.3$ ppm; $\Delta\sigma = 70$ ppm; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$] and quadrupole (⁷Li, $C_Q = 65$ kHz) interactions; the width of the $m = 1/2 \rightarrow m = -1/2$ transition in the static ⁷Li NMR spectrum (Figure 2c; fwhm = 4.1 kHz) can be traced back to nonaveraged homo- and heteronuclear dipolar interactions. Upon incorporation of the ionic liquid and the LiTf into the SiO₂ matrix, distinctive changes in the appearance of the NMR spectra can be observed. Contrasted to the spectra for pristine LiTf, the number and intensity of the spinning sidebands in the ⁷Li MAS NMR spectra as well as the line width of the signal in the static ⁷Li NMR spectra are found to be drastically reduced. The reduction of the line width of the static ⁷Li NMR signal originates in an averaging of the homo- and heteronuclear dipolar interactions due to motional narrowing; the almost complete loss in spinning sideband intensity in the ⁷Li MAS NMR spectra indicates an averaging of the quadrupolar coupling of the ⁷Li nuclei, again due to the dynamics of the Li cations. A close inspection of the line widths and residual spinning sideband intensities discloses gradual changes in the Li mobility within the ionogel-glasses. Both parameters, the residual spinning sideband intensities and the static ⁷Li NMR line width (cf. Table 1), exhibit a decrease with increasing [BMIM]BF₄/LiTf ratio, thus indicating a corresponding increase in Li mobility. This increase in the mobility with increasing [BMIM]BF₄/LiTf ratio is also borne out by the ¹⁹F-MAS NMR spectra. Whereas for sample *ig_1* the majority of the triflate anions remains immobile with the corresponding signal resembling that of pristine LiTf ($\delta_{\text{iso}} = -79.3$ ppm; $\Delta\sigma = 60 \pm 5$ ppm), the ¹⁹F-MAS NMR spectra for samples *ig_2* and *ig_3* display a single narrow signal at -79.3 ppm with only marginal spinning sideband intensity, suggesting high triflate mobility within the pore system of the SiO₂ network in these samples (Figure 3). Contrasted to this, the BF₄ anions (from the ionic liquid) are found to be mobile within the SiO₂ network, irrespective of the [BMIM]BF₄/LiTf ratio. For the corresponding signal (cf. Figure 2a), only two spinning sidebands of rather minor intensity can be observed for all studied ionogel-glasses. Nevertheless, the same principal trend as for the ⁷Li MAS NMR signal and the ¹⁹F MAS NMR signal of the triflate anions, a decrease in the spinning sideband intensity with increasing [BMIM]BF₄/LiTf ratio, is followed by this signal. Interestingly, the isotropic position of the BF₄ signal experiences a shift to higher field with decreasing [BMIM]BF₄/LiTf ratio. Thus, according to the solid-state NMR results, in the ionogel-glass samples with high [BMIM]BF₄ ratio (sample *ig_3*), the Li cations, triflate anions, BF₄ anions, and [BMIM] cations (as evidenced from the ¹H MAS NMR spectra and ¹³C MAS NMR spectra, cf.

