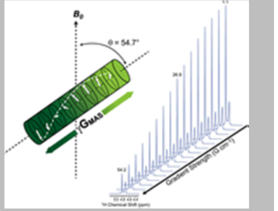
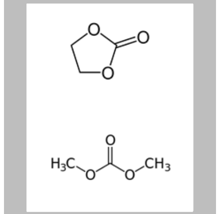
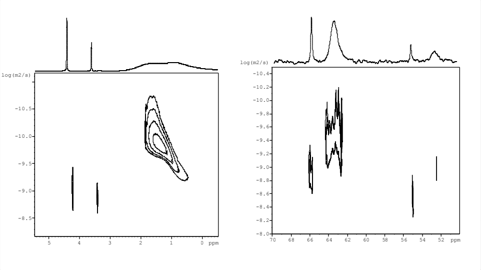
SAND2014-16162PE

Exploring the Interactions between Carbonate-Based Solvents and Nanoporous Carbon







Measuring Relaxation and Diffusion Properties of Heterogeneous Electrolyte-Electrode Samples with HR-MAS NMR

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UC Berkeley Physical Chemistry Ph.D. Program

Sandia National Laboratories

Exceptional service in the national interest

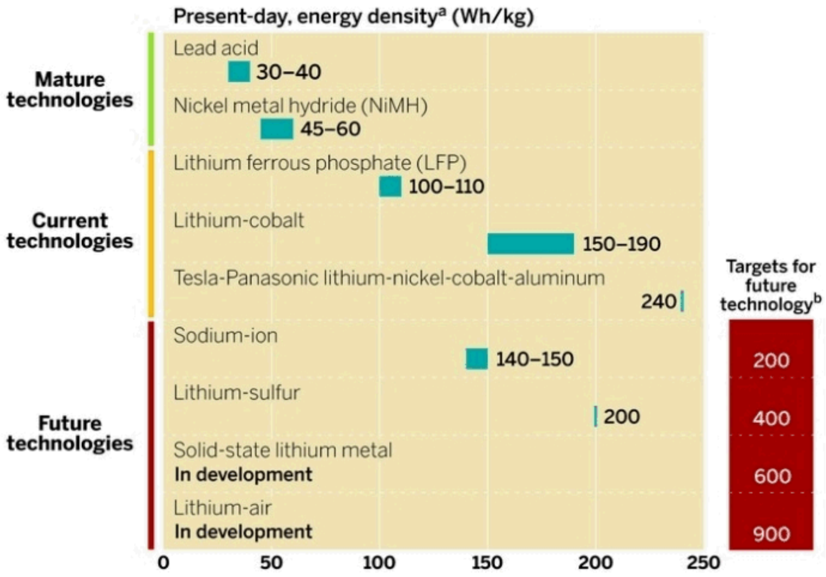
Student Intern Program (SIP) Presentation

July 24, 2014

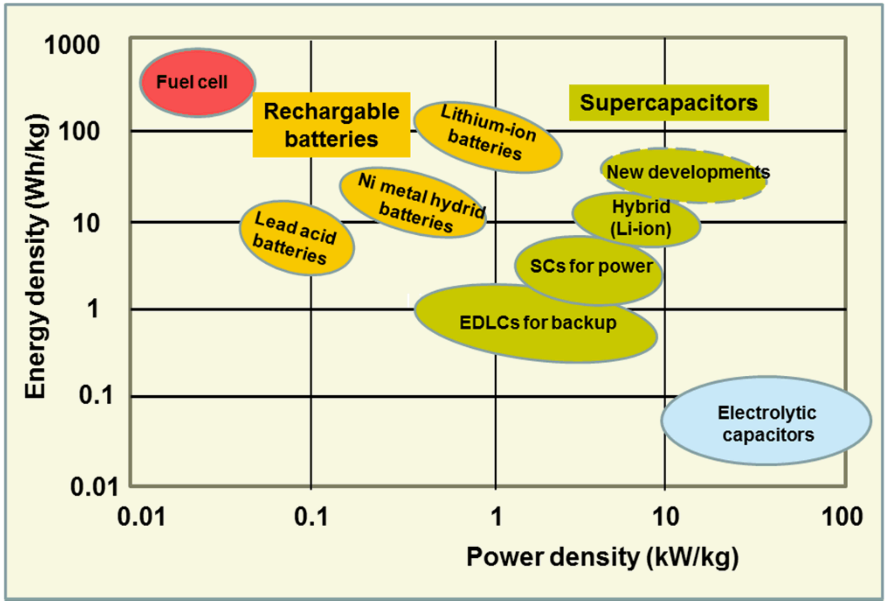
U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

Background



- **Advances in Energy Storage are Necessary**
  - Electric cars, other technologies require better energy storage technologies



Ragone Chart- Power density vs. Energy density of common energy storage devices

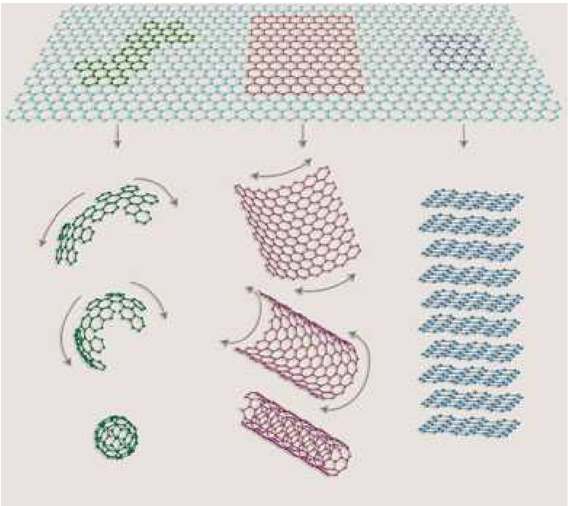
- **Improving Lithium Ion Batteries**
- **Development of Supercapacitors**
  - Low energy density compared to batteries, but high power density (10-100x greater than batteries)

Chemical and Engineering News Weekly, Volume 92 Issue 28 | pp. 11-15; Wikimedia Commons

Motivation for Project

- **A great deal of research effort is being put into improving these energy storage devices**
  - Novel Materials
  - Computational Studies

- **Diffusion properties of the electrolyte molecules used in these devices are only known for bulk quantities of the electrolyte**
  - Increasingly, advances in Li-Ion batteries and supercapacitors make use of nanomaterials
  - Nanoscale molecular physical properties are known to differ greatly from bulk physical properties

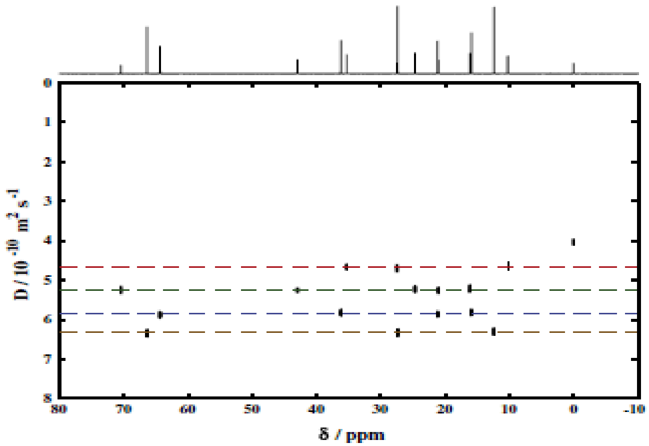


Graphite nanomaterials- buckyballs, nanotubes, and graphene- are used extensively in new energy storage devices

Geim, A. K., & Novoselov, K. S., 2007, *Nature Materials*, *6*, 3, 183-191.

