



Natural abundance ^{17}O nuclear magnetic resonance and computational modeling studies of lithium based liquid electrolytes



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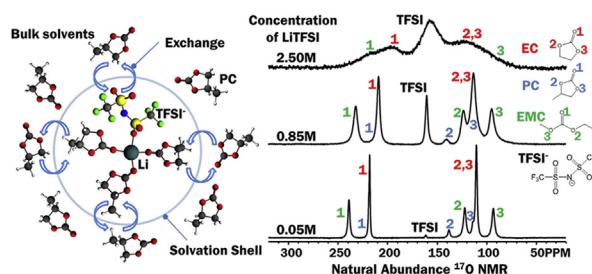
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HIGHLIGHTS

- We obtain high SNR spectra of natural abundance O-17 NMR.
- Solvation structures are verified by chemical shift calculation.
- Coordination number of first solvation shell is four.
- Coordinated and free solvent molecules exchange fast with each other.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural abundance ^{17}O NMR measurements were conducted on electrolyte solutions consisting of Li [CF₃SO₂NSO₂CF₃] (LiTFSI) dissolved in the solvents of ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC), and their mixtures at various concentrations. It was observed that ^{17}O chemical shifts of solvent molecules change with the concentration of LiTFSI. The chemical shift displacements of carbonyl oxygen are evidently greater than those of ethereal oxygen, strongly indicating that Li⁺ ion is coordinated with carbonyl oxygen rather than ethereal oxygen. To understand the detailed molecular interaction, computational modeling of ^{17}O chemical shifts was carried out on proposed solvation structures. By comparing the predicted chemical shifts with the experimental values, it is found that a Li⁺ ion is coordinated with four double bond oxygen atoms from EC, PC, EMC and TFSI⁻ anion. In the case of excessive amount of solvents of EC, PC and EMC the Li⁺ coordinated solvent molecules are undergoing quick exchange with bulk solvent molecules, resulting in average ^{17}O chemical shifts. Several kinds of solvation structures are identified, where the proportion of each structure in the liquid electrolytes investigated depends on the concentration of LiTFSI.

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1. Introduction

Electrolytes, responsible for transferring ionic components, play a critical role in energy storage systems such as rechargeable

lithium ion batteries (LIBs) and redox flow batteries (RFBs), with the former based on solid-state electroactive materials while the latter on those dissolved in the electrolytes. The LIB technology has become increasingly important recently benefited from the combined high energy and high power density. Today, LIBs are widely used on cell phones, laptop computers and other portable devices, and are recently employed to revolutionize ground

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transportation via electric vehicles (EV) and hybrid electric vehicles (HEV) [1–3]. On the other hand, RFB has enjoyed a recent renaissance fueled by the rapidly evolved global energy profile and the need for large-scale stationary energy storage devices. By providing wider electrochemically stable voltage windows, the emerging nonaqueous RFB (NRFB) has great potential to overcome the low energy density challenge present in current state-of-the-art aqueous RFB technologies [4–7]. Typically, LIBs and NRFBs share the electrolytes with similar formulations including the solvents, the charge carrier salts, the additives, and their concentrations [8,9]. Therefore, an in-depth fundamental understanding of the electrolyte systems could shed light on both systems aiming at performance improvement.

The choice of electrolyte (i.e., solute + solvent) plays a key role in the Li^+ -based energy storage systems regardless of LIBs or NRFBs. The conductivity of the electrolytes directly influences the rating performance of the batteries, and their electrochemical stability determines the cycle life and safe operation of the batteries [10]. Alkyl carbonates were found to be the most suitable solvents for electrolytes [11], attributed to their high electrochemical stability, a reasonable temperature range between freezing and boiling points, sufficiently low toxicity, and acceptable safety features [12]. The current model electrolyte systems prevalently use mixtures of alkyl carbonates including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl-methyl carbonate (EMC) as the solvent [2,3,10,12–14]. On the other hand, among the many Li salts, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is one of the most attractive options because the TFSI⁻ is a large anion with delocalized charge and usually has lower binding to Li^+ thus yielding more free Li^+ cations available for charge transport (Chart 1) [15]. Selection of the electrolyte compositions and determination of their relative ratios usually are driven by the requirements for advanced battery performance such as high conductivity, good chemical and electrochemical compatibility, low volatility of the electrolyte, etc. [2,12,16]. The solvation phenomenon where the ions actively interact with the solvent molecules commonly exists in electrolyte systems and plays an important role in determining the properties of the electrolyte. In-depth understanding of the solvation structures of ions is critically important for designing improved electrolytes that offer optimized properties for the electrolyte and enhanced performance for batteries. Up to now, there are only a few investigations on understanding the properties of the mixed electrolytes with Li salt, where molecular dynamics (MD) simulations and diffusion measurements were employed [15,17–23]. As this is an emerging field of research, there are indeterminate understandings reported from prior studies on the Li^+ solvation structure and the ion association in carbonate solvent [15,24–26]. For example, in the case of EC the number of molecules bound to the Li^+ ion reported by Borodin et al. is 3.8 on average in LiTFSI/EC system [15], while Bhatt et al. concluded that the leading component is the four-coordinated complex, $\text{Li}^+(\text{EC})_4$. For PC, on the other hand, Kameda et al. proposed a coordination number of 4.5 for LiPF₆/PC electrolyte [24], and similar result has been calculated by Smith et al. with X-Ray absorption spectroscopy [25], but in the study of Brooksby et al., the number of solvating PC molecules around the Li^+ ions is more consistent with 3 [26]. For the mixed solvent, Vatamanu et al. obtained a total coordination number around 3.7 in the system of LiPF₆ in the mixture of EC and DMC [22]. Furthermore, little is known on the detailed changes of the solvation structures and molecular dynamics as a function of the increased solute concentration primarily due to the serious lacking of an enabling experimental investigation method.

