6,7Li NMR study of ion mobility on the molecular scale in lithated imidazole complexes

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Abstract

Two model compounds, lithium imidazolium (LiIm) and lithium 2-undecylimidazolium (und-LiIm), were synthesized. These materials are chosen as models of potential lithium ion conductors for use as electrolytes in lithium batteries. Solid-state NMR was used to provide information on the microscopic interactions including ionic mobility and ring reorientations which govern the efficiency of conductivity. Lithium imidazolium was mixed with lithium methylsulfonate, generating a doped complex in which a doubly lithiated imidazole ring was inferred based on the 7Li NMR chemical shifts. Our research includes 6,7Li variable temperature MAS NMR experiments at intermediate spinning speeds, relaxation studies to determine spin-lattice relaxation times (T1) of lithium ion hopping, and 2D exchange spectroscopy to determine possible chemical exchange processes. The possibility of 2-site ring reorientation for the doubly lithiated imidazole ring was supported by exchange spectroscopy. Comparisons of spin-lattice relaxation times and corresponding activation energies of the lithium imidazolium and the doped complex point to a higher degree of mobility in the latter.

Lithium 2-undecylimidazolium was prepared and exhibited a lower melting point than the parent lithium imidazolium, as expected. This small molecule was chosen as representative of a side-chain functionalized polyethylene-based material. 7Li MAS spectra show mainly the presence of the doubly lithiated imidazole ring in pure und-LiIm, and in the LiCH3SO3–und-LiIm mixture. The data clearly indicate local mobility of the lithium ions in the materials.

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1. Introduction

The electrolyte is a critical component for optimum performance in high energy density secondary lithium batteries. A successful polymer electrolyte must be able to act as a mechanical separator, an electronic insulator and a good ionic conductor. Moreover, it has to be electrochemically stable and easily processable. To address safety concerns and to add flexibility of cell design, materials research in the last decade has focused on designing polymer and gel electrolytes which meet the desired criteria. A wide variety of materials have been studied with the focus on polyethylene oxide based systems with large anions, such that ionic conductivity arises primarily from lithium ion transport [1,2]. Lithium transport in such systems depends strongly on polymer-backbone flexibility and the coordination of the lithium ions. More recent studies include nanocomposite materials of lamellar clays with intercalated polymer chains, or polymers that incorporate nanoparticles of a robust material such as TiO2 or Al2O3 [3,4]. As well, polymer gel electrolytes have been a major contender as useful electrolytes for secondary lithium batteries. They combine the mechanical properties of the solid polyelectrolyte (poly(methylmethacrylate), PMMA, or poly(acrylonitrile), PAN), with the high ionic conductivity of liquid electrolytes. The liquid electrolyte usually contains a mixture of two or more solvents (EC, PC, gBL or DMC) and a lithium salt such as LiPF6, LiClO4 or LiCF3SO3. The challenge remains to optimize all components to achieve a highly conductive material with good mechanical properties.

Recently, polymers incorporating heterocycles such as imidazole, benzimidazole, and pyrazole have been investigated as proton-conducting materials with potential applications as...
membrane materials in polymer electrolyte membrane fuel cells [5–10]. To our knowledge, related compounds have not yet been considered as electrolytes for lithium ion batteries. Moreover, as stated by Armand and Tarascon, achieving high ionic conductivity in Li-based polymer electrolytes requires a better understanding of the fundamentals of ion dissociation and transport [11]. Thus, both the consideration of heterocycles as lithium ion conductors and the detailed study of their ion transport mechanisms are warranted.

Recent efforts in our group have focused on the possibility of using imidazolium-based materials as an alternative polyelectrolyte for lithium ion batteries, in which protons in imidazole are replaced by lithium ions. Lithium transport in these novel lithiated imidazole-based materials may not depend strongly on polymer-backbone flexibility or coordination of the Li+ ions and thus, polymers with higher glass transition temperatures and therefore good mechanical integrity may be viable. The objective of our study is to synthesize new materials based on lithiated imidazole and characterize their ionic mobility using solid-state NMR.