Summer Project

- **Explore a research opportunity for which Sandia is uniquely equipped to tackle—using Nuclear Magnetic Resonance Spectroscopy (NMR) to obtain diffusion constants for electrolytes near and within the pores of a nanoporous carbon electrode material**
    - Requires the use of Pulsed Field Gradients (PFG) and High Resolution Magic Angle Spinning (HR-MAS)



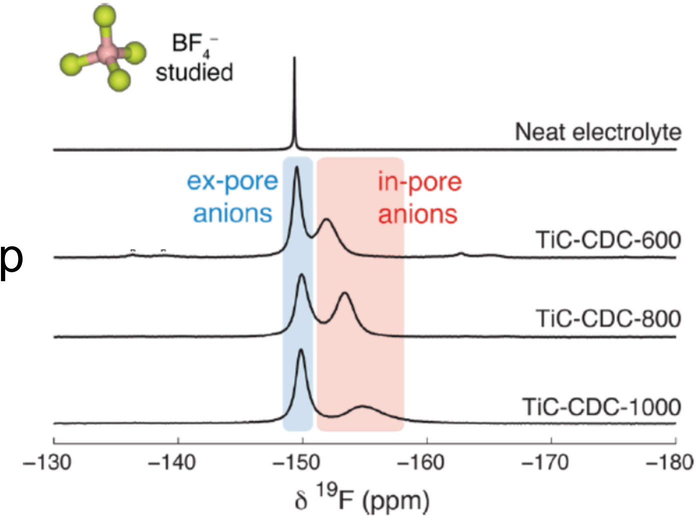
^{13}C Diffusion-Ordered SpectroscopY (DOSY) of a mixture of alcohols. This experiment enables resolution of a complex spectrum by sorting spectra by diffusion constant.

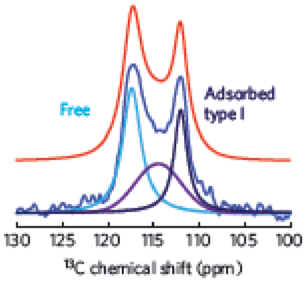
- **Spectral peak deconvolution and nuclear spin relaxation studies to discern different molecular environments for electrolytes in nanoporous carbon**

Botana, Adolfo, et al., 2011, *Journal of Magnetic Resonance* 211.1: 25-29.

Previous NMR Studies of Materials used in Energy Storage Applications

- **Forse *et al.* (2014) used ^{19}F solid state NMR on BF_4^- to show that electrolyte resonances experienced upfield shifts to lower ppm when inside pores of porous carbon materials compared to the free (ex-pore) electrolyte resonances**
  - This effect was attributed to ring currents from delocalized π-electrons between carbon atoms
  - The π-electrons of the carbons that make up the pore cause a diamagnetic shielding effect, resulting in a reduced local magnetic field around the electrolyte enclosed in the pore and thus a lower chemical shift



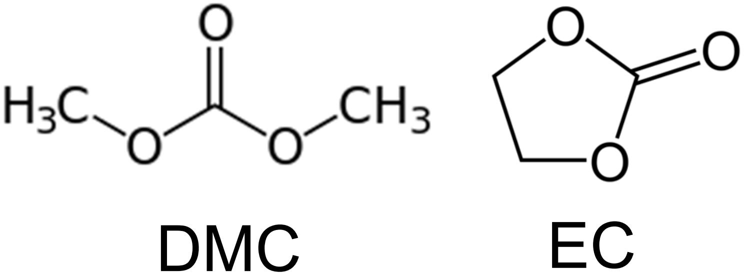


- **Deschamps *et al.* (2013) observed an organization of electrolytes in porous carbon electrodes with ^{11}B and ^{13}C solid state NMR, and observed multiple molecular environments which were elucidated with spectral peak deconvolution**

Forse, Alexander C. *et al.*, 2014, *J. Phys. Chem. C,* 118, 14, 7508-7514; Deschamps, M. *et al.*, 2013, *Nature Materials*, *12*, 4, 351-358.

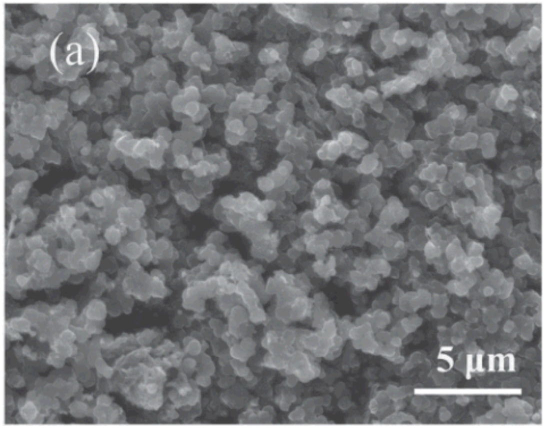
Carbonate Solvents and Porous Carbon

- **Carbonate solvents**
  - Used as electrolytes, especially in lithium-ion batteries
  - Large electrochemical window (1.0-4.7V operating range), but can have low flash points (flammable)
  - Mixtures often used to reduce flammability- 1:1 DMC/EC



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

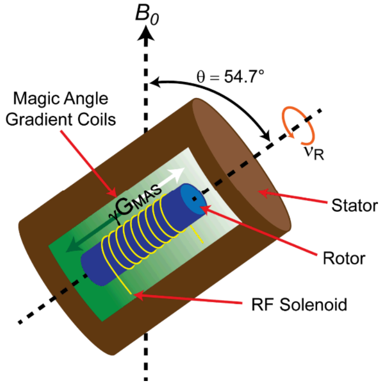
- **Nanoporous Carbon (nPC)**
  - Good electric conductivity
  - Can be amorphous ("activated carbon") or have well defined porosity (Carbide-derived Porous Carbons)
  - Porous nanostructures of sp^2-hybridized carbons (pore size ~2 nm)
  - High surface area



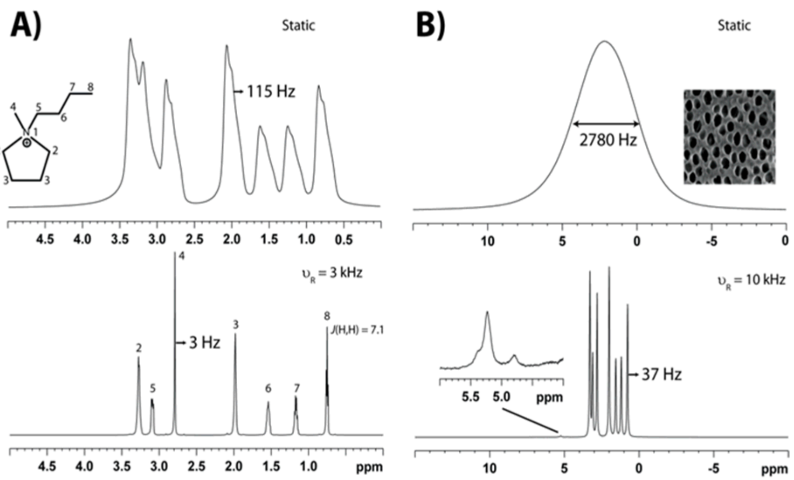
SEM Image of nanoporous carbon

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

High Resolution-Magic Angle Spinning (HR-MAS)



$$\Delta B \sim P_2(\cos\theta) = 3\left(\cos^2\theta - \frac{1}{2}\right)$$



- **Changes in magnetic susceptibility across heterogeneous samples result in broad lineshapes**
- **Spinning the sample (pressurized N_2) at the “magic angle”- 54.7º causes the susceptibility term of the Hamiltonian to go to zero**
  - Dipolar couplings and Chemical Shift Anisotropy are also averaged when spinning at the magic angle for the same reason

Todd M. Alam and Janelle E. Jenkins, “ HR-MAS NMR Spectroscopy in Material Science”, in Advanced Aspects of Spectroscopy

