Exploring the Interactions between Carbonate-Based Solvents and Nanoporous Carbon by Measuring Diffusion and Relaxation Properties with PFG HR-MAS NMR

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Abstract

Nanoporous carbons and carbonate-based solvents are commonly used as electrode and electrolyte materials in lithium-ion batteries and supercapacitors. To better characterize the interactions between electrolyte molecules and nanoporous carbon, pulsed-field gradient (PFG) high-resolution magic angle spinning (HR-MAS) NMR is used to study the diffusion properties of dimethyl carbonate (DMC) and ethylene carbonate (EC) in an equimolar mixture added to a sample of nanoporous carbon powder. Diffusion constants are obtained using a ^{1}H pulsed-gradient stimulated echo pulse sequence and a ^{13}C-detected pulsed-gradient stimulated echo with DEPT for coherence transfer. Distinct in-pore and ex-pore environments are observed, with the diffusion constants differing by an order of magnitude between the two environments. Relaxation measurements and spectral peak deconvolution gives further insight into the electrolyte organization in the system, revealing four different electrolyte environments: ex-pore bulk, ex-pore restricted, in pore bulk, and in-pore restricted. Both dimethyl carbonate and ethylene carbonate are observed in all four environments. Changes in the distribution of electrolyte between the environments are observed at different MAS rates and at different ratios of electrolyte to nanoporous carbon powder.

Introduction

Currently, there is a growing need for improvements in energy-storage devices such as lithium-ion batteries and supercapacitors. In order to optimize the design of these devices, it is necessary to better characterize the interactions between electrolyte molecules and electrode materials.

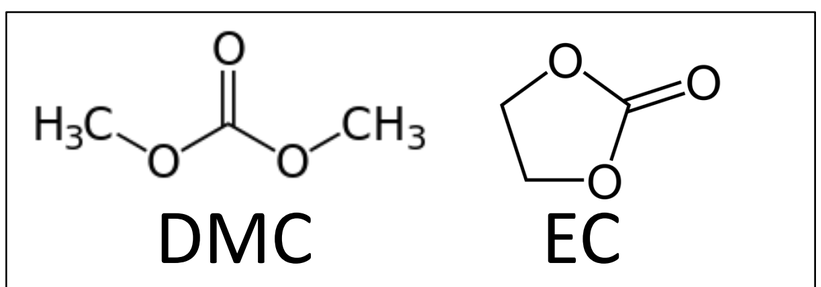
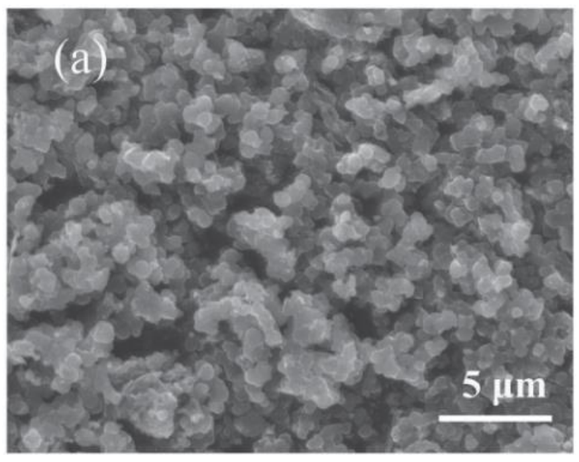


Figure 1. *Molecular structure of dimethyl carbonate (DMC) and ethylene carbonate (EC).*

While diffusion properties of molecules in electrolyte solutions have been previously studied with PFG-NMR, to date no studies have been performed looking into the diffusion properties of electrolyte molecules near electrode surfaces using this technique. To perform PFG NMR diffusion studies on electrolytes near the surface of electrode materials requires the use of high-resolution magic angle spinning (HR-MAS) to reduce magnetic field inhomogeneity within the sample.



Zheng et al. 2014, Adv. Funct. Mater., 24, 4156-4163.

