
Molecular interactions in lithium ion batteries: Identification of lithium species in non-aqueous propylene carbonate electrolyte by NMR

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Abstract

The electrolytic dissociation of lithium hexafluorophosphate (LiPF₆) in non aqueous cyclic propylene carbonate has been investigated in the 0.2 – 3.5 M concentration range by ⁷Li solution state NMR spectroscopy. ⁷Li NMR spectra provide evidence for the presence of different cationic species in the electrolyte. Using a spectral deconvolution procedure we have determined their relative composition at any given salt concentration. In the solvent rich regime (0.2 - 1.4 M) the free dissociated Li⁺ ions and the solvent separated ion-pairs (SSIP) are the dominant species, whereas in the salt rich regime the contact ion-pairs (CIP) become the dominant species. Additionally, our results show that the Li exchange among these sites occurs on a sufficiently slow NMR chemical shift time scale at room temperature ($k < 15$).

Key Words: Li-ion battery, electrolyte, non-aqueous carbonate solvent, ⁷Li NMR spectroscopy, lithium speciation

Introduction

Lithium ion batteries (LIBs) power our digital life and are extensively used in electronic devices. LIBs consist of electrodes, electrolyte and a separator. The most widely used electrolyte for LIBs is LiPF₆ in a non-aqueous carbonate solvent mixture, consisting of a cyclic carbonates, e.g, ethylene carbonate (EC), with one or more linear carbonates, e.g, dimethyl carbonate (DMC). The key to the battery performance is the Li-ion conduction in the liquid electrolyte medium which, in turn, is determined by the nature of Li ion species that exist in solution and the factors that govern the dynamics of the ion pairs. Considerable research has been reported in the last few years to better understand the nature of the Li-ion species formed in terms of solvation and coordination using a

variety of experimental and theoretical studies.

In so far as studies of Li-ion complexation in non-aqueous carbonate solvent is concerned, recent studies have dealt with the application of various techniques such as Raman,¹⁻² vibrational, infrared²⁻³ and molecular rotation^{1,3} spectroscopy. NMR spectroscopy, using ¹³C and ¹⁷O of the solvent molecule, has also been employed to glean valuable atomic level insights from the observed chemical shifts and analyzing them in term of the Li-ion coordination with the organic solvent molecules to determine the coordination number.³⁻⁵ Theoretical studies based on molecular dynamics simulations and density functional theory as well as quantum chemical calculations have been reported which not only complement the experimental findings but have enabled the determination of thermodynamic parameters.⁶

By and large, the studies on neat and mixed electrolytes reported thus far are mostly solvent focused and invariably studied in the solvent rich regime. While they do provide valuable insights on the

nature of primary and secondary solvation and also enable the determination of the solvent coordination number, no information about the non-solvated cation environments, such as the contact ion pairs (CIP) are provided from such studies.

The direct observation of Li-cation using ⁷Li NMR spectroscopy as a molecular characterization tool offers new opportunities to probe the cationic environments in the electrolyte at the atomic level. The lithium cation can be expected to exist in either of the three major species, namely, (i) the solvated and fully dissociated Li⁺; (ii) the solvent separated ion pair (SSIP) and (iii) the contact ion pair (CIP), which are the major species formed during the electrolyte dissociation.^{2,4} ⁷Li NMR thus enables the inspection of all these cation environments and hence affords their characterization. Besides, the evolution and build up of the different Li-species can be monitored and ascertained when ⁷Li NMR studies are conducted as a function of salt concentration. ⁷Li NMR offers a high detection sensitivity due to its large natural abundance (92.6 %) and, despite being quadrupolar (I=3/2), a high spectral

resolution is expected due to its small quadrupole moment. ^7Li NMR, therefore, provides a direct access to the local Li environments present under high resolution conditions and renders a study of lithium speciation in electrolytes readily feasible.

The present work deals with the direct application of ^7Li NMR spectroscopy to study the dissociation of LiPF_6 in non-aqueous cyclic propylene carbonate (PC) over the salt concentration range of 0.2 - 3.5 M with the main objective of providing first hand information on lithium ion speciation and their relative population at each concentration.

Experimental

Lithium hexafluorophosphate was purchased from Sigma Aldrich and used without further purification. Commercially available battery grade carbonate solvents, propylene carbonate (PC) was obtained from Sigma Aldrich and used after distillation. Electrolyte solutions of different concentrations (0.2 - 3.5 M with 0.2M incremental step) in PC solvent were prepared in an argon filled glove box (both H_2O and $\text{O}_2 < 0.1$ ppm) and transferred into

5 mm NMR tube and stored under a moisture free environment.