HR-MAS Sample Preparation

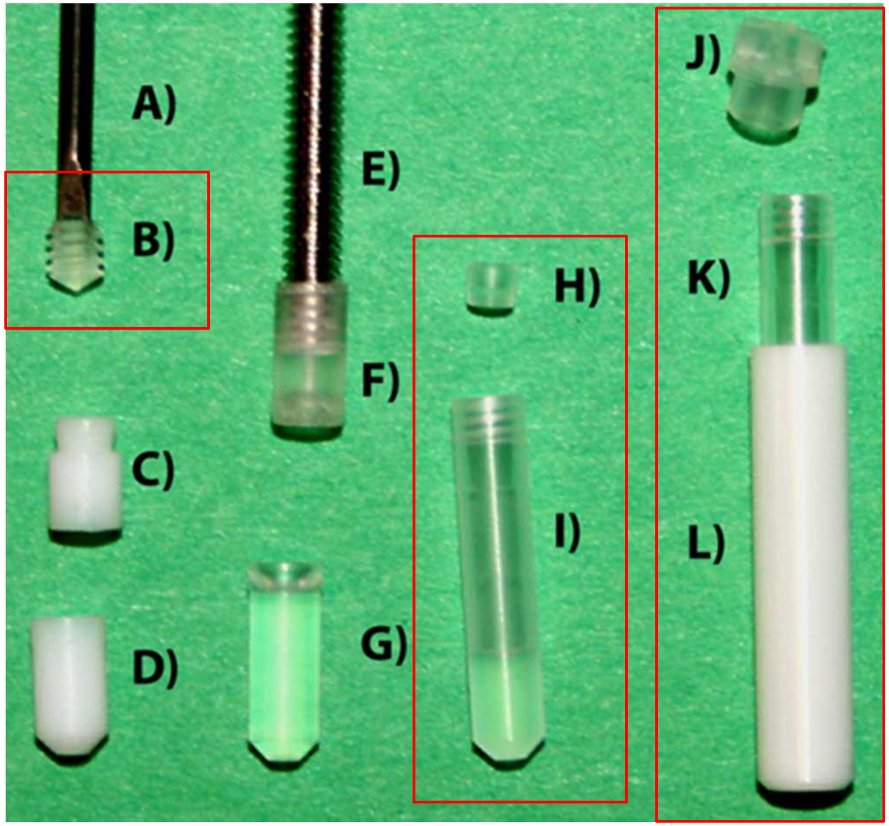
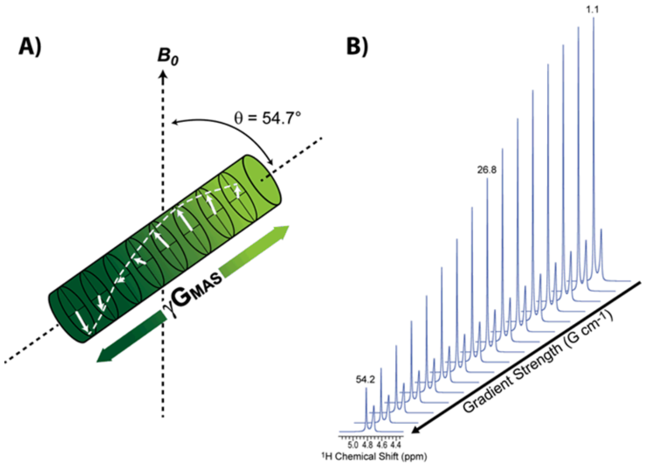


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 μL volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F® insert for 12 μL sample volume, H) plug for disposable insert, I) disposable 30 uL Kel-F® insert, J) 4 mm rotor cap, K) disposable inserted partially in a 4 mm rotor, L) 4 mm zirconia MAS rotor. All these parts are for the Bruker HR-MAS system, and may vary between vendors.

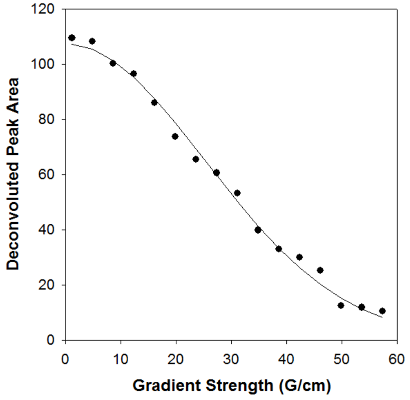
- **Spinning samples containing both liquid and solid sample at kHz requires measures to combat centrifugation effects**
- **Mixtures of nPC powder and 1:1 EC/DMC liquid electrolyte were packed into Kel-F MAS inserts and placed into a zirconia MAS rotor and spun at 10 kHz**

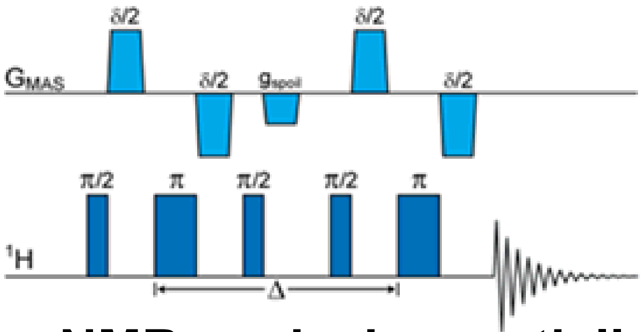
Todd M. Alam and Janelle E. Jenkins, “ HR-MAS NMR Spectroscopy in Material Science”, in Advanced Aspects of Spectroscopy

Diffusion NMR



$$\frac{E(q,\Delta)}{E(0,\Delta)} = \exp\left[-q^2 D\left(\Delta - \frac{\delta}{3}\right)\right]$$



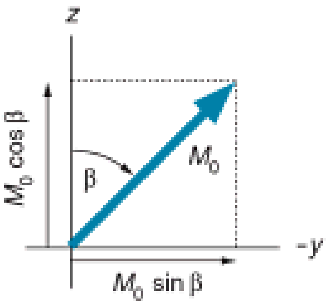


- **Diffusion NMR works by spatially encoding spins using a magnetic field gradient pulse to apply a phase shift to the spins based on their position along the axis of the rotor**
  - After a delay, a second gradient pulse attempts to correct the phase shift, but as the molecules have diffused away from their original position, there is a loss of signal
- **Obtain diffusion constant from decay of signal as a function of gradient strength, Stejskal-Tanner Equation**

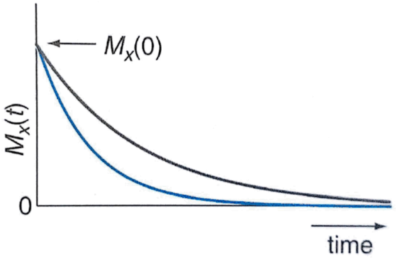
Todd M. Alam and Janelle E. Jenkins, " HR-MAS NMR Spectroscopy in Material Science", in Advanced Aspects of Spectroscopy

Nuclear Spin Relaxation

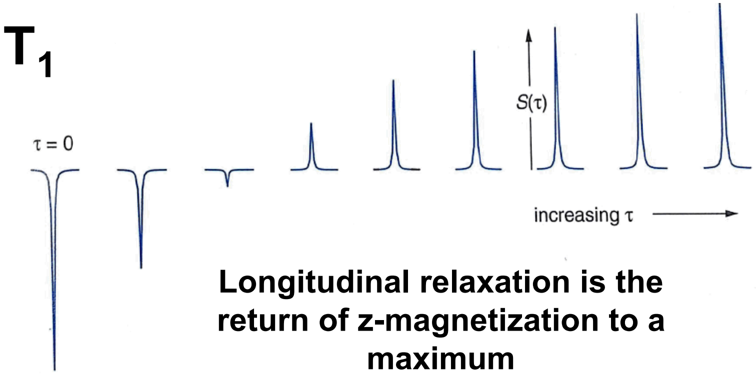
- **The initial equilibrium state in an NMR experiment is where the net magnetization of the sample is along the axis of the external field (z axis)**
- **In pulsed NMR, RF pulses tip the magnetization vector to a non-equilibrium position**



T_2 **Transverse relaxation is the decay of xy-plane magnetization**



T_1



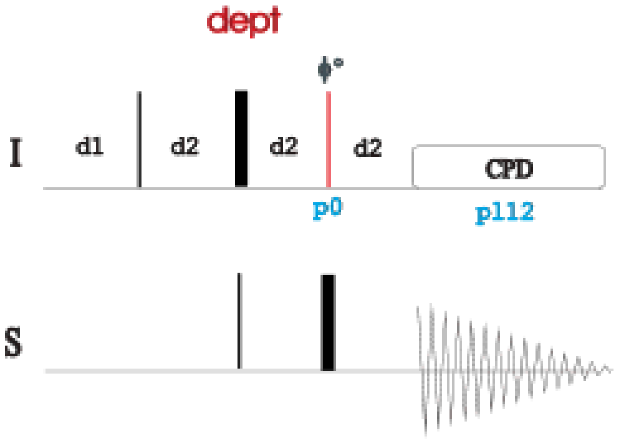
Longitudinal relaxation is the return of z-magnetization to a maximum

- **After a pulse, spins relax from a non-equilibrium state to the equilibrium state by various relaxation mechanisms**
- **Relaxation is characterized by longitudinal relaxation (T_1) and transverse relaxation (T_2)**
  - T_1 and T_2 values are sensitive to chemical environment

Keeler, J. (2013). *Understanding NMR spectroscopy*. John Wiley & Sons.