Figure 2. *SEM Image of nanoporous carbon.*

In the present study, the carbonate-based solvent electrolytes ethylene carbonate and dimethyl carbonate (Fig. 1) are observed with HR-MAS NMR in a heterogeneous mixture with nanoporous carbon (Fig. 2). A 1:1 mixture of EC:DMC is commonly used as an electrolyte solvent. The relaxation and diffusion properties of the electrolytes in nanoporous carbon are then measured.

Methods

An equimolar mixture of EC and DMC was added to a sample of nanoporous carbon and packed into an HR-MAS insert. T_2 relaxation measurements are made using the CPMG echo decay experiment. Diffusion of the electrolytes are measured with respect to the diffusion of protons in the sample using a pulsed dipolar gradient stimulated-echo sequence as seen in Fig. 3.

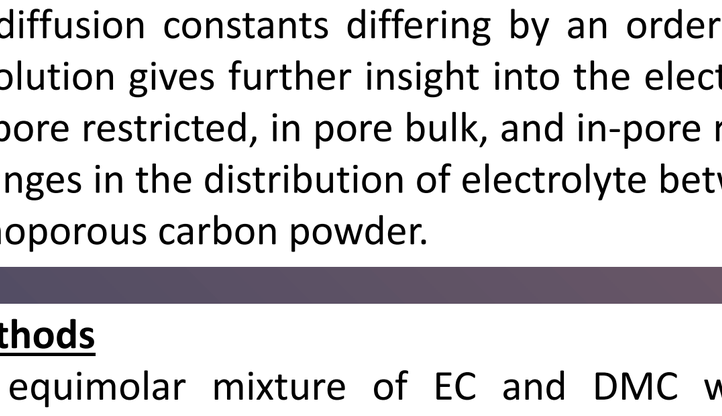


Figure 3. *PFG stimulated echo with dipolar gradients and spoil gradient for ^{1}H-detected diffusion measurements. G_{MAS} indicates the gradient is applied at the magic angle.*

Two variations of the diffusion pulse sequence are used, one with ^{1}H signal detection and the other with ^{13}C signal detection via coherence transfer from ^{1}H by the DEPT pulse sequence. The diffusion measurements were performed under HR-MAS experimental conditions, the setup of which is shown in Fig. 4.

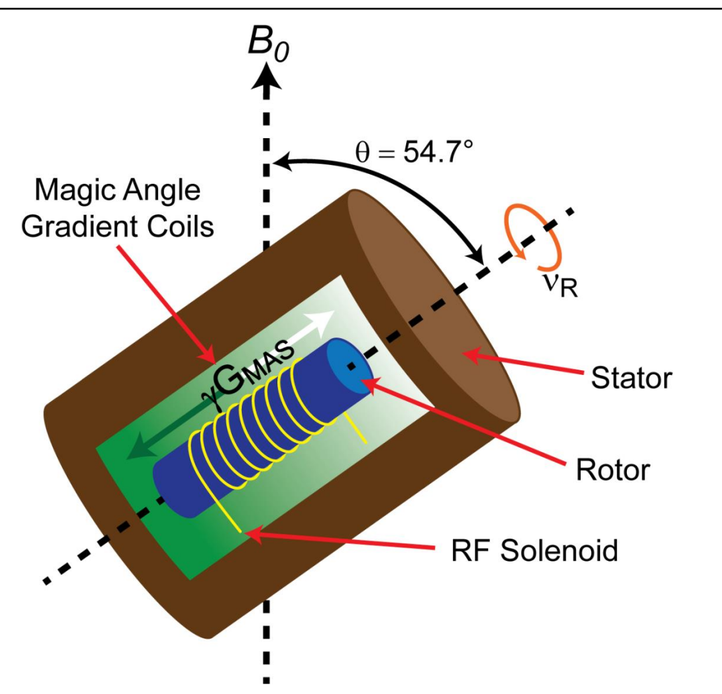


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Figure 4. *PFG HR-MAS NMR conditions. A stator is tipped at the magic angle with respect to the external field B_0, with a gradient coil along the magic angle axis. A 4mm sample rotor can be spun pneumatically up to rates of about 10 kHz.*

