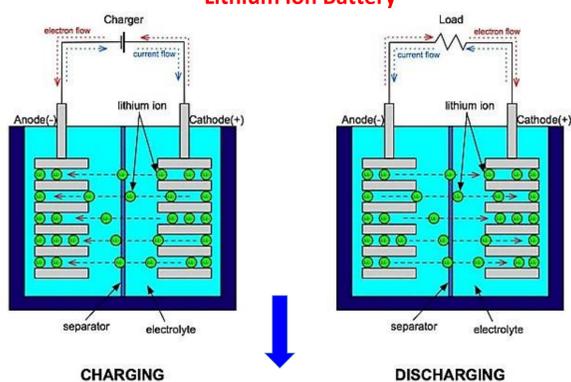


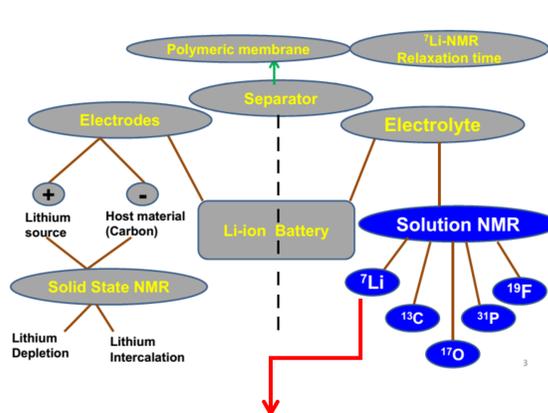
ABSTRACT

Lithium ion batteries (LIBs) power our digital daily life and are extensively used in electronic devices and tools. The key to the battery performance is the Li-ion conduction in the liquid electrolyte medium and this is crucially determined by the kind of Li species that exist and the various factors governing these species. Much of the research efforts in the last few years are focused on studying the effects of solvation. While valuable insights are provided from observed chemical shifts leading to the determination of the solvent coordination number, no information about the non-solvated cation environments, such as the contact ion pairs (CIP), is provided as such studies are invariably done in the solvent-rich regime (< 1.4 M). The present work deals with a study of electrolytic dissociation of lithium hexafluorophosphate (LiPF_6) in non-aqueous cyclic propylene carbonate (PC) in a large 0.2 – 3.5 M concentration range by ^7Li solution state dynamic NMR spectroscopy under high sensitivity and resolution. Relaxation and diffusion measurements have been used in conjunction with ^7Li NMR spectral measurements to know the kind of dissociated cationic species that exist in the electrolyte solution.

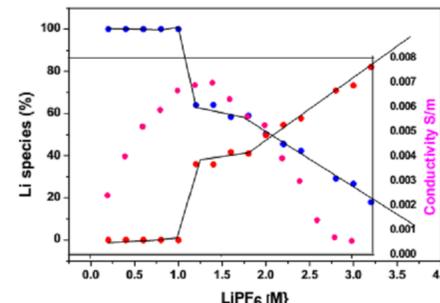
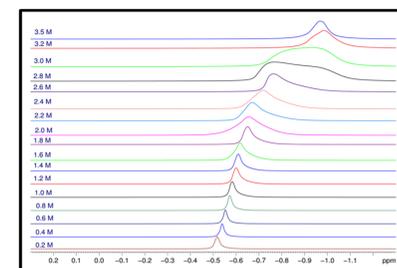
Lithium Ion Battery



NMR for Li-ion Batteries

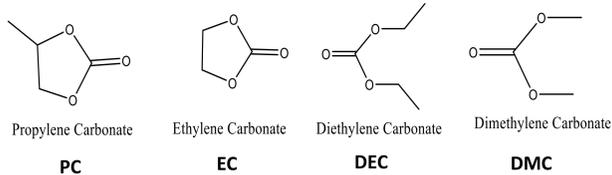
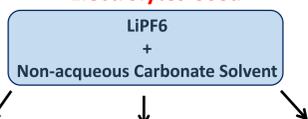


^7Li NMR of LiPF_6 in PC



- Marked changes in ^7Li chemical shift and the line shape.
- Two distinct Li species revealed by spectral deconvolution beyond 1 M. Dissociated Li distributed among two chemically distinct species.
- Dominance of entirely PC-solvated Li at 1 M and below.
- Emergence of Li^+ ion-paired to PF_6^- at 1.2 M and above and increase in relative population of CIP species beyond 2M.
- ^7Li NMR observations are in good accord with conductivity data providing molecular basis for the bulk behavior.
- ^7Li NMR evidences that for optimal battery performance the electrolyte concentration is best chosen at 1 – 1.2 M and is validated in actual use..

