



Multinuclear magnetic resonance investigation of cation-anion and anion-solvent interactions in carbonate electrolytes

Jing Peng^{a,b}, Mallory Gobet^a, Matthew Devany^c, Kang Xu^d, Arthur von Wald Cresce^d, Oleg Borodin^d, Steven Greenbaum^{a,*}

^a Department of Physics & Astronomy, Hunter College of the City University of New York, New York, NY 10065, USA

^b Doctoral Program in Chemistry, The Graduate Center of City University of New York, New York, NY 10016, USA

^c Department of Chemistry and Biochemistry, Hunter College of the City University of New York, New York, NY 10065, USA

^d Electrochemistry Branch, Sensor and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, MD 20783, USA

HIGHLIGHTS

- Ion-ion and ion-solvent interactions in carbonate electrolytes were investigated.
- The solvation behaviors of LiPF₆ and LiBF₄ in EC/DMC were studied by NMR.
- Spectroscopic results on ion solvation and pairing borne out by NMR diffusometry.

ARTICLE INFO

Keywords:

Ion-solvent
Ion-ion interactions
Nuclear magnetic resonance
Carbonate electrolyte
Lithium ion battery

ABSTRACT

The investigation of ion-solvent interaction in electrolytes is crucial for basic understanding of ion transport through the bulk electrolyte as well as interphase formation processes on both electrodes, which dictate performances of lithium ion batteries (LIBs). In this report, nuclear magnetic resonance (NMR) was used to study the solvation behaviors of two typical lithium salts (lithium hexafluorophosphate, or LiPF₆, and lithium tetrafluoroborate, or LiBF₄) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) mixtures. With increasing salt concentration and DMC percentage in both systems, ¹⁹F NMR experiences an upfield shift along with decreasing $J_{31P-19F}$ and $J_{11B-19F}$, which evidence the stronger interaction between the Li⁺ and F⁻ in an environment with diminishing presence of high dielectric medium. The quadrupolar relaxation of ¹¹B dominates the ¹⁹F relaxation mechanism and demonstrates that LiBF₄ mainly exists as ion pairs in solution either at high salt concentration or in a medium of low polarity. ⁷Li, ¹⁹F, ¹H NMR diffusion measurements were conducted to characterize the relative mobility of cation, anion and solvent molecules, the results of which support the conclusion above. Salt concentration and solution polarity have a much stronger effect on cation-anion aggregation and solvation in the LiBF₄ system than in the LiPF₆ system.

1. Introduction

Lithium ion batteries (LIBs) are in ever-increasing demand for their wide applications in markets of portable electronic devices, plug-in Hybrid Electric Vehicles (PHEV), and large-scale grid-storage units *etc.* In all these LIB devices, electrolyte consisting of lithium salt dissolved in aprotic polar solvents is a critical component that dictates the cycle life, power density and safety of LIBs. Among the organic solvents available, only a limited number of carbonate esters were found to be able to support the reversible intercalation chemistries employed by LIBs, and in most cases mixtures of cyclic and acyclic carbonates have

to be used to reach an optimum balance of diversified considerations including ion transport, viscosity and interfacial chemical behaviors [1]. Despite the many possible combinations of cyclic and acyclic carbonate esters, one cyclic solvent, ethylene carbonate (EC), is indispensable because of its especially high dielectric constant and its outstanding ability to protect the graphite anode [2]. Dimethyl carbonate (DMC) is a popular acyclic carbonate and is frequently paired with EC in standard LIB electrolyte formulations. Among the salts, lithium hexafluorophosphate (LiPF₆) was proposed as an electrolyte salt in the 1960s. After decades of screening, it stood out above numerous lithium salts and was eventually adopted by commercial LIBs manufacturers.

* Corresponding author. 695 Park Avenue, Room 1220N, New York, NY 10065, USA.
E-mail address: sgreenba@hunter.cuny.edu (S. Greenbaum).