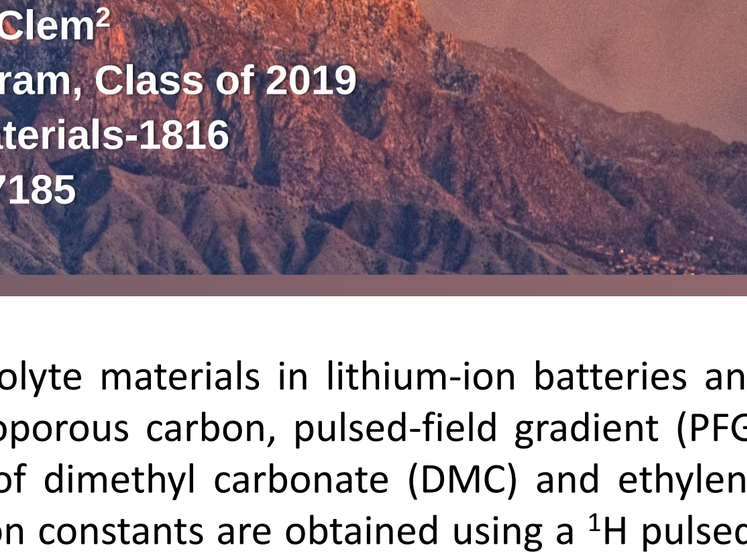

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Figure 5. A) *Effect of a gradient pulse along the axis of the magic angle.* ***B)*** *The signal decays with increasing gradient strength.*

Diffusion NMR works by spatially encoding spins using a magnetic field gradient to applying a phase shift to the spins based on their position along the axis of the rotor, as pictured in Fig. 5a. The intention of applying a gradient pulse is to then apply it a second time after a delay. If no molecules diffuse, the spatially-encoded phase shift will be perfectly reversed, and the signal will have only decayed due to inherent relaxation processes. However, when molecules do diffuse, the second gradient pulse is unable to reverse the effects of the initial phase shift, leading to a signal loss which increases with increasing gradient strength, as seen in Fig. 5b. To obtain the diffusion constant D, the decay is fit to the Stejskal-Tanner equation, seen in Fig. 6.

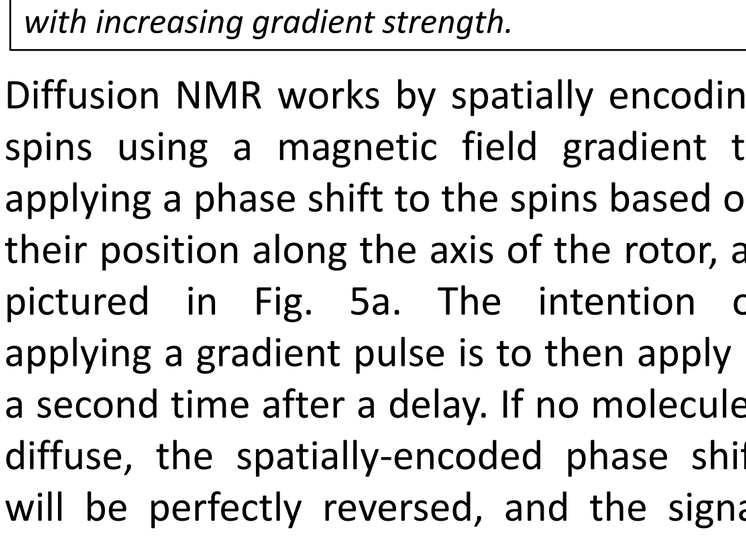

Figure 6. *A decay of signal intensity from a diffusion experiment, fit to the Stejskal-Tanner equation*