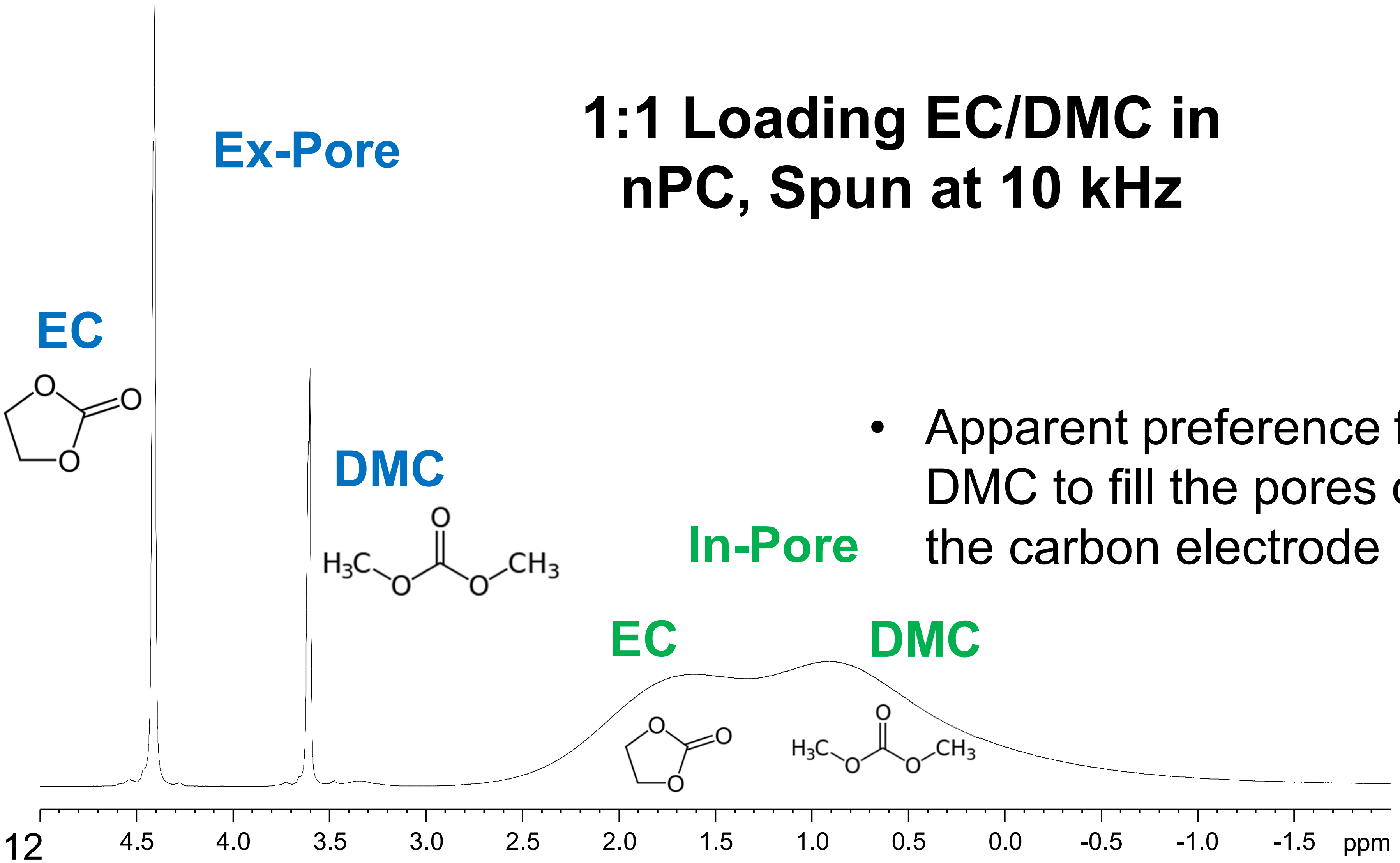
Experiments

- **Diffusion (^{1}H DOSY, ^{1}H-^{13}C DEPT-DOSY)**
  - Detecting ^{1}H for diffusion could limit the ability to obtain accurate diffusion constants, as broadened peaks may overlap.
  - Implement the **^{1}H-^{13}C DEPT** (Distortionless Enhancement by Polarization Transfer) pulse sequence following the DOSY to observe diffusion with the increase in resolution afforded by ^{13}C, though at the cost of signal-to-noise ratio



- **Relaxation (^{1}H CPMG)**
  - **T_2 — Carr-Purcell-Meiboom-Gill Echo Train**
    - Increasing delays between pulses as spins evolve in the xy-plane lead to an exponential decay of magnetization defined by T_2