However, LiPF₆ also brought restrictions because of its comparatively high moisture sensitivity and low thermal stability [3,4]. Compared with LiPF₆, lithium tetrafluoroborate (LiBF₄) has been known as relatively safe [5], less moisture-sensitive [6] and delivers better performance under certain conditions [7]. With these advantages over LiPF₆ in mind, the lower dissociation constant and low ion conductivity of LiBF₄ constitute obstacles to its extensive applications in LIBs [1,8,9].

A high ionic conductivity and consequently a low ionic association are generally preferred for a successful electrolyte in supporting the cell reactions. Designing an ideal Li-ion electrolyte requires a better understanding of the fundamental mechanisms of ion dissociation and transport. Ding et al. concluded that cation-solvent interactions play a dominant role in determining the charge transport ability, while solvent interactions with the anion influence the formation of cation-anion aggregates [10,11]. Hence, it is important to understand how solvent molecules interact with anions, since such interactions predict the formation and states of aggregates in the electrolytes, thereby influencing the charge transfer ability and kinetics of cell reactions.

Nuclear Magnetic Resonance (NMR) spectroscopy is a sensitive tool used to probe the local environments of ions and solvent molecules, which in turn reflects respective solvation and interaction behaviors. Previous works employing NMR have concentrated on cation solvation. Cation solvation can be clearly identified by NMR because cation-solvent interactions change the electronic environment of certain nuclei in both cation and solvent, resulting in NMR chemical shift variation. Early ¹³C NMR studies suggested preferential Li⁺ solvation by cyclic EC rather than by acyclic diethyl carbonate (DEC) and DMC [12]. Such an observation was confirmed using ¹⁷O-NMR, which directly monitors the nuclei that interact with Li⁺ [13,14]. Another important parameter obtained from NMR, the *J* coupling constant, also exhibits the species-specific interaction information. Research has shown that the ¹¹B-¹⁹F coupling constant of LiBF₄ tends to increase in environments with higher LiBF₄ concentration (i.e. more aggregation) [15] and lower dielectric constant [16]. Inter-ionic interactions, such as ion pairing, is reported to be very effective at distorting the electric field gradient of an anion nucleus with a quadrupole moment, which influences the lineshape and relaxation time of certain nuclei on anions [17–21]. In addition, NMR diffusometry provides supplemental information on ion pairing interactions [22].

In this report, we focus on the solvent effects by applying NMR techniques on two electrolyte systems with LiPF₆ and LiBF₄ salts, respectively. *J* coupling constants and relaxation time, which determine the lineshape of NMR spectra [23], are carefully examined for ¹⁹F and ¹¹B nuclei, as ionic association affects spectral parameters as well as self-diffusion coefficients. Systematic studies on temperature dependence of self-diffusion coefficients for cations, anions and solvents have been previously reported for LiBF₄ and LiPF₆ salts in EC, propylene carbonate (PC), and DEC single solutions and EC/DEC binary solution system [22,24], but the current work here pays more attention to the effects of salt concentrations and co-solvent ratios in awareness of recent thrusts on super-concentrated electrolytes and the numerous new properties they exhibit [25,26]. As described by Stokes-Einstein equation (1), the effective ion radius is related to the diffusion coefficient of the ion:

$$r = \frac{k_B T}{6\pi\eta D} \quad (1)$$

where *r* is the effective radius of an ion, *k_B* is Boltzmann's constant, *T* is temperature, *η* is the viscosity, and *D* is the diffusion coefficient. The pulse field gradient NMR method accurately measures the self-diffusion coefficient of individual cation, anion and solvent by appropriate choice of a particular nucleus [22,27,28]. To augment the anion solvation studies on LIBs electrolytes, in this work we monitor ¹⁹F, ¹¹B NMR spectra (chemical shift, *J* coupling constant), ¹¹B spin relaxation, detailed lineshape analysis and ¹H, ⁷Li, ¹⁹F diffusion measurements in an

effort to better understand the ionic association and solvent interaction in these systems.