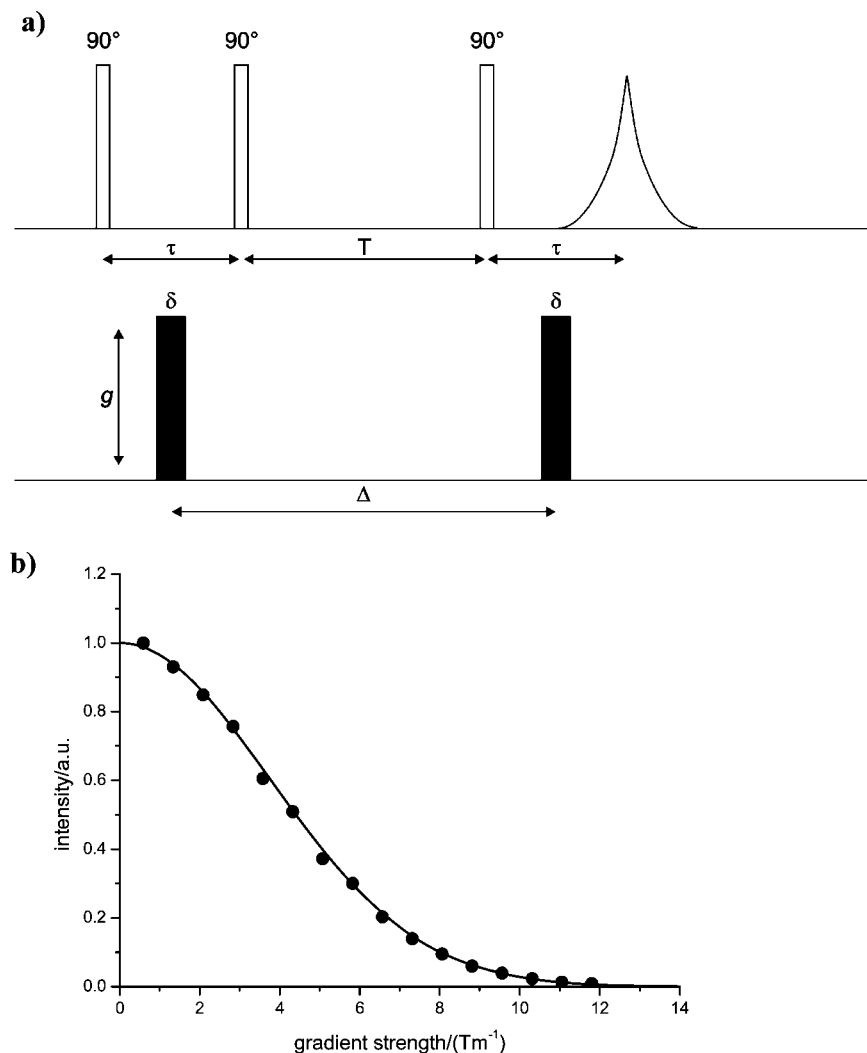


Figure 6. (a) Stimulated echo pulse sequence used for the PFG NMR experiments. The commercial PFG probe allows gradient strengths (g) of up to 11.8 T/m. (b) Results of a ^1H PFG NMR experiment employing the pulse sequence in part a for sample [BMIM] BF_4/LiTf . The intensity of the stimulated echo is plotted as a function of the gradient strength g . Experimental details: $\delta = 1.5$ ms; $\Delta = 50$ ms; $\pi/2$ pulse length = $4.5 \mu\text{s}$; $\tau = 3.7$ ms; relaxation delay = 6 s; line broadening = 0.3 Hz; spectral width = 20 000 Hz. From the decay, the self-diffusion coefficient D is obtained by fitting the decay to $I_{(g)} = I_{(0)} \exp[-D\gamma^2 g^2 (\Delta - \delta/3)]$.

Table 2. Room Temperature Diffusion Coefficients (from PFG NMR) and Ionic Conductivities (from impedance spectroscopy) for the Samples Investigated in This Work^a

sample	diffusion coefficients D / ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)				ionic conductivity σ ($10^{-4} \text{ S cm}^{-1}$)				
	[BMIM] $^+$	Li^+	Tf^-	BF_4^-	calculated from D for individual ions				from impedance spectroscopy
[BMIM] BF_4	11	—	—	11	—	—	—	—	—
[BMIM] BF_4/LiTf	4.5	1.5	1.9	2.5	—	—	—	—	—
ig_2	—	0.5	0.8	0.9	—	—	—	—	6.3
ig_3 ^b	4.5	1.3	2.8	3.6	15	1.1	2.3	12	30
ig_3.2 ^b	2.4	0.7	1.2	1.4	8	0.6	1.1	5	15

^a The individual contributions to the total ionic conductivity were calculated from the diffusion coefficients employing $\sigma = \sum_{\text{ion}} \sigma_{\text{ion}} \propto \sum_{\text{ion}} \lambda_{\text{ion}}^{\text{ion}} D_{\text{ion}}$.

^b Repeated batches of the same compositions gave somewhat different absolute values for the ionic conductivity and the diffusion coefficients (cf. samples ig_3 and ig_3.2). This, however does not affect the observed overall dependence of these values on the [BMIM] BF_4/LiTf ratio.

Figure 2) are performing an almost liquidlike dynamic within the pore system of the fully condensed SiO_2 network. However, the presence of minor spinning sideband intensity in the ^1H , ^{19}F , and ^7Li MAS NMR spectra indicates some restriction of the dynamics due to the confinement of the ionic liquid/LiTf within the pores of the SiO_2 network.

The perpetuation of the high Li mobility down to subambient temperatures constitutes a prerequisite for a good Li ion conductor for use in battery applications. This was

confirmed by temperature-dependent ^{19}F MAS, ^1H , and ^7Li NMR on sample ig_3. The corresponding spectra (cf. Figure 4) convincingly prove that the mobility of the cations ([BMIM] $^+$, Li^+) and anions (triflate, BF_4^-) extends down to a temperature of 240 K. Below this temperature, the distinct line broadening in the ^1H and ^7Li NMR spectra and the appearance of considerable spinning sideband intensity in the ^{19}F MAS NMR spectra indicate a freezing of the motion of the various ionic species present in the system.