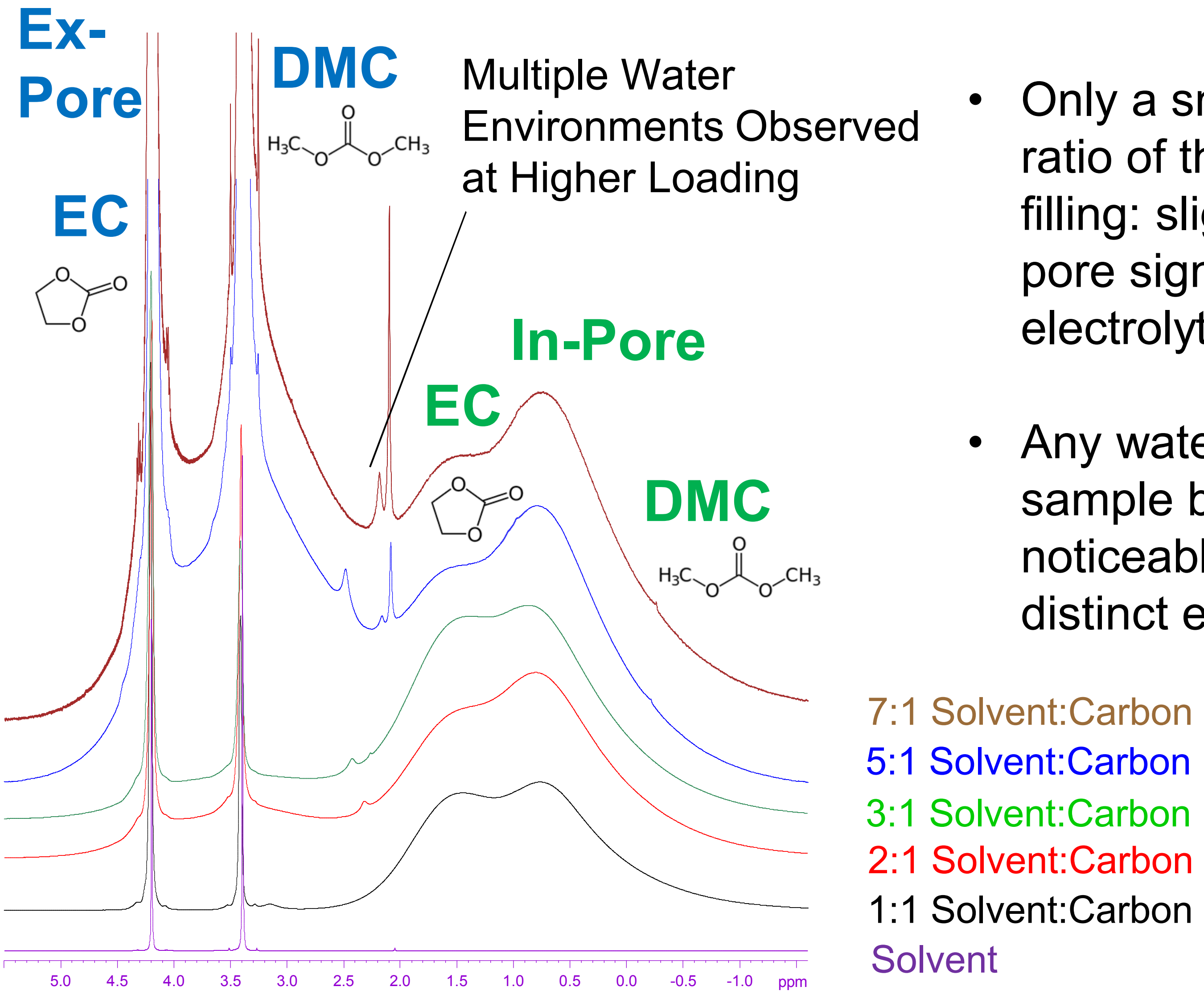
^{1}H HR-MAS NMR Spectrum



1:1 Loading EC/DMC in nPC, Spun at 10 kHz

- Apparent preference for DMC to fill the pores of the carbon electrode

Effects of the Ratio of Electrolyte to Carbon

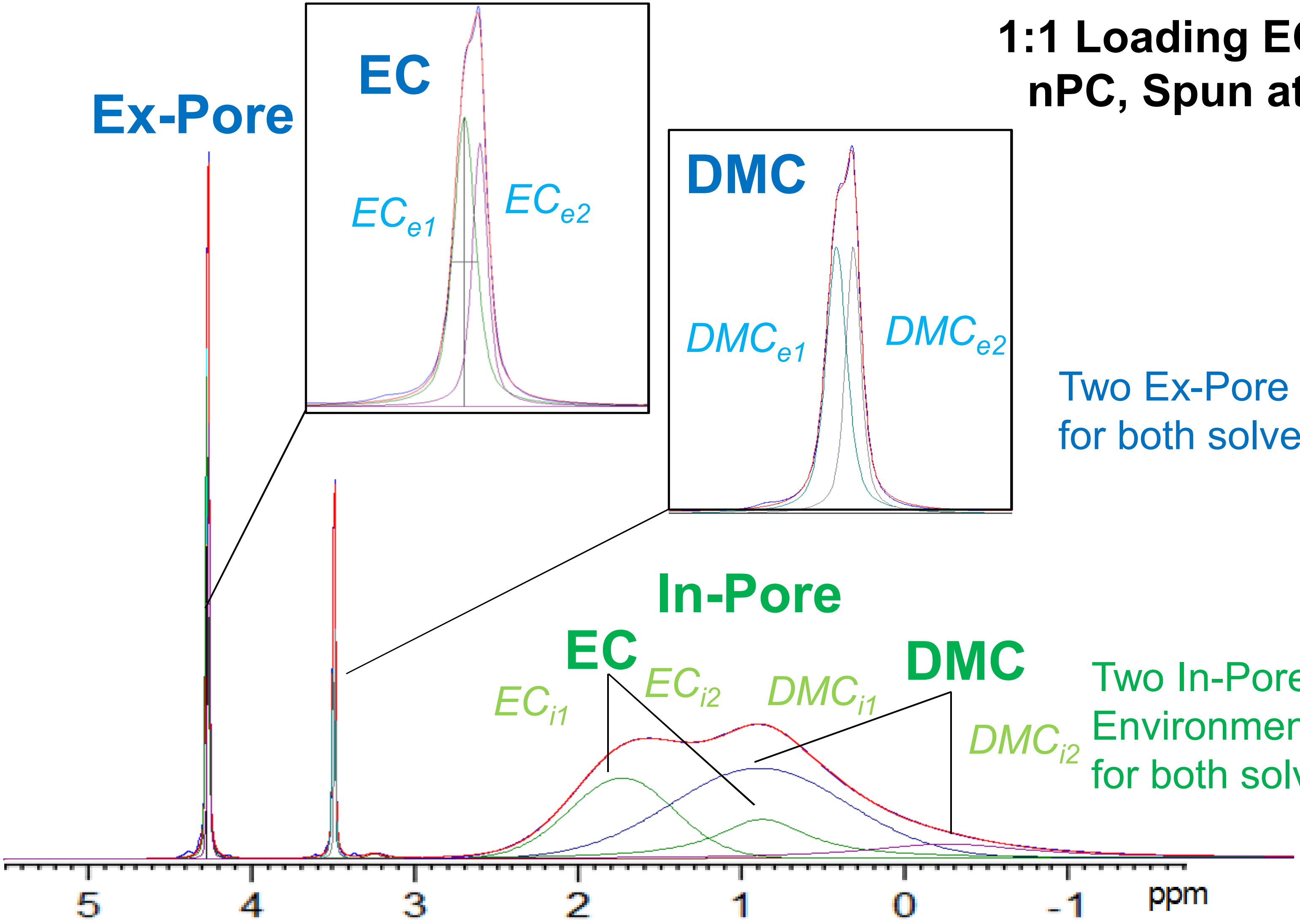


Multiple Water Environments Observed at Higher Loading

- Only a small change in the ratio of the preference of pore-filling: slightly more DMC in pore signal than EC as electrolyte is added
- Any water present in the sample becomes immediately noticeable at higher loadings, distinct environments seen

^{1}H NMR Spectral Peak Deconvolution

1:1 Loading EC/DMC in nPC, Spun at 10 kHz



Two Ex-Pore Environment
for both solvents

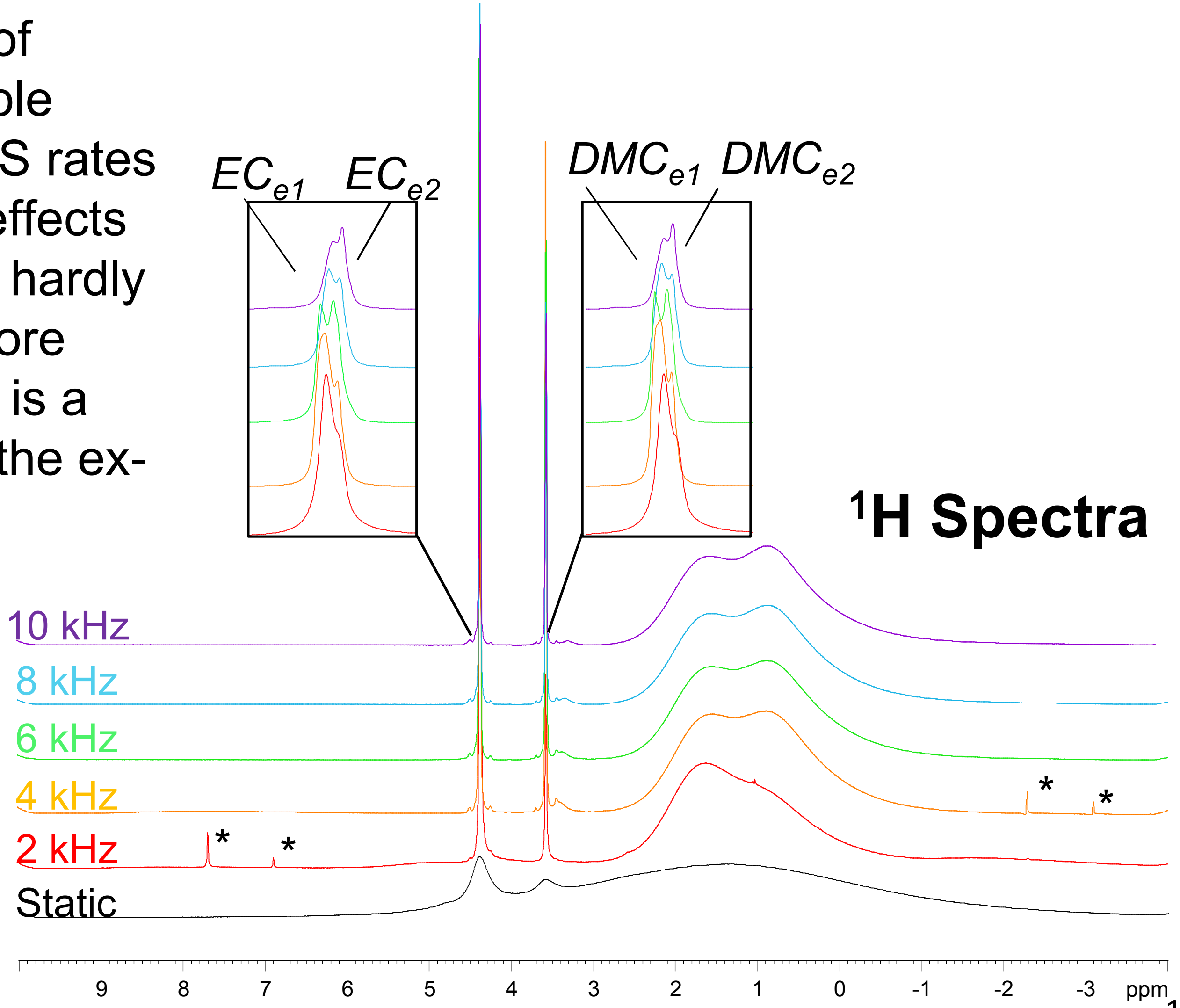
Two In-Pore
Environments
for both solvents