Investigations of proton transport in imidazole-based materials using solid-state NMR have provided insight into the mechanism (Grotthus vs. vehicle) of proton-mobility in such materials [12,13]. The Grotthus mechanism in imidazole involves a single migration event along the hydrogen-bonded chain followed by a planar rotation of all the imidazole molecules prior to further proton transfer [14]. The activation energy of the ring flip was determined via 13C solid-state NMR measurements [9]. Here we apply a related NMR approach to investigate lithium ion mobility in lithiated versions of similar imidazole containing materials.

We present solid-state NMR results of lithium imidazolium (LiIm), lithium 2-undecylimidazolium (und-LiIm) and both systems doped with lithium methanesulfonate. These results provide the first step toward understanding the lithium local mobility mechanism in imidazole-based materials, and act as a foundation for further investigations of polymer-tethered lithium imidazolium materials. Our spectroscopic approach combined 1D 6Li and 7Li MAS NMR, 2D 6Li EXSY exchange spectroscopy [15] and 7Li saturation recovery spin-lattice relaxation time (T1) experiments [16] to characterize the local lithium environments and their molecular level mobility and exchange processes.

2. Experimental section

Lithium imidazolium (LiIm) was obtained as a product of the reaction of 1H-imidazole with butyl lithium in toluene according to a procedure described in literature [17]. 1H-imidazole was used as received from Aldrich. 1H NMR (200 MHz, DMSO): δ 67.25 (s, 1H), 6.77 (s, 2H). 13C NMR (200 MHz, DMSO): δ 140.9, 123.8. 7Li MAS NMR (300 MHz): δ 3.2.

Lithium 2-undecylimidazolium (und-LiIm) was synthesized in the reaction of 2-undecyl-1H-imidazole with butyl lithium [13]. 1H NMR (200 MHz, DMSO): δ 0.81 (t, 3H), 1.24 (m, 16H), 1.54 (m, 2H, m), 2.41 (t, 2H), 6.52 (s 2H). 13C NMR (200 MHz, DMSO): δ 20.9, 29.5, 35.4, 35.5, 36.0, 36.6, 39.5, 123.0, 160.1. 7Li MAS NMR (300 MHz): δ 2.01.

2-Undecyl-1H-imidazole was obtained according to a procedure described in literature [18]. At 0 °C, an ammonia solution in methanol (ca. 7 N, 20 mL, 139.20 mmol) was added to a solution of dodecyl aldehyde (10.28 mL, 46.39 mmol) and a 40% solution of glyoxal hydrate (5.3 mL, 46.40 mmol) in methanol (100 mL). After the reaction mixture was stirred for 6 h at 0 °C, the mixture was refrigerated (3 °C) for 6 days. Water was added and the product was extracted using ethyl acetate. The combined organic layers were dried over sodium sulfate and after removing the solvent the crude product was crystallized from hexane giving the product as a white powder with 70% yield. The purity of the product thus obtained was checked by 1H and 13C NMR. 1H NMR (200 MHz, CDCl3): δ 0.88 (t, 3H), 1.24 (m, 16H), 1.69 (m, 2H), 2.72 (t, 2H), 6.95 (s 2H), 10.30 (s, 1H). 13C NMR (200 MHz, CDCl3): δ 20.9, 29.5, 35.4, 35.5, 36.2, 36.4, 38.7, 128.0, 155.8.

Lithium methanesulfonate (LiCH3SO3) was synthesized by the reaction of methanesulfonic acid with lithium chloride. The purity of the product was checked by 1H and 7Li NMR. 1H NMR (200 MHz, DMSO): δ 2.28 (s, 3H). 7Li MAS NMR (300 MHz): δ −0.17. Subsequently, LiIm and und-LiIm were mixed with lithium methylsulfonate (LiCH3SO3) in a 1:1 molar ratio. The ionic complexes [Li–Im–LiCH3SO3] and [und-LiIm–LiCH3SO3] were prepared by grinding the mixture of imidazolium compound with 3LiCH3SO3 for 5 min in an agate mortar and pestle in an argon glove box.