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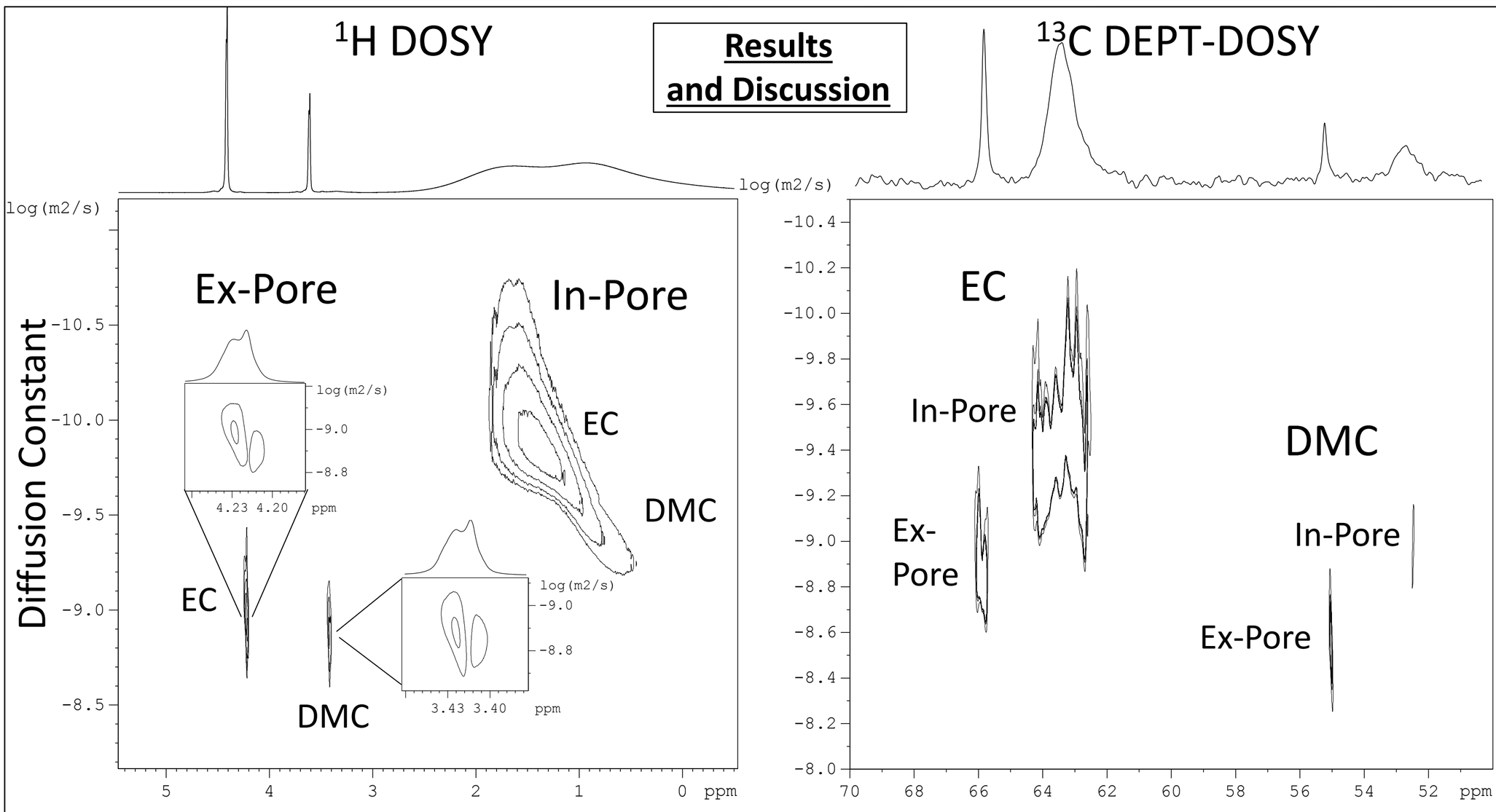