Effect of MAS Rate on Electrolyte Distribution

- A slight redistribution of electrolyte in the sample occurs at different MAS rates due to centrifugation effects
- For the most part, it is hardly noticeable for the in-pore resonances, but there is a change in the ratio of the ex-pore environments

- Asterisks denote spinning sidebands

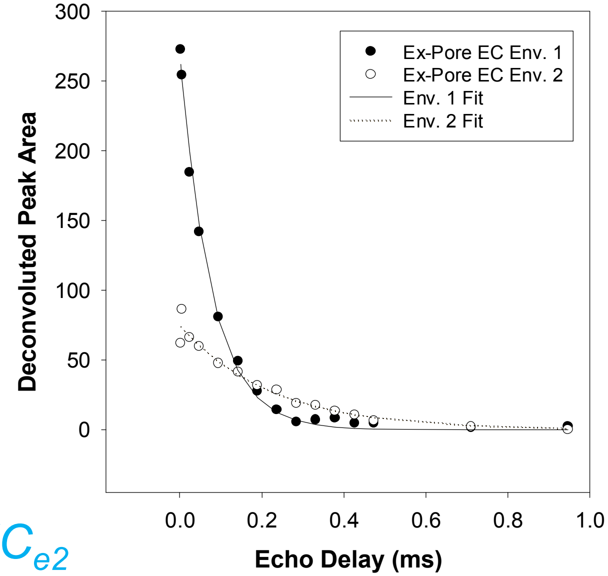
- Note the spectrum obtained for Static, poor resolution



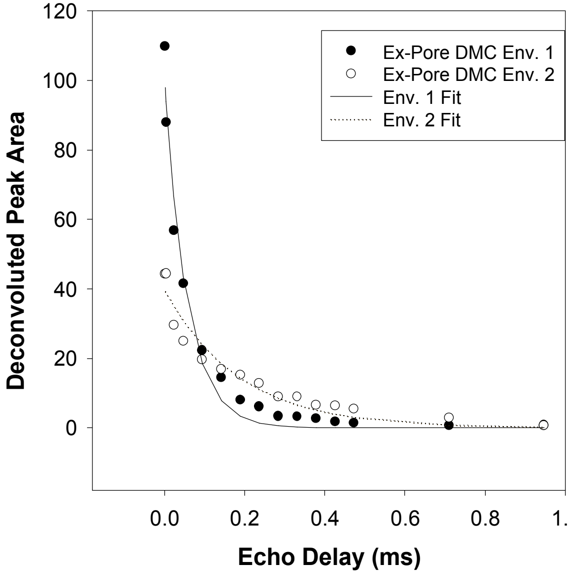
Characterization of Environments by T_2 Relaxation

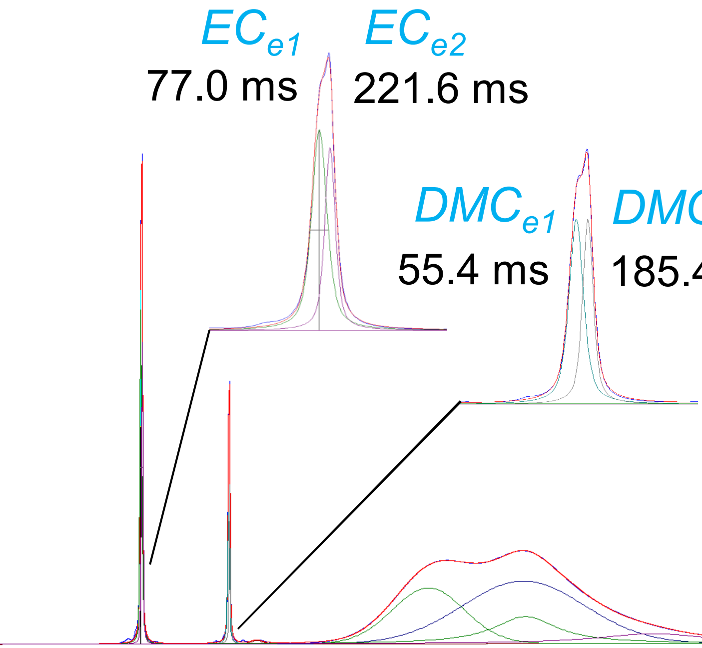
- The two deconvoluted ex-pore environments have very distinct T_2 values

Ex-Pore EC CPMG Echo Decay
Env. 1 T2: 77.0 ms
Env. 2 T2: 221.6 ms



Ex-Pore DMC CPMG Echo Decay
Env. 1 T2: 55.4 ms
Env. 2 T2: 185.4 ms



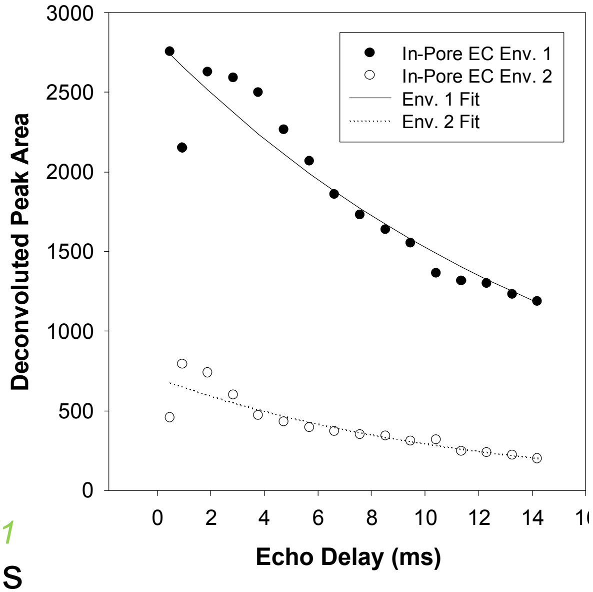


- Free liquids have long T_2 values, therefore environment 2 is likely the “bulk” ex-pore electrolyte, while environment 1 could be a “surface-adsorbed” ex-pore environment

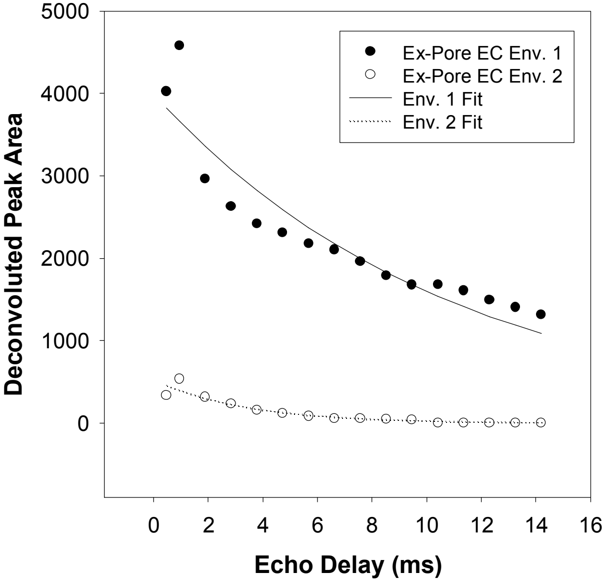
Characterization of Environments by T_2 Relaxation