Fig. 1. 7Li MAS NMR spectra of a. Lithium imidazolium and b. Lithium methanesulfonate.
Solid-state NMR. Spectra were acquired on an AV 300 Bruker spectrometer, at Larmor resonance frequencies of 116.62 MHz for $^7$Li, and 44.16 MHz for $^6$Li. All spectra were acquired under magic angle spinning (MAS) at 10 kHz using 4 mm zirconia rotors. Samples were packed in a glove box under an inert argon atmosphere. Spectra were referenced to $^6,^7$LiCl(s) at 0.0 ppm. Typical acquisitions used 30° radio frequency pulses, and 10 s recycle delays, with a total of 1024 transients averaged for each 1D spectrum. $^7$Li spin-lattice relaxation data, $T_1$, were acquired using a saturation recovery sequence, due to the unusually long $T_1$ values of these materials. Experimental parameters included variable delays between 1 ms and 3600 s, and 16 scans per increment. Activation energies for spin-lattice relaxation were extracted from linear fits of ln (1/$T_1$) versus inverse temperature over a temperature range from 300–360 K.

Powder X-ray Diffraction. The synthesized lithiated imidazole complex [Li–Im$^+$–Li CH$_3$SO$_3^-$] was analyzed by X-ray powder diffraction using a Bruker D8 diffractometer with Cu Kα radiation and an exit beam graphite monochromator. Sample was measured from 2$\theta$=5–50° at a step size of 0.040° and a step time of 2 s.

3. Results and discussion

3.1. Lithium imidazolium and its complexes

Fig. 1 present the $^7$Li MAS NMR spectra of a) Lithium Imidazolium (LiIm) and b) Lithium Methanesulfonate (LiCH$_3$SO$_3$). The lithium atom in LiIm is covalently bonded to the nitrogen atom in the imidazole ring, which has a corresponding chemical shift of 3.20 ppm. In contrast, the chemical shift of the Li resonance in LiCH$_3$SO$_3$ (~0.17 ppm) indicates the presence of the more commonly found ionic lithium species in this compound.

Single pulse $^7$Li MAS NMR experiments in the temperature range of 300–370 K for pristine lithium imidazolium did not show any changes upon heating (data not shown), which confirmed the absence of ionic motion. This is consistent with the high melting point ($T_m$>623 K), and an associated high lattice energy for the material. For the mixture of LiIm and LiCH$_3$SO$_3$, $^7$Li MAS NMR experiments at various temperatures (300 K, 320 K, 350 K and 370 K) (Fig. 2) show the presence of two strong lithium signals (3.20 ppm and ~0.17 ppm) corresponding to lithium imidazolium and lithium methanesulfonate. The height of the LiIm lithium resonance increases with increasing temperature, as the corresponding linewidth decreases. The line narrowing is attributed to ionic mobility, enabled by the less rigid and noncrystalline structure of the mixture. Structural changes upon mixing are discussed in more detail with reference to the powder diffraction studies below. The relative intensity of the lithium methanesulfonate resonance decreases, attributable to the lack of significant change in the linewidth of this signal. The most significant observation in this series of spectra is the appearance of the new peak at about 1.70 ppm assigned to an intermediate lithium species, and its increasing intensity with temperature. This resonance was not seen in the $^7$Li MAS spectra of either pure LiIm or pure LiCH$_3$SO$_3$. We attribute this new peak to a lithium imidazolium complex, the structure of which is shown in Scheme 1.

The proposed mechanism of formation of the lithium imidazolium complex is shown in Scheme 1, and involves the attack of the lone pair electrons of nitrogen on the lithium ion of the lithium methanesulfonate. The resonance structures illustrate the charge localized on the nitrogen centers. To test the reproducibility and sensitivity of the mixture to grinding, a second mixture was prepared in which the starting materials were ground together for 5 min in an agate mortar and pestle under inert atmosphere. There is precedent in the literature for such solid-state reactions, where co-grinding of non-conducting lithium salts produced ionically conducting species [19]. The second treatment was identical to that of the original sample.