Nuclear magnetic resonance (NMR) spectroscopy, a non-destructive and atomic specific tool, is ideal for such an investigation because it can offer a molecular view of the chemical sites of ions in the solvation structure. ¹³C and ¹⁷O NMR have been attempted to investigate the Li^+ solvation structures in electrolytes related to Li-ion batteries [27–29]. ¹⁷O NMR is more attractive due to the large chemical shift range, i.e., a couple of thousands ppm that is a potentially very sensitive probe for investigating the subtle changes of the interaction between an O atom and a Li^+ . However, ¹⁷O NMR investigations are challenging because of the extremely low natural abundance (0.037%) of the NMR-active ¹⁷O, making it one of the most difficult nuclei to observe by NMR spectroscopy [30,31]. Most of the ¹⁷O NMR in the literature used isotopic enrichment for enhanced signal to noise ratio (SNR), or took a very long time for signal averaging [32]. But isotope enrichment is often prohibitively expensive, and long-time data acquisition is too time-consuming and is unable to capture the transient changes in the structures, both making the ¹⁷O NMR insufficiently practical for most research and limiting its broad application. Bogle et al. employed ¹⁷O NMR for the first time as a molecular probe to understand how Li^+ from LiPF₆ interacts with EC and DMC [27], where the resonances corresponding to EC and DMC, each contributing only two well resolved peaks, were well separated from each other over the LiPF₆ concentration studied (a favorable case for NMR study) [27]. A solvation structure of Li^+ with the first solvation sheath containing four EC and the 2nd solvation sheath containing six EC molecules in the mixture of EC was proposed based on results obtained by varying the ratio of EC to DMC while keeping the concentration of LiPF₆ constant, i.e., at 1.0 M. Key conclusions from these authors included that a maximum number of six EC molecules can be associated with one Li^+ and there exists fast exchange of EC molecules in the 2nd solvation sheath with bulk EC molecules under the condition of excessive EC molecules; and EC preferentially bonds with Li^+ than DMC.

In this work, a highly sensitive ¹⁷O NMR technique using a combination of a large-sample-volume (LSV) NMR probe and an ultrahigh magnetic field of 21.1 T was employed to study the solvation structures of LiTFSI in pure and mixed solvents of EC, PC and EMC based on changes in chemical shift and linewidth. A total of eight resonant ¹⁷O NMR peaks were observed on a mixture containing EC, PC and EMC, a case that was much more challenging than previous investigation. To obtain a detailed physical picture on how a Li^+ interacts with EC, PC and EMC, computational modeling of the ¹⁷O NMR chemical shifts were used to accurately interpret the experimental results and related the experimental observations to the detailed molecular interaction associated with Li^+ solvation structures.

2. Experimental

2.1. Materials and sample preparations

LiTFSI, EC, PC and EMC were purchased from BASF (Florham Park, NJ) and were used as received. All the sample preparations were performed in a MBraun Labmaster Ar-filled glove box (Stratham, NH) with water and O₂ contents less than 1 ppm. A variety of samples were prepared by dissolving LiTFSI in the specified solvents, whose concentrations and compositions are summarized in Table 1.

2.2. NMR measurements

Since EC is a solid at room temperature, EC was dissolved in dichloromethane-*d*₂ (CD₂Cl₂) at saturated concentration to obtain the ¹⁷O NMR for neat EC. The effect of CD₂Cl₂ will be discussed in

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