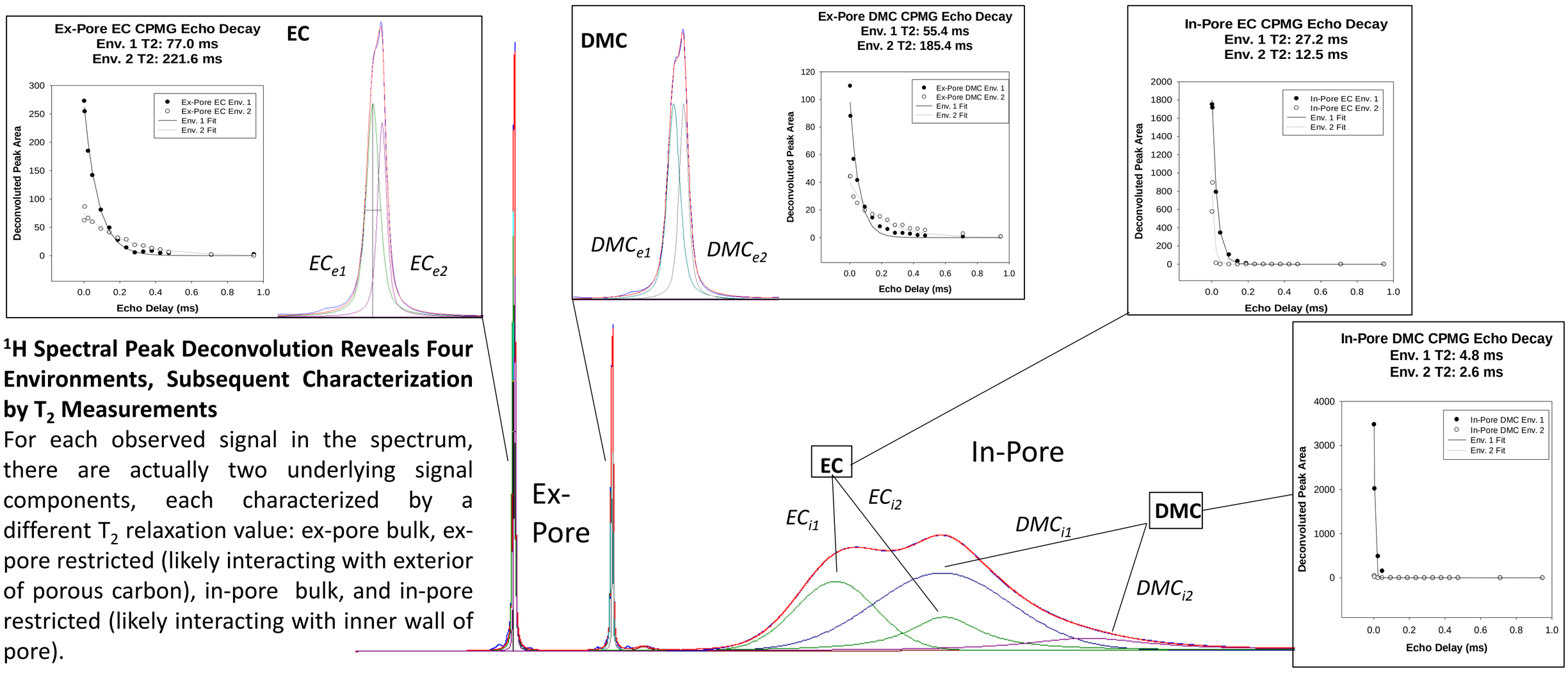
Results and Discussion