NMR experiments were carried out in the solution state at ambient room temperature (22-24 °C) on a Bruker Avance III 400 MHz NMR spectrometer at the Larmor frequency of ^7Li (155.506 MHz). ^7Li NMR spectra were acquired in the single pulse mode with a 30° flip angle pulse (4 μsec) and a 1 sec relaxation delay. Typically 40 free induction decays were acquired and Fourier-transformed with 1 Hz exponential line broadening. The ^7Li chemical shifts were referenced externally to 1M LiCl solution. All the spectral deconvolutions were carried out using DMFIT software.⁷ A mixed Gaussian/Lorentzian line shape (G/L =0.5) was used and the experimental spectra were iteratively fitted to arrive at the lithium species present and estimate their relative population.

Results and Discussion

Figure 1 (A) shows the ^7Li -NMR spectra of LiPF_6 at different concentrations in the range 0.2 – 3.5 M in non-aqueous organic propylene carbonate solvent. The NMR spectra mainly show a dominant signal with clearly noticeable shift of the resonance with

increasing concentration. A careful inspection of the ^7Li -NMR spectra shows that the line shape is not a single Lorentzian as expected for an exchange narrowed line which is typical for a dynamically averaged cationic environment in dynamic equilibrium. This is clearly not the case as seen by the marked asymmetry in the line

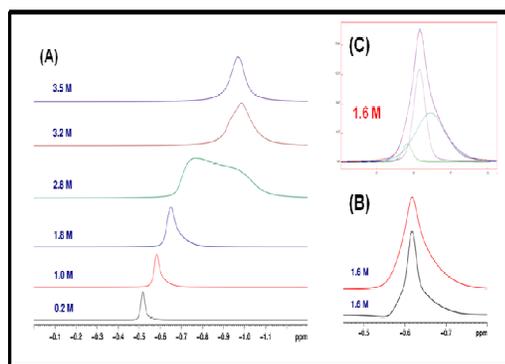


Figure 1. (A) ^7Li -NMR spectra of LiPF_6 in propylene carbonate at different salt concentrations. (B) Resolution enhanced ^7Li -NMR spectrum of 1.6 M. (C) Spectral deconvolution of (B) using a mixed Gaussian/Lorentzian (0.5) line shape function.

shape which can be noticed in **Figure 1**, especially in the spectra recorded at higher concentrations. This can be attributed to the spectral overlap among distinctly different lithium sites which have small difference in their chemical shifts. The observed signal line shape and the intensity profile are entirely governed by the lithium species

present and their actual composition in a given concentration. This can be more readily seen from the resolution enhanced spectrum, such as the one shown in **Figure 1 (B)** for 1.6 M solution, which clearly shows that there are three overlapping signals which constitute the observed ^7Li spectral line shape. Independent ^7Li spin-lattice (T_1), spin-spin (T_2) relaxation time measurements of 1.6 M solution reveal a triple exponential relaxation behaviour for the total integrated signal intensity and additionally confirm our above spectral interpretation.

The observed ^7Li NMR spectra at each concentration was de-convoluted to reveal the various lithium species present. De-convolution of the of 1.6 M solution is shown in **Figure 1 (C)** and the presence of three distinct lithium sites is at once identified. The concentration dependence of the ^7Li NMR response shows that at low concentrations down to 1.4 M the NMR spectrum comprises only two components, whereas, at higher concentrations an additional component is required to fit the observed ^7Li line shape. These observations and the de-convolution procedure that we have used have therefore enabled us to

monitor not only the Li species formed, but also get quantitative estimates of their relative population at any given concentration. The lithium cation speciation from ^7Li NMR has also enabled the determination of ^7Li chemical shifts at each concentration for the different species present. It may be remarked that the chemical shifts ascribed to each species are determined more accurately in the present study when compared to previous studies which assume that the ^7Li NMR spectrum consists of a single unresolved resonance.⁸ This has, in turn, allowed monitoring the NMR behaviour for the dissociated Li-ion, SSIP and CIP species in a way that had not been possible before.