Electrolytes Used



The choice of the electrolyte is key to the battery performance. The concentrations such that it should provides a high carrier density and at the same time a facile movement of the Li ion in the medium. Li-ion shuttling from cathode to anode (during charging) and anode to cathode (during discharging) is greatly influenced by the types of cationic species that are formed during the dissociation process.

Experimental

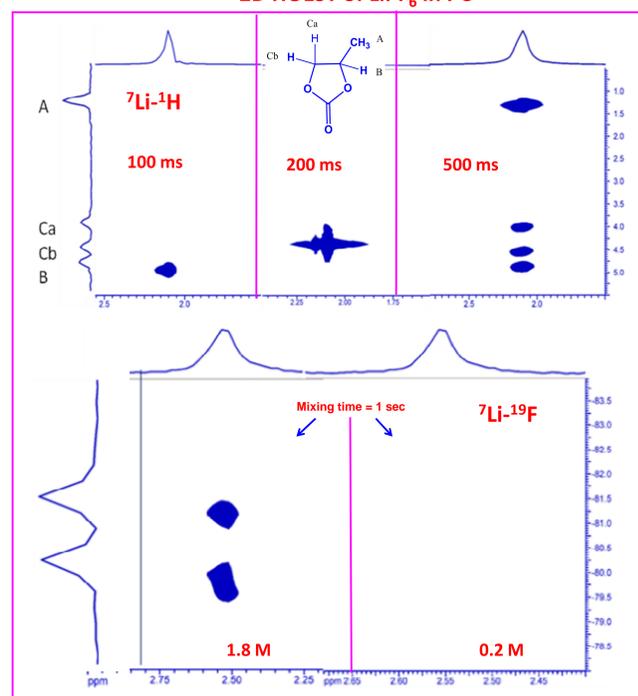
Electrolyte solutions of LiPF_6 in PC were prepared in argon filled glove box with H_2O and O_2 level < 0.1 ppm. Sample solutions were prepared from stock solution (LiPF_6 in PC) and 0.5 ml solution were transferred into 5 mm NMR tube in the concentration range from 0.2 to 3.5 M (total of 17 samples for the present studies).

NMR spectra and relaxation time (T_1 , T_2) data were acquired in the solution state at ambient room temperature (22-24 °C) on a Bruker Avance III 400 MHz spectrometer at the ^7Li Larmor frequency of 155.506 MHz, employing the standard inversion recovery and CPMG sequences and using 55 (T_2) or 85 (T_1) tau delays. The 90° pulse was 8 usec and 16 scans were acquired for each of the delays used. Relaxation data were fitted using the Dynamic Center module available in Topspin 3.5.

Diffusion experiments were performed on a JEOL 500 MHz NMR spectrometer operating at the Larmor frequency of 194.38 MHz and equipped with a diffusion accessory providing a maximum gradient strength of 30 G/cm. All diffusion measurements were performed with the bipolar pulse pair longitudinal encode-decode (BPPLD) pulse sequence. In the diffusion measurement, the experimental variables gradient duration (d) and diffusion time (D) were fixed at 10 ms and 200 ms, respectively, while the amplitude of the gradient (g) varied from 20 to 280 mT/m in 15 steps. The diffusion coefficients were obtained by nonlinear fitting of the experimental data to the Stejskal-Tanner equation. All the NMR spectral, relaxation and diffusion measurements were carried out at ambient probe temperature (23 -25 °C) .

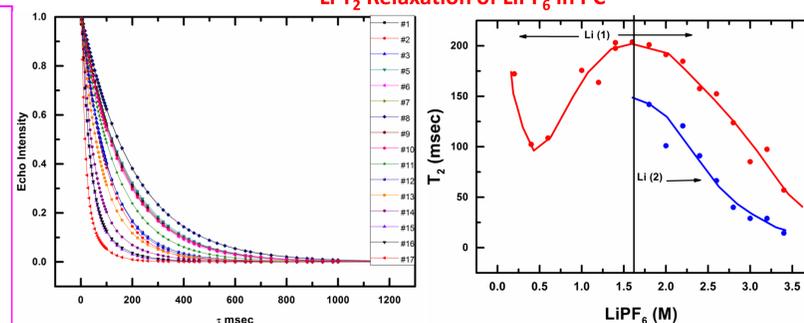
For the LiPF_6 + PC system, ^7Li NMR spectroscopy offers the following advantages: 1) High detection sensitivity even at lower concentrations; 2) Minimal life time broadening due to small quadrupole effects and vanishing electric field gradients; 3) Affords faster spectral and relaxation measurements and derive information about the types of Li species that exist; 4) Further extension of these measurements under actual battery cycling conditions *in situ*,