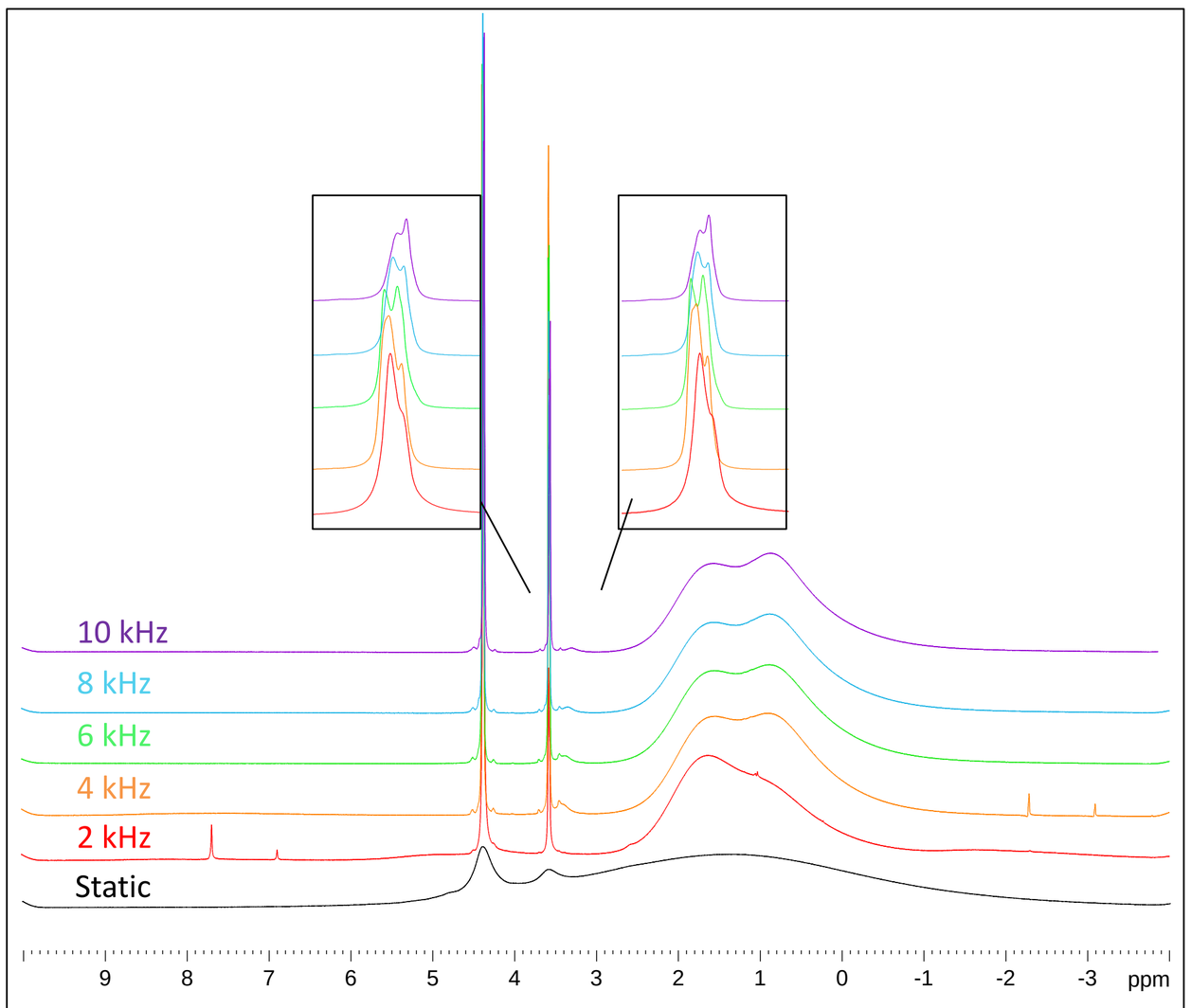
Diffusion-Ordered Spectroscopy (DOSY)