The lithium cation speciation of LiPF_6 in propylene carbonate is shown in **Figure 2**. The three lithium species detected from ^7Li NMR are labeled as Li (1), Li (2) and Li (3), respectively. Plots in **Figure 2** show the variation of the relative population for the above three Li species as a function of the salt concentration. Li (1) and Li (2) begin to emerge at the lowest concentration of 0.2 M with a large number of lithium cations getting preferentially populated at Li

(1) sites. This enables us to associate the two species Li (1) and Li (2), detected in the 0.2 - 1.4 M range, to the dissociated and charged Li^+ ions in the propylene carbonate solvent and the solvent separated ion pairs (SSIP), respectively.⁶ Initial confinement of lithium

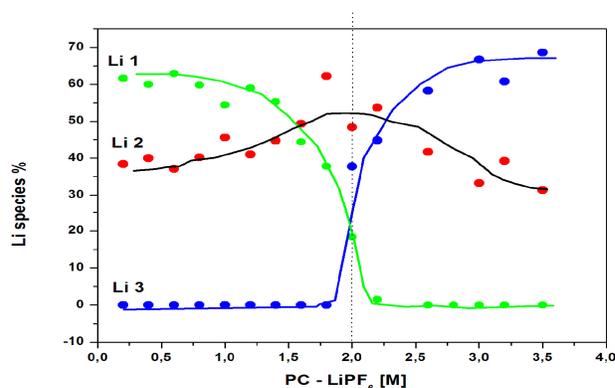


Figure 2. Lithium speciation determined from ^7Li -NMR and the variation in lithium site population for the electrolyte solution of LiPF_6 and propylene carbonate.

into the Li (1) and Li (2) environments and the large deficiency at Li (2) sites tends to allow the Li (2) population to grow as more and more lithium is consumed from the electrolyte at increasing concentrations. Since the total lithium is distributed only among Li (1) and Li (2) sites, increase in the population of Li (2) sites would tantamount to a progressive decrease of the Li (1) site population as the concentration of the salt solution is increased. This is indeed noticed

in **Figure 2** in the concentration range 0.2 - 1.6 M until an equitable distribution of lithium into Li (1) and Li (2) sites is seen to occur at 1.6 M. Remarkably, Li (3) emerges only beyond 1.6 M and becomes the dominant species at 2.6 M and above. Since for the cyclic carbonate contact ion pairs are favoured only at high salt concentrations, Li (3) can be readily assigned to the lithium cation belonging to CIPs. Our ^7Li NMR results show that in the solvent rich regime the lithium speciation occurs in a way that the fully dissociated and solvated charged (Li^+) and solvent separated ion pairs (Li^+ - solvent - PF_6^-), i.e., Li (1) and Li (2), respectively, are the dominant species. On the other hand, in the high salt rich regime, cations in the contact ion pairs ($\text{Li}^+\dots\text{PF}_6^-$) are the dominant species, although the fully solvated lithium ions are by no means insignificant in number.

Conclusions

^7Li -NMR spectroscopy has been utilized to study the lithium cation speciation in the electrolyte solution of LiPF_6 in non-aqueous organic propylene carbonate. Lithium belonging to the solvated and fully dissociated (Li^+), solvent separated and ion

paired (SSIP) and contact ion pairs (CIP) have been identified from ^7Li NMR spectra and their populations at different salt concentration have been quantitatively determined. The dominance of the former two species in the solvent rich regime and that of the latter two species at high salt concentrations have been borne out from these studies.

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References

1. Qiao, H.; Luan, H.; Fang, X.; Zhou, Z.; Yao, W.; Wang, X.; Li, J.; Chen, C.; Tian, Y. *J. Mol. Stru.* **2008**, *878*, 185.
2. Burba, C. M.; Frech, R. *J. Phys. Chem. B* **2005**, *109*, 15161.
3. Seo, D. M.; Reininger, S.; Kutcher, M.; Redmond, K.; Euler, W. B.; Lucht, B. L. *J. Phys. Chem. C* **2015**, *119*, 14038.
4. Yang, L.; Xiao, A.; Lucht, B. L. *J. Mol. Liq.* **2010**, *154*, 131.
5. Bogle, X.; Vazquez, R.; Greenbaum, S.; Cresce, A. v. W.; Xu, K. *J. Phys. Chem. Lett.* **2013**, *4*, 1664.
6. Aroca, R.; Nazri, M.; Nazri, G. A.; Camargo, A. J.; Trsic, M. *J. Sol. Chem.* **2000**, *29*, 1047.
7. Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli,

B.; Gan, Z.; Hoatson, G. *Mag. Reson. Chem.*
2002, *40*, 70.

8. Kondo, K.; Sano, M.; Hiwara, A.; Omi, T.;
Fujita, M.; Kuwae, A.; Iida, M.; Mogi, K.;
Yokoyama, H. *J. Phys. Chem. B* **2000**, *104*,
5040.