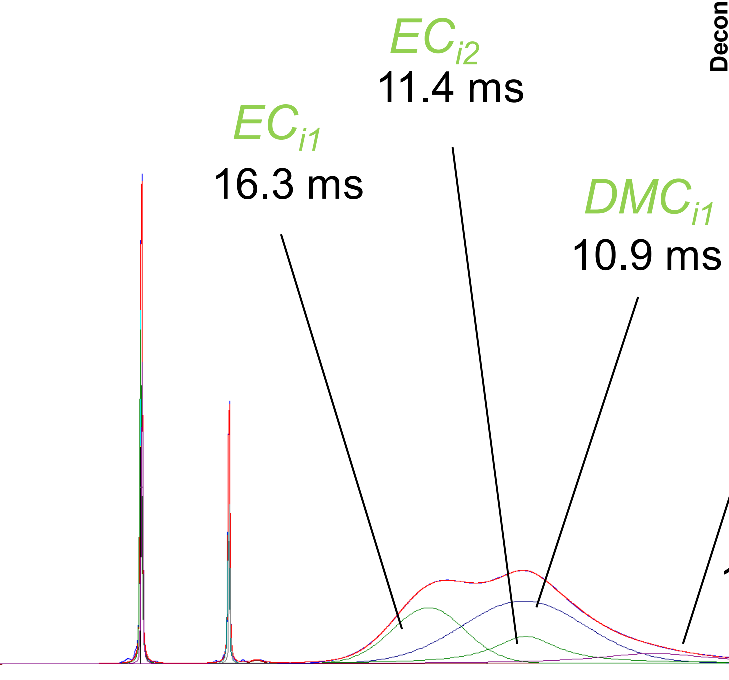
- The two deconvoluted in-pore environments also have very distinct T_2 values, and much shorter than the ex-pore values

In-Pore EC CPMG Echo Decay
Env. 1 T2: 16.3 ms
Env. 2 T2: 11.4 ms



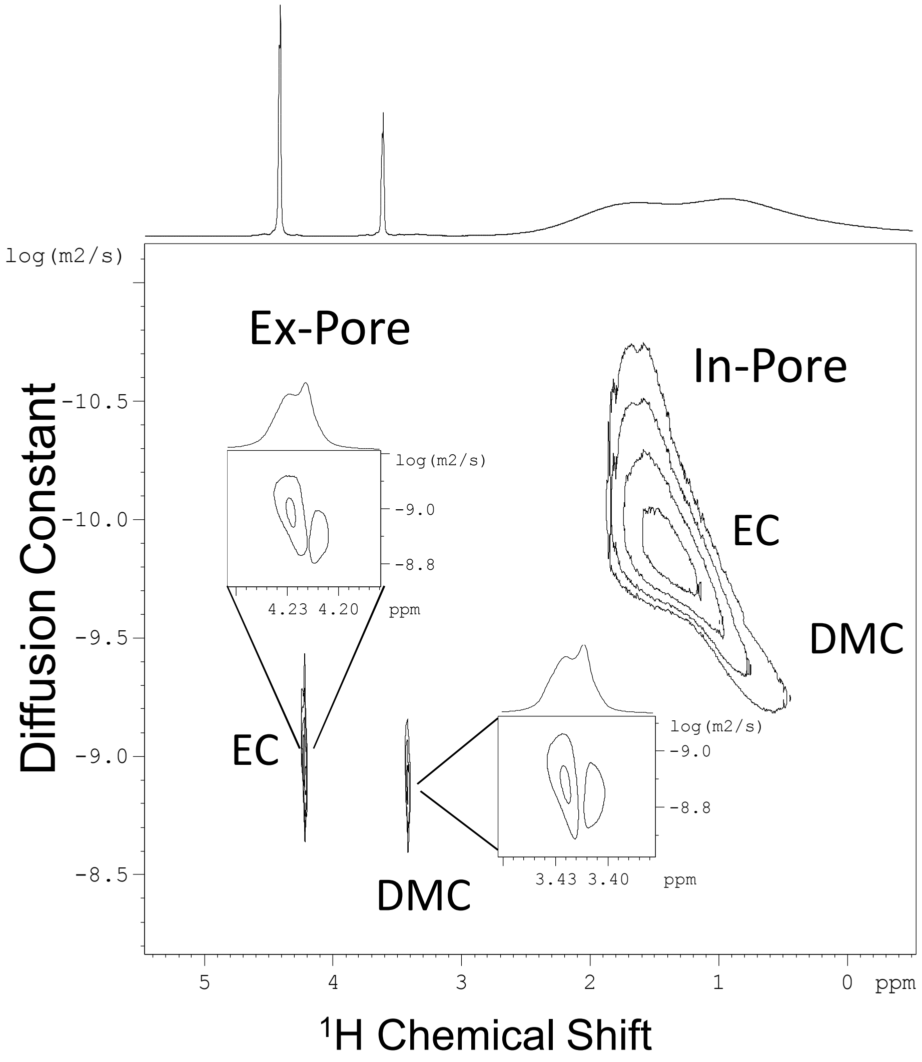
In-Pore DMC CPMG Echo Decay
Env. 1 T2: 10.9 ms
Env. 2 T2: 3.4 ms





- As env. 2 is even more diamagnetically shifted than env. 1 and has a shorter T_2 value, it is likely a surface-adsorbed in-pore environment, while environment 1 is likely the "bulk" or the center of the pores

Diffusion NMR- ^{1}H DOSY



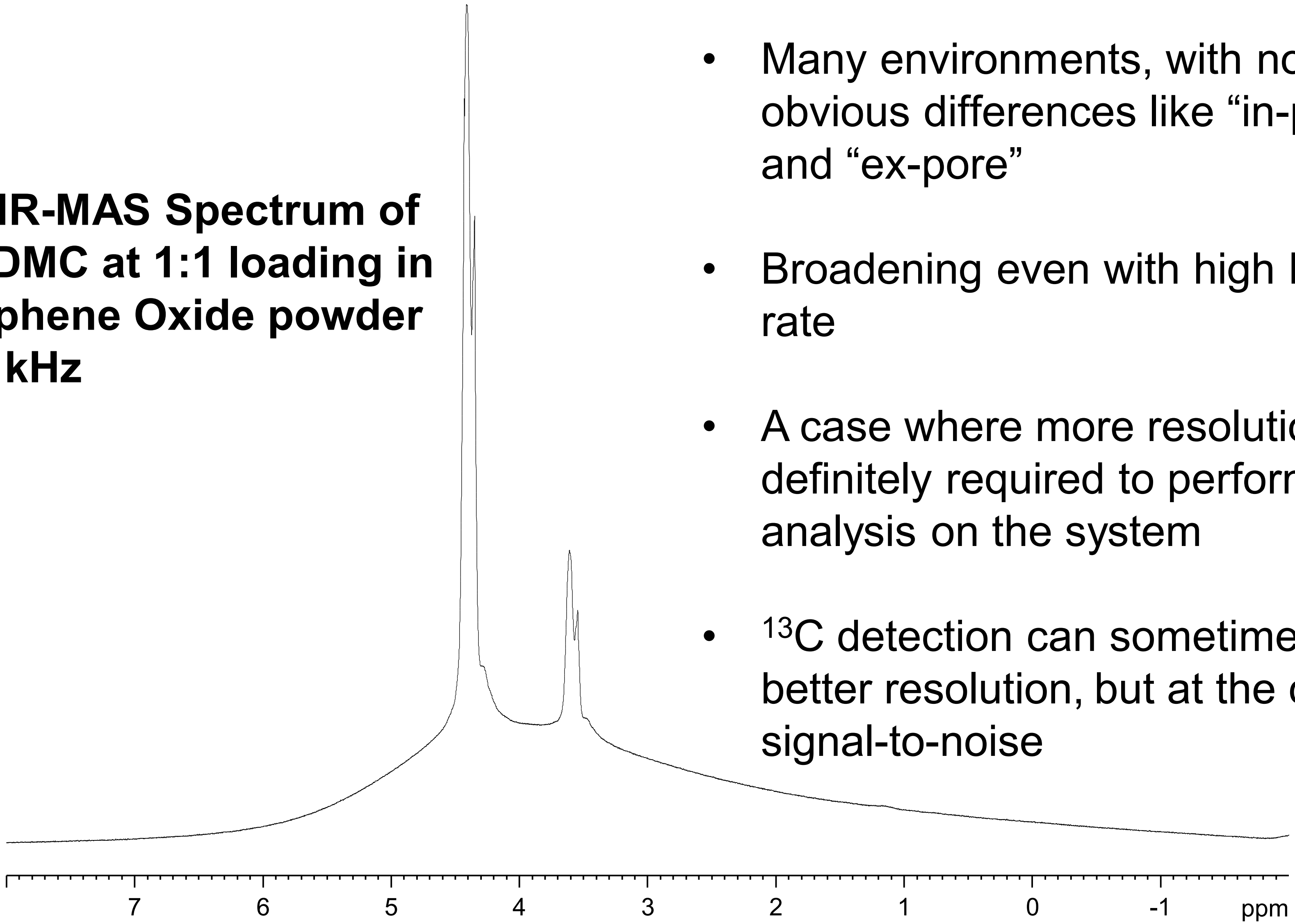
- An order of magnitude difference between in-pore and ex-pore electrolyte diffusion constants

