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Nuclear magnetic resonance studies of the solvation structures of a high-performance nonaqueous redox flow electrolyte

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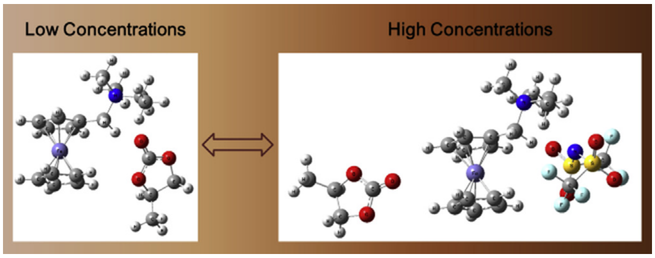
HIGHLIGHTS

- Dissolution mechanism of new active material is figured out.
- Solvation structures are verified by chemical shift calculation.
- Coordinated and free solvent molecules exchange fast with each other.
- High SNR spectra of natural abundance O-17 NMR are obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding the solvation structures of electrolytes is important for developing nonaqueous redox flow batteries that hold considerable potential for future large scale energy storage systems. The utilization of an emerging ionic-derivatived ferrocene compound, ferrocenylmethyl dimethyl ethyl ammonium bis(trifluoromethanesulfonyl)imide (Fc1N112-TFSI), has recently overcome the issue of solubility in the supporting electrolyte. In this work, ^{13}C, ^{1}H and ^{17}O NMR investigations were carried out using electrolyte solutions consisting of Fc1N112-TFSI as the solute and the mixed alkyl carbonate as the solvent. It was observed that the spectra of ^{13}C experience changes of chemical shifts while those of ^{17}O undergo linewidth broadening, indicating interactions between solute and solvent molecules. Quantum chemistry calculations of both molecular structures and chemical shifts (^{13}C, ^{1}H and ^{17}O) are performed for interpreting experimental results and for understanding the detailed solvation structures. The results indicate that Fc1N112-TFSI is dissociated at varying degrees in mixed solvent depending on concentrations. At dilute solute concentrations, most $Fc1N112^{+}$ and $TFSI^{-}$ are fully disassociated with their own solvation shells formed by solvent molecules. At saturated concentration, $Fc1N112^{+}$-$TFSI^{-}$ contact ion pairs are formed and the solvent molecules are preferentially interacting with the Fc rings rather than interacting with the ionic pendant arm of Fc1N112-TFSI.

1. Introduction

As a promising stationary energy storage technology, redox flow batteries (RFBs) have experienced a recent renaissance fueled by the rapidly evolving global energy profiles because of the growing

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deployment of renewable energy resources. The cell design of energy-bearing liquid electrolyte stored outside the electrodes offer significant advantages including the decoupling of energy and power, excellent scalability, modular manufacturing, active thermal management, intrinsic safety, etc. [1–4] Benefiting from wider electrochemically stable voltage windows, the emerging nonaqueous RFB (NRFB) holds great potential for overcoming the low energy density challenge present in current state-of-the-art aqueous RFB technologies [3–6]. Recent research on NRFBs focuses on the development of redox active materials including organometallic compounds [7–9], redox organic materials [10–12], redox active polymers [13], and the synergy between flow battery and Li-ion or Li-metal battery chemistries [14–20]. However, the current performance of NRFBs has lagged far behind their inherent capability. To date, most of them have failed to demonstrate energy density and cycling durability even close to their aqueous counterparts.

One of the major technical hurdles for NRFBs is the low solubility of redox materials leading to limited energy density [7,8,12]. Often, low solubility originates from insufficient solvation interactions occurring between the redox materials and solvent molecules. A good understanding of the solvation phenomena is able to offer insights to questions such as preferred functionalities and chemical sites of interactions, solvation structure evolution upon concentration changes, effects of solvation structure on material properties, etc. According to such information obtained, one can rationally design the redox molecules, improve the supporting electrolyte systems, and tune the flow cell conditions as redox material concentration increases. Especially, deliberate molecular engineering strategies to increase material solubility can advance the development of high energy density NRFB systems. In solvation studies, nuclear magnetic resonance (NMR) and computational modeling have proven to be powerful tools.