2. Experimental

2.1. Electrolyte preparation

LiPF₆ (Morita Chemical Industries) and LiBF₄ (Ferro) were stored in an argon-filled glovebox (Vacuum Atmospheres Nexus One, < 1 ppm O₂, < 1 ppm H₂O). EC (BASF) and DMC (BASF) were dried over 3 Å molecular sieves and then filtered to store in an argon-filled glovebox until needed. LiPF₆ and LiBF₄ were dissolved in EC and DMC binary mixture at mole ratio of 80/20, 50/50, 20/80 and 0/100. The LiPF₆ solutions were prepared at five concentrations of 0.01 M, 0.05 M, 0.5 M, 1.0 M, and 1.2 M, while the concentration of LiBF₄ was 0.01 M and 1 M. Preparation of electrolyte solutions was conducted in a glove box under argon atmosphere.

2.2. NMR characterization

The NMR experiments were done with a 400 SB Bruker Avance III spectrometer (9.4 T). The samples were sealed in NMR tubes in the glovebox in order to prevent moisture absorption and air exposure. Each sample was placed in a 4 mm Teflon tube and inserted in a 5 mm NMR tube containing a chemical shift reference in deuterated solvent. This set-up prevents any possible reaction between the electrolyte sample and the reference material, and allows for an optimal chemical shift referencing, and adjustment of magnetic field homogeneity (i.e. shimming) using a ²D lock signal for each sample. The external reference solutions (set to 0 ppm) were CFCl₃ in CDCl₃ for ¹⁹F experiments and boric acid in D₂O for ¹¹B experiments. All spectra were collected using a direct excitation single pulse sequence, while ¹¹B spin-lattice relaxation times (*T*₁) and ¹¹B spin-spin relaxation times (*T*₂) were collected by using inversion-recovery and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences, respectively. Multiplet line shapes were simulated using Dmfit software (*J* multiplet mode) [29].

The diffusion NMR experiments were performed using a double-stimulated-echo sequence [30] at 25 °C. The gradient pulse duration *δ* was 1.2–4 ms, the diffusion delay *Δ* = 150–400 ms. The diffusion coefficient *D* is measured as the only fitting parameter by plotting the signal intensity *I* versus gradient strength using the Stejskal-Tanner equation (2) [31,32]. The diffusion of the EC and DMC molecules, cation and anion were measured using ¹H, ⁷Li and ¹⁹F NMR operating at (400, 155.5 and 376.5) MHz respectively.

$$I = I_0 * e^{-D(\gamma g \delta)^2 (\Delta - \frac{\delta}{3})} \quad (2)$$

In Equation (2), *I*₀ is the signal in absence of the field gradient, *g* is the gradient strength, and *γ* is gyromagnetic ratio of the studied nucleus.

3. Results and discussion

3.1. PF₆⁻ analysis

¹⁹F NMR experiments were performed on five LiPF₆ electrolytes series (five concentrations ranging from 0.01 M to 1.2 M with several EC/DMC ratios of 80/20, 50/50, 20/80 and 0/100). Since the melting point of EC is ~35 °C, the electrolyte with EC/DMC ratio of 100/0 was not prepared for measurements. The digital resolution of ¹⁹F NMR was 0.3 Hz. ¹⁹F and ³¹P are both 100% natural abundance isotopes with nuclear spin ½, therefore ¹⁹F NMR spectrum (not shown) of LiPF₆ exhibits typical lineshape of a doublet characterized by a large *J* coupling between fluorine and phosphorus nuclei. The absence of additional fluorine resonance evidences the stability of LiPF₆ in EC/DMC solvents.

Download English Version:

<https://daneshyari.com/en/article/7724781>

Download Persian Version:

<https://daneshyari.com/article/7724781>

[Daneshyari.com](https://daneshyari.com)