![Scheme 1](image-url)

Scheme 1. Mechanism of formation of dilithiated imidazolium ring with methanesulfonate counteranion. Both resonance structures shown as products, as well as the delocalized charge on the imidazolium ring.
with the exception of the extended grinding time. The spectrum of this well-ground mixture LiIm and LiCH$_3$SO$_3$ contains only the signal at 1.70 ppm. Thereby, we confirm that the intimate mixture of the two starting materials generates an intermediate complex, the relative amount of which can be controlled by varying the grinding time. Since the $^7$Li signal was quite broad, we repeated the experiment using $^6$Li to establish that this single resonance was present in the well-ground material and to probe lithium ion exchange.

$^6$Li MAS spectra of a mixture of LiIm and $^6$LiCH$_3$SO$_3$ at different grinding times are shown in Fig. 3. The data show improved resolution typical of $^6$Li, which has a lower quadrupolar coupling constant and less dipolar coupling due to the lower magnetogyric ratio relative to $^7$Li. The spectrum of the well-ground material indeed shows a single resonance at 1.70 ppm. Most importantly, these spectra confirmed that the Li$^+$ ions are exchangeable, as the signal intensities of the different species are comparable to those obtained by $^7$Li NMR for the original mixture, although the only 6-Li source is the $^6$LiCH$_3$SO$_3$ salt. The $^6$Li$^+$ ions introduced in the lithium methanesulfonate salt, are present in the product, associated with the imidazolium rings, as evidence by their higher frequency shift. In the absence of a crystal structure, this is our strongest proof of the lithiated imidazolium complex.

Attempts to prepare this type of doped lithiated imidazole complex [Li–Im$^+$–Li CH$_3$SO$_3$] from solution chemistry routes have been unsuccessful to this point, likely due to the high lattice energy of the LiCH$_3$SO$_3$ salt. We are working on alternate syntheses involving larger anions. However, the success and reproducibility of the solid-state reaction is clearly demonstrated by the intermediate chemical shift observed in the $^6,^7$Li NMR spectra. Moreover, the relative intensity of this resonance is shown to grow with grinding time. This NMR data is an important confirmation of the possibility of creating such positively charged, doubly lithiated imidazole rings in the solid-state. Such structures will act as carriers of dopant lithium ions to increase carrier concentration and promote ionic conductivity in polyelectrolytes.

To confirm the solid-state NMR results indicating the formation of a new structure, namely, a doped lithiated imidazole complex [Li–Im$^+$–Li CH$_3$SO$_3$], powder X-ray diffraction analysis was performed. The X-ray powder diffraction pattern of the mixture of Li–Im with LiCH$_3$SO$_3$ that was prepared by grinding of these two compounds for 5 min is shown at Fig. 4 (curve a). This pattern is different than lithium imidazolium (curve b) and crystalline lithium methanesulfonate (curve c) patterns. Comparisons of the reflections of the starting materials and the mixture are consistent with a molecular level rearrangement of the structure upon formation of the lithium complex [Li–Im$^+$–Li CH$_3$SO$_3$] by grinding Li–Im with LiCH$_3$SO$_3$. The weak reflections that are observed in the new material indicate some local ordering; however, no single crystals were obtained, so a complete structural assignment is not possible. The product is nevertheless not a simple physical mixture of the two parent materials, since these reflections are no longer visible in the diffraction pattern. This demonstrates the presence of a new local structure.