2D HOESY of LiPF_6 in PC

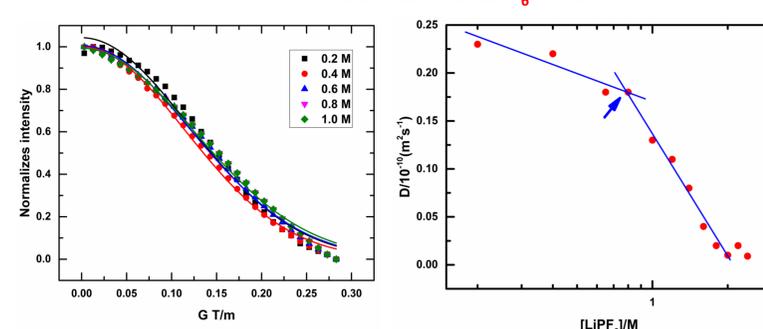


- 2D ^7Li - ^1H and ^7Li - ^{19}F HOESY experiments were performed on 0.4 M LiPF_6 in PC. with an aim to probe the Li-solvent and Li ion-pair interactions, respectively.
- In the former case, Li-solvent interaction is clearly evidenced and the mixing dependent study shows that the Li interaction with the solvent is strongest at the carbonyl oxygen site.
- No HOESY signal can be detected in the ^7Li - ^{19}F HOESY except when the electrolyte concentration is quite high (e.g., 1.8 M) and this evidences the formation of contact ion pair (CIP) and additionally supports the ^7Li NMR spectral results and analysis.

^7Li T_2 Relaxation of LiPF_6 in PC



^7Li Diffusion of LiPF_6 in PC



- ^7Li spin-spin relaxation (T_2) is well fitted to a single component behavior at early concentrations (0.2 – 1.6 M) but shows a biexponential decay at higher concentrations.
- Li interaction with the solvent (PC) molecules and the increase in the relaxation rate upon solvent binding in the solvent rich regime is clearly evidenced..
- The emergence of the ion-paired Li at > 1.8 M is clearly evidenced and its increased relaxation efficiency in comparison to the solvated Li species is also borne out.
- Li interaction with the solvent (PC) molecules and the increase in the relaxation rate upon solvent binding in the solvent rich regime is clearly evidenced.
- ^7Li diffusion measurements depict distinct profiles for the spin-echo decay acted on by translational cation mobility (A).
- To a first degree the diffusion data were fitted to a single component decay and a plot of diffusion coefficient versus the electrolyte concentration (B) shows a variation which can be characterized by Li ion in two distinct environments with different translational degree of freedom.
- Further improvement to observe the entire decay and fit the experimental data to two or more components need much stronger field gradient strengths than that is presently available.

CONCLUSIONS

^7Li -NMR spectroscopy has been utilized to study the lithium cation speciation in the electrolyte solution of LiPF_6 in non-aqueous organic carbonate solvents (PC, DMC and EC/DMC).

Lithium belonging to the solvated and fully dissociated solvent associated Li^+ and ion paired (CIP) $\text{Li}^+ \cdot \text{PF}_6^-$ have been identified from ^7Li NMR spectra and their relative population at each electrolyte concentration has been estimated. 2D HOESY experiments show that for the cyclic propylene carbonate the Li-solvent interaction is the strongest at the carbonyl oxygen. Strong ion-pair interaction is also evidenced at high electrolyte concentrations.

Spin-spin relaxation results additionally support the above conjecture and lends for further analysis of the dynamic data to assess the relative population of the Li species present in the electrolyte.

Diffusion measurements indicate a break point and demarcates two different Li species, namely the solvated species at low concentrations and the ion-paired species at high concentrations. Much stronger gradients are warranted in further studies and for proper fitting of the ^7Li diffusion data.

Overall, ^7Li NMR results show that for good bulk Li conductivity in the electrolyte medium, the salt concentration is optimum at 1 – 1.2 M.

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