- Both ex-pore environments are able to be resolved by their diffusion constant, with environment 1 (surface-adsorbed) diffusing slightly slower

- Can we get better resolution?

Another Example- Graphene Oxide

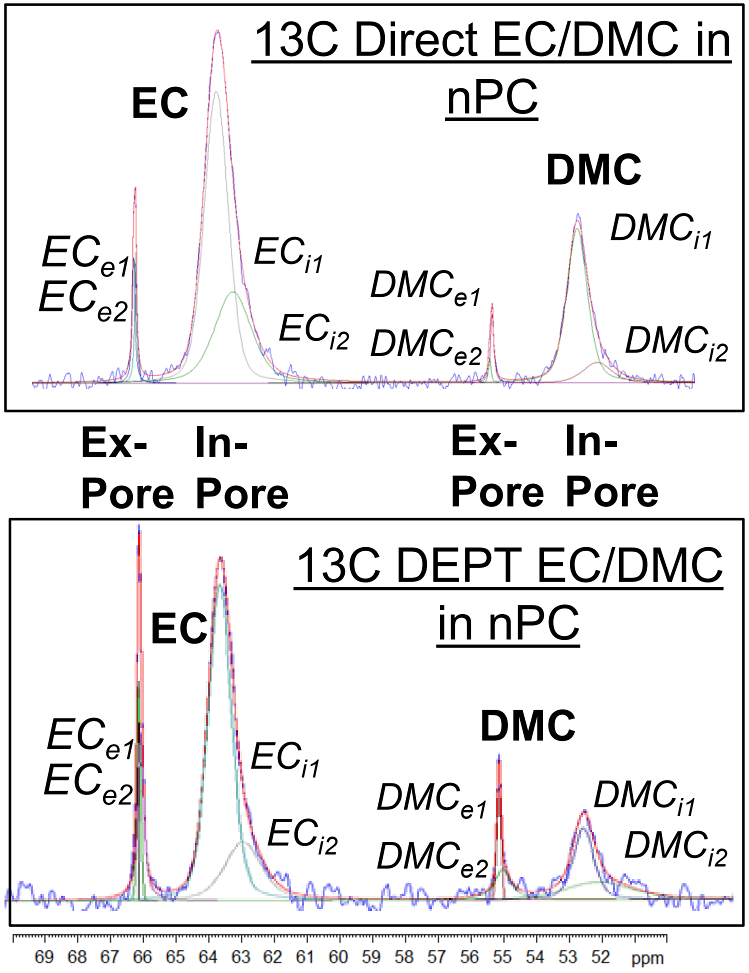
^{1}H HR-MAS Spectrum of EC/DMC at 1:1 loading in Graphene Oxide powder at 8 kHz

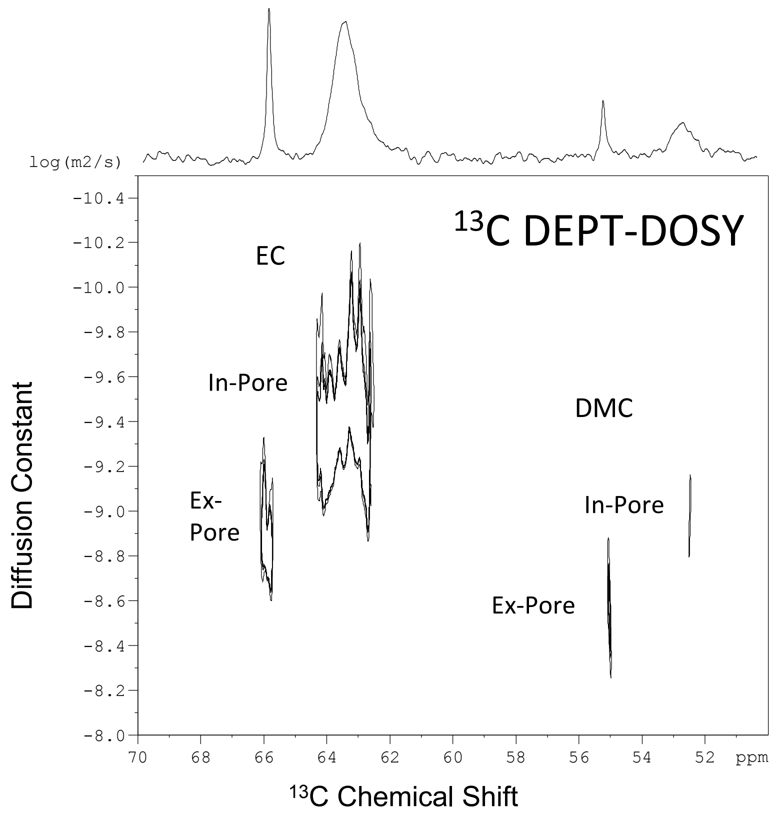


- Many environments, with no obvious differences like “in-pore” and “ex-pore”
- Broadening even with high MAS rate
- A case where more resolution is definitely required to perform any analysis on the system
- ^{13}C detection can sometimes afford better resolution, but at the cost of signal-to-noise

^{13}C Detection, ^{1}H-^{13}C DEPT DOSY of EC/DMC in nPC

- 13C DEPT Signal of In-Pore electrolyte is decreased due to additional 13 ms spent in the xy-plane during the DEPT sequence which allows for additional T_2 relaxation





Conclusions and Future Directions

- **For the first time ever, diffusion data for electrolytes in the pores of a porous electrode material have been obtained using HR-MAS PFG NMR**
  - An order of magnitude difference between diffusion constants of in-pore and ex-pore environments (~10^9 ex-pore, ~10^{10} in-pore)
- **Four distinct chemical environments were observed for both solvents: *ex-pore bulk, ex-pore adsorbed, in-pore bulk, in-pore adsorbed***
- **Future directions**
  - Explore the nuances of the binary mixture (implications for Solid-Electrolyte Interface-SEI)
  - Get diffusion constants for other electrolyte solvents
  - Add lithium salts, measure ^{7}Li, ^{19}F, ^{31}P diffusion to obtain in-pore and ex-pore diffusion for cations and anions

Acknowledgments

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Kimberly Childress
Ellie Friedmann
Vitaliy Dernov

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Sandia National Laboratories

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Group photo

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