![Fig. 3. $^6$Li MAS spectra of mixtures of LiIm and LiCH$_3$SO$_3$ at 10 kHz MAS. — 30 s grinding, and — 5 min grinding.](image)

![Fig. 4. XRD diffraction patterns of Li–Im, LiCH$_3$SO$_3$, and a ground mixture of Li–Im with LiCH$_3$SO$_3$.](image)
2D EXSY is a well-established NMR method for characterizing dipolar couplings and chemical exchange phenomena in the solid state [15]. The mixture of LiIm and LiCH₃SO₃ was studied using 2D ⁶Li EXSY exchange spectroscopy at variable contact times between 1 ms and 1 s to investigate the possible exchange interactions between the various lithium sites. The dominant feature in the 2D spectra (Fig. 5a) arises along the diagonal, corresponding to the three resonances observed in the 1D study. The correlation between these lithium atoms is observed in the spectrum obtained with a longer mixing time (50 ms) as a pair of cross peaks CB and BC (Fig. 5b). The BC cross peaks are evidence of correlation between lithium ions in these two environments. This is possible either through spin-diffusion driven by dipolar coupling, or through chemical exchange, via 2-site imidazole ring flips. Given the short time scale (50 ms) on which cross peaks are observed for this low gamma nucleus, we attribute the cross peaks to evidence of ring reorientation in the lithiated imidazole complex. This is the first evidence demonstrating local lithium ion mobility, and suggesting possibility of ion transport in this class of materials based on microscopic level ion mobility. This motion has been proposed to be the rate-limiting step in proton transport for imidazole-based proton conductors. Therefore, we interpret this data as positive support for the utility of lithiated imidazoles as lithium ion conductors.

Our research includes ⁷Li relaxation investigations to determine the activation energies of lithium ion hopping for pure and doped lithium imidazolium. We calculated relaxation spin-lattice times \( T_1 \) at different temperatures within the range 300–370 K for both materials. The very long \( T_1 \) of lithium imidazolium \( (T_1 = 135 \text{ s at ambient temperature}) \) suggests a rigid molecular structure, whereas the \( T_1 \) value decreases in the case of doped LiIm (the mixture of LiIm and LiCH₃SO₃) by roughly a factor of two. The \( T_1 \) relaxation time of ⁷Li in the dopant salt, lithium methanesulfonate, was 57.6 s at ambient temperature. The relatively long \( T_1 \) in the salt is attributed to the highly symmetric environment of the lithium ions, which minimizes the electric field gradient of the quadrupolar nuclei \( (7\text{Li } I = 3/2) \). Surprisingly, this value is quite similar to that of the doped LiIm material. The fact that the \( T_1 \) of doped LiIm is not simply the average of the two \( T_1 \)'s for the salt and pure lithium imidazole, nor a bi-exponential function including both \( T_1 \)'s, is a further confirmation that the intermediate ⁷Li resonance of the new complex is indeed attributable to a new material, and not simply a physical mixture of the components.

Comparison between pure and doped lithium imidazole systems shows lower activation energies for ⁷Li spin-lattice relaxation in the doped lithium imidazole (Fig. 6). Pure LiIm data has an activation energy of 17.2 kJ/mol, whereas the doped complex’s activation energy is 13.2 kJ/mol. The obtained activation energy may describe the energy requirement for lithium ion transport, but more studies should be done. Nevertheless, the differences between pure LiIm and the doped complex are significant and can be attributed to greater local mobility in the doped complex.

3.2. Lithium 2-undecylimidazole and its complexes

This target molecule (Scheme 2) was synthesized as a model of a polyethylene based membrane material except no oxygen atoms are present. Thus the lithium is complexed only by the

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Fig. 5. 2D ⁶Li EXSY of a mixture of LiIm and ⁶LiCH₃SO₃ at 10 kHz with mixing time at 360 K a. 1 ms; b. 500 ms.

Fig. 6. Dependence of the relationship between 1000/\( T \) and ln \(|1/T_1|\) for LiIm and the mixture of LiIm with LiCH₃SO₃.
imidazole nitrogen atoms. The envisioned polymer would have a comb-like structure with imidazole rings strung out at the tips of the comb teeth, giving the tooth length as a variable in tuning the mechanical properties of the membrane.

To obtain an understanding of the ion transport mechanism in polymer-tethered lithium imidazolium materials, we studied lithium 2-undecylimidazolium (und-LiIm) which contains a long alkyl chain attached to the ring at the 2-carbon position. At room temperature, the $^7$Li MAS NMR spectra of this material show the presence of one broad lithium signal with a chemical shift of 2.0 ppm. The intermediate value between covalently and ionically bonded lithium atom suggests the presence of the intermediate species, as was seen in the case of the lithium complex $[$Li–Im$^+–$Li CH$_3$SO$_3^-$].