Recently, Wei et al. studied a new active redox species with high solubility in nonaqueous electrolytes by functionalizing pristine ferrocene (Fc) to embody an ionically charged tetraalkylammonium (TAA) pendant arm with a bis(trifluoromethanesulfonyl)imide (TFSI) counter anion (hence denoted as Fc1N112-TFSI) [6]. This compound was electrochemically tested in a Li/organic redox flow battery configuration with a cell potential of ~3.5 V. Previous work verified that the ionic pendant intensifies interactions between Fc1N112-TFSI and the mixed solvents composed of ethylene carbonate (EC), propylene carbonate (PC) and ethyl methyl carbonate (EMC), demonstrated by proton NMR experiments and density function theory (DFT) calculations [6]. Chart 1 shows a representation of the structures of all major components in this system. The major hypothesis is that the solute–solvent interactions take place predominantly at the ionic pendant arm of Fc1N112-TFSI with fully dissociated TAA^+ and $TFSI^-$ at Fc1N112-TFSI concentrations ranging from 0.1 M to 1.7 M in the solvent. However, with ^1H NMR alone, the complicated details of the solvation structures have not been sufficiently decoded. Additional studies utilizing Pulsed Field Gradient (PFG) NMR measurements of diffusion [21] coupled with molecular dynamics simulations argue that the PC solvent interacts with $Fc1N112^+$ strongly relative to the other solvent molecule. More theoretical and experimental evidence is still needed to gain comprehensive understandings of the solvation mechanism.

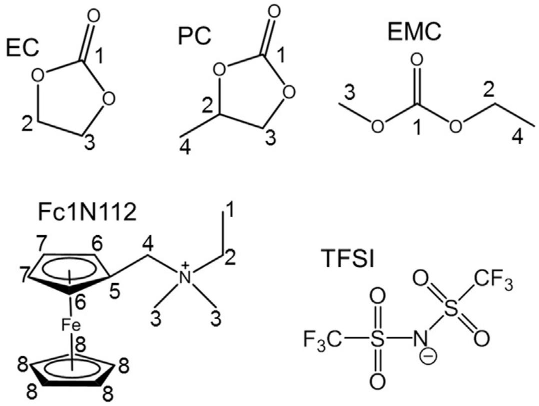

Chart 1. The labeling of the carbon sites and the formula of EC, PC, EMC $Fc1N112^+$ and $TFSI^-$.

Here, we continue this study through using natural abundance ^{13}C and ^{17}O solution-state NMR to acquire a more accurate molecular view of the solvation structures as reported by the chemical shift values or linewidths of these two nuclides. Both, ^{13}C and ^{17}O NMR have played important roles in the development of liquid electrolytes as these methods reveal more in-depth structural details when combined with ^1H NMR [22–24]. Quantum chemical calculations of ^1H, ^{13}C, and ^{17}O NMR chemical shifts using a variety of solvation models are carried out to complementarily interpret the experimental results and observations related to the detailed molecular interactions.

2. Experimental

2.1. Materials and sample preparations

The preparation of Fc1N112-TFSI is reported in detail elsewhere [6,25]. Briefly, Fc1N112-TFSI was synthesized in two steps: (dimethylaminomethyl)ferrocene (96%, Sigma–Aldrich) reacted with bromoethane (98%, Sigma–Aldrich) in anhydrous acetonitrile (99.8%, Sigma–Aldrich) to produce the intermediate of ferrocenylmethyl ethyl dimethylammonium bromide, followed by anion exchange with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, BASF) in deionized water to afford the Fc1N112-TFSI in an overall yield of 91%. The NMR sample solutions were prepared simply by mixing the Fc1N112-TFSI and the solvents at specified concentrations in an argon-filled glove box (Mbraun, Stratham, NH) with moisture and oxygen levels less than 1 ppm. Battery grade PC, EC and EMC were purchased from BASF. Since EC is in solid form at room temperature, NMR spectra for neat EC were acquired by dissolving EC in deuterated chloroform ($CDCl_3$).

2.2. NMR measurements

All ^{13}C NMR experiments were carried out on a Varian 600 MHz NMR spectrometer equipped with a Z axis gradient 5 mm triple resonance probe. The corresponding Larmor frequency was 150.933 MHz. A single 90° hard pulse with gated decoupling during data acquisition period was used. About 512 to 2048 scans were acquired for each spectrum with an acquisition time of about 0.9 s and a recycle delay time of 5 s. ^{13}C NMR spectra were externally referenced to TMS (assigned a value of 0.0 ppm). The peak assignments for the ^{13}C NMR spectra of EC, PC, EMC and TFSI were according to those in computer databases, i.e., ACD/NMR Databases from ACDLabs (http://www.acdlabs.com). Natural abundance ^{17}O NMR experiments were performed on a Varian-Agilent 900 MHz NMR spectrometer equipped with a home-built large-sample-volume probe (15 mm outer diameter). Details of the probe design and performance will be published in a separate paper [24]. The corresponding Larmor frequency was 122.041 MHz. A 25 μs long pulse was used for spectral excitation. The spectra were collected in 1000–30,000 scans depending on the linewidth of the peaks, with an acquisition time of 25 ms and a recycle delay time of 0.5 s. ^{17}O NMR spectra were referenced to the oxygen resonance from