The established very high ionic mobility extending to temperatures down to 240 K in an albeit solid-state electrolyte system will only translate into good macroscopic ionic conductivity if the hosting SiO₂ matrix provides a connected pore system. Le Bideau and Vioux reported a conductivity of $\approx 10^{-3}$ S cm⁻¹ at ambient temperature in related, LiTf-free ionogel-glasses, from which the presence of a connected pore system, enabling macroscopic transport, could be concluded.¹⁶ The ionic conductivities of the samples investigated in this work were determined from temperature-dependent impedance spectroscopy (cf. Figure 5). Again, the sample with the highest [BMIM]BF₄/LiTf ratio exhibits the best performance; a value of 0.5×10^{-2} S cm⁻¹ at 300 K is observed. The temperature dependence of the conductivity at high and low temperatures follows an Arrhenius behavior with resulting activation energies of $E_A = 44 \pm 4$ kJ mol⁻¹ at high temperatures and $E_A = 150 \pm 4$ kJ mol⁻¹ at low temperatures with a change over at $T = 226$ K, i.e., roughly the same temperature at which the cation and anion dynamics is frozen (cf. Figure 3). The main interest in these samples, however, is not related to their overall ionic conductivity but to the Li ion conductivity. Since from the results of the impedance measurements it is not possible to separate the contributions from the various ions from one another, additional pulsed field gradient NMR experiments were performed. With PFG NMR the mobility of the various cations and anions present in the solid electrolytes can be studied individually via an evaluation of the respective diffusion coefficients. Thus, ¹H, ⁷Li, and ¹⁹F PFG NMR experiments were performed to obtain the diffusion coefficients for [BMIM]⁺ (¹H), BF₄⁻ (¹⁹F), Li⁺ (⁷Li), and triflate (¹⁹F). The pulse sequence employed and a representative ¹H-PFG NMR data set for [BMIM]BF₄/LiTf are given in Figure 6, the results are compiled in Table 2. The diffusion coefficients for pristine [BMIM]BF₄ and a [BMIM]BF₄/LiTf mixture (ratio 4:1, corresponding to ig_3) were determined as references. According to our results, the mobility of the [BMIM]⁺ cation and BF₄⁻ anion decreases by a factor of 2 and 4, respectively, upon addition of LiTf. Within this mixture, the Li cations, although representing the smallest ions in the system, exhibit the lowest diffusion coefficient, followed by Tf and BF₄, whereas [BMIM], constituting the largest ion, shows the highest diffusion coefficient. Interest-

ingly, the confinement of the [BMIM]BF₄/LiTf mixture into the pore system of the silica glass (sample ig_3) does not entail a further deterioration of the ionic mobility. Rather, the diffusion coefficients are found to be more or less identical to those of the mixture. Again, the mobility is found to scale with the inverse of the ion size, in accordance with published data for various binary ionic liquid/lithium salt systems.^{26,27} As outlined in ref 27, this indicates that whereas the larger [BMIM] cation diffuses as a single ion, neither the TF⁻ and BF₄⁻ anions nor the Li cations diffuse as single ions, but rather are involved in the formation of temporary lithium–anion complexes, which also explains the observed stronger effect of salt addition on the anion mobility. (cf. Table 2). A rough estimate for the Li conductivity in the samples—ignoring any correlation effects such as ion pairing or the formation of larger anion–cation agglomerates—may be calculated from the diffusion coefficients obtained from PFG NMR using $\sigma = \sum_{\text{ion}} \sigma^{\text{ion}} \propto \sum_{\text{ion}} x^{\text{ion}} D^{\text{ion}}$. The obtained individual ionic conductivities are incorporated in Table 2. As expected, the ions from the ionic liquid provide the dominant contribution to the total ionic conductivity; nonetheless, the ionic conductivity obtained for the Li cations (1.1×10^{-4} S cm⁻¹ at ambient temperature) presents an encouraging high value for a solid Li ion conductor.

Conclusions

To conclude, the high ionic conductivity that extends down to subambient temperatures in combination with the high mechanical stability of the fully condensed SiO₂ network renders this class of material a particular promising prospect for a solid electrolyte for battery applications. Owing to the large degree of chemical flexibility (variation of the glass matrix, the ionic liquid, and the Li salt), further improvement of the material may be anticipated in the near future.

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