$^6$Li MAS NMR experiments of the freshly prepared mixture of und-LiIm with $^6$LiCH$_3$SO$_3$ in the range of temperatures from 300–360 K is presented in Fig. 7a. Again, in this case the resonance corresponding to the lithium ion from LiCH$_3$SO$_3$ ($-0.30$ ppm) is present in the mixture. At room temperature the peak corresponding to the intermediate lithium species is very broad and probably overlaps with the covalently bonded lithium at about 3.14 ppm. The lithium resonance of und-LiIm increases and the corresponding linewidth decreases with temperature more intensely than in the lithium imidazolium mixture. This is consistent with the earlier onset of ion mobility, as expected in this softer material. A decreasing intensity of the lithium methanesulfonate resonance and a corresponding increase in intensity of the new intermediate lithium species (1.52 ppm) with increasing the temperature was observed. This confirms that the lithium ions from the salt become incorporated into the und-LiIm complex, with methanesulfonate as a spectator ion.

Above 340 K, the resonance from lithium covalently bonded into the imidazole ring becomes clearly resolved and increases continuously, confirming the original formation of the covalent bond and supporting the interpretation of local mobility within the structure.

Interestingly, the sample comprised of a well-ground mixture of und-LiIm and LiCH$_3$SO$_3$ after 2 weeks of aging showed

\[ \text{Scheme 2. Synthesis of a. Lithium imidazole and b. Lithium 2-undecylimidazole.} \]

Fig. 7. $^7$Li MAS spectra of a mixture of und-LiIm and LiCH$_3$SO$_3$ at 10 kHz a. fresh sample at different temperatures b. comparison of the original sample (below) and the material after 2 weeks of aging (above).
mainly the presence of the intermediate dilithium 2-undecylimidazolium (0.74 ppm) and the ionic lithium species at −0.22 ppm. Single pulse $^7$Li MAS NMR experiments of this freshly prepared and aged material at room temperature are shown in Fig. 7b. The intensity of this resonance is dominant even at room temperature. Since the und-LiIm–LiCH$_3$SO$_3$ mixture became uniformly comprised of the intermediate species upon aging, 2D exchange experiments to examine exchange rates between the parent resonances of und-LiIm and the salt became irrelevant. Clearly, the possibility of exchange is most strongly evidenced by this transformation of the material into a homogenous compound.

Conductivity measurements by impedance spectroscopy have been attempted, but as yet have been unsuccessful due to the highly moisture-sensitive nature of the lithiated samples, and the lack of an appropriate sample chamber. Efforts to this end are ongoing in our laboratory. Such measurements would substantiate the long-range ion transport capabilities which are at this point inferred from the local mobility and exchange processes detected by solid-state NMR.

4. Summary and outlook

$^7$Li NMR studies confirm the synthesis of lithium imidazolium (LiIm), 2-undecylimidazolium (und-LiIm), the ionic salt LiCH$_3$SO$_3$, and the doped intermediate complexes, [Li−Im$^–$−Li CH$_3$SO$_3$] and [und-Li−Im$^–$−Li CH$_3$SO$_3$]. Exchange spectroscopy of a well ground mixture of the LiIm salt LiCH$_3$SO$_3$ supports the possibility of a 2-site ring reorientation for this doubly lithiated imidazole ring. Comparisons of $T_1$ spin-lattice relaxation values and the corresponding activation energies of the LiIm and the doped complex point to a higher degree of mobility in the latter.

$^7$Li MAS NMR spectra of pure lithium 2-undecylimidazolium and of the aged mixture [und-Li−Im$^–$−Li CH$_3$SO$_3$] mainly show the presence of the doubly lithiated imidazole at room temperature. This data supports the hypothesis that the material may exchange and transport lithium ions.

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