Comparison of the resulting ^{1}H DOSY and ^{13}C DEPT-DOSY of a sample of porous carbon and equimolar EC/DMC at a 1:1 ratio by weight, spun at 10 kHz. The in-pore *D* value for both electrolyte species is an order of magnitude smaller than for the ex-pore signals. The ^{13}C DEPT-DOSY shows a more rapid decay, resulting in larger *D* values. This is likely due to T_2 relaxation, which has an increased effect due to the additional time for relaxation during the DEPT section of the pulse sequence.



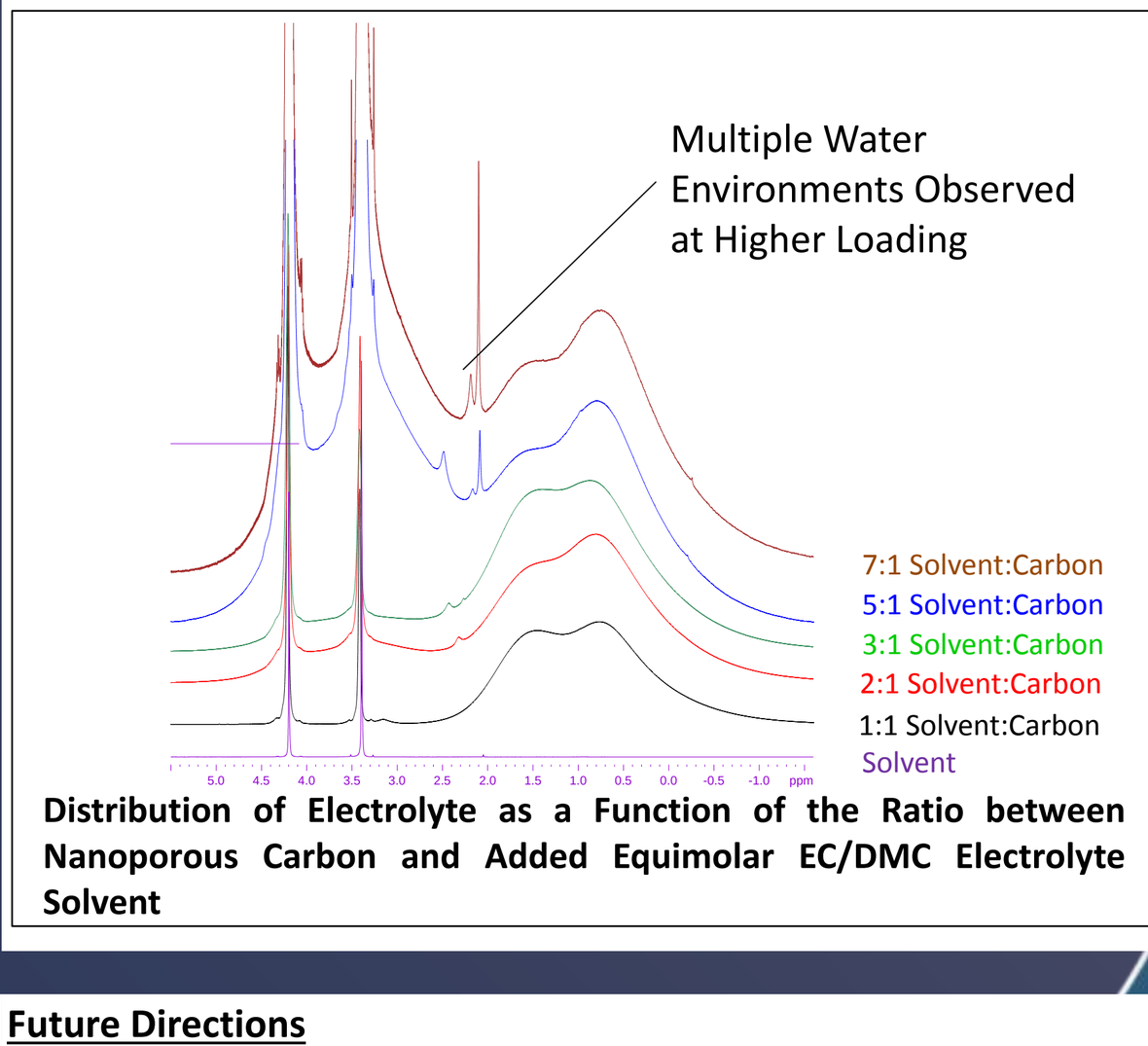
^{1}H Spectral Peak Deconvolution Reveals Four Environments, Subsequent Characterization by T_2 Measurements

For each observed signal in the spectrum, there are actually two underlying signal components, each characterized by a different T_2 relaxation value: ex-pore bulk, ex-pore restricted (likely interacting with exterior of porous carbon), in-pore bulk, and in-pore restricted (likely interacting with inner wall of pore).



Effect of MAS Rate on the Distribution of Electrolyte in a 1:1 Ratio of equimolar EC/DMC Solvent to Nanoporous Carbon

Extra peaks in the 2 and 4 kHz spectrum are spinning sidebands. Resolution enhancement from static is obtained at just 2 kHz.



Distribution of Electrolyte as a Function of the Ratio between Nanoporous Carbon and Added Equimolar EC/DMC Electrolyte Solvent

Future Directions

- **Perform NOESY experiments to better understand the organization of electrolytes in the pores**
- **Dissolve lithium salts in solution to observe differences between the in-pore and ex-pore diffusion rates of the cation and anion**

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