National Ultrahigh-Field NMR Facility for Solids

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Program

8 th Annual Solid-State NMR Workshop

May 26, 2013, Québec City Convention Centre, Quebec, Canada

Session 1 (QCCC, Room 304B)

Chair Michèle Auger (Université Laval)

13:00-13:30 **Younès Messaddeq** (Université Laval) "New Glassy Materials Based on Heavy Oxides: Properties and Applications"

13:30-14:00 **Jun Xu** (Western University) "Determining the Number of Crystallographically Non-equivalent Sites for Each Element in MOF α-Mg$_3$(HCOO)$_6$ by Multinuclear Solid-State NMR at 21.1 T"

14:00-14:30 **Kristopher Harris** (McMaster University) "Solid-State NMR Studies of Lithium-Ion Battery Materials"

14:30-15:00 **Kevin Burgess** (University of Ottawa) "Alkaline-Earth Metal Solid-State NMR Study of Mg, Ca, and Sr Complexes in Organic Molecular Environments"

15:00-15:15 **Coffee Break**

Session 2 (QCCC, Room 304B)

Chair Isabelle Marcotte (Université du Québec à Montréal)

15:15-15:45 **Michèle Auger** (Université Laval) "^{2}H NMR Study of the Insertion of the Myristoyl Group of Neuroral Calcium Sensor Proteins in Lipid Bilayers"

15:45-16:15 **Qasim Saleem** (University of Toronto) "Lipids in motion: Lateral Diffusion of Lipids in Bilayers Measured via ^{31}P CODEX"

16:15-16:45 **Martine Monette** (Bruker Ltd.) "Lock, Gradients and Inverse Detection - from High-Resolution to Solid-State NMR"

16:45 **Reception** sponsored by Bruker Ltd. (Canada)

Determining the Number of Crystallographically Non-equivalent Sites for Each Element in MOF α-Mg$_3$(HCOO)$_6$ by Multinuclear Solid-State NMR at 21.1 T

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Metal-organic frameworks (MOFs) are a novel type of crystalline porous materials that have shown great potential in a variety of applications including gas separation and storage, selective recognition and catalysis. The topology of frameworks as well as the size, shape and connectivity of pore systems is of fundamental importance for the applications of MOFs. Therefore, thorough structural characterization is essential as it allows one to understand the relationships between the properties of MOFs and their structures. The structures of many MOFs have to be determined from the more limited powder XRD data due to the lack of suitable single crystals for X-ray diffraction. In such cases, an unambiguous structure solution requires additional information from other techniques such as solid-state NMR (SSNMR). SSNMR is complementary to XRD because it is sensitive to the short range ordering and local environments around the nuclei of interest.

One particular area which we have been working on is to develop multinuclear SSNMR as an effective approach to determine the number of non-equivalent sites for all the elements in unit cell. The ability of differentiating multiple sites is critical because it allows one to directly compare the NMR spectra with the X-ray determined structure. In this talk, we present our recent work on an important MOF, microporous α-Mg$_3$(HCOO)$_6$. Attempts were made to resolve 4xMg, 6xC, 6xH and 12xO sites by ^{25}Mg, ^{13}C, ^{1}H and ^{17}O SSNMR at 21.1 T for three microporous α-Mg$_3$(HCOO)$_6$ samples including as-made (*i.e.* containing solvent DMF molecules), activated (empty framework), and benzene-loaded phases. Among the interesting results, the ability of achieving ultrahigh-resolution for proton by the combination of performing MAS experiments under ultrafast spinning and isotope labeling is of particular importance because the structural information from ^{1}H NMR complements that from XRD which is limited in accurately locating hydrogens.

Solid-State NMR Studies of Lithium-Ion Battery Materials

Kristopher J. Harris,[1] Zoë E.M. Reeve,[1] Dongniu Wang,[2] Xifei Li,[2] Xueliang Sun,[2] and Gillian R. Goward[1]

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Lithium ion batteries (LiBs) find use in applications ranging from personal electronics to electric vehicles, and are particularly desirable when light-weight, rechargeable storage is required. Current research into new materials for LiBs is driven by the need to improve capacity-to-weight ratios, charge/discharge rates, spontaneous flammability ratings, electrolyte compatibility, environmental sustainability, and manufacturing costs [1]. In common with many topics in materials chemistry, improved LiB materials are increasingly being generated through the synthesis of nanostructured materials. As such materials are often amorphous and heterogeneous, solid-state NMR is an ideal spectroscopic tool. We present here a study of a recently developed anode material composed of approximately 100 nm tin-core/carbon-shell nanoparticles supported on graphene nanosheets, Sn@C-GNs [2]. The results of a ^{1}H, ^{13}C, and ^{119}Sn study of the structure and chemistry of the pristine material will be discussed. It was extremely difficult to obtain ^{13}C spectra; however, the low sensitivity proved to have its source in dephasing of the NMR signal by an unusually high degree of disorder, an effect that can be countered via the use of a rotor-synched echo train (i.e., CPMG/MAS). Further application of this method to other fully unsaturated carbon materials of technological importance such as graphites, graphenes, fullerenes, nanotubes, etc. is being explored.

The use of ^{1}H NMR spectroscopy to search for low-weight-percentage impurities was enabled by the use of a background suppression technique developed by D. Brouwer et al. Tin-119 spectra of the pristine material show that the tin oxide starting material is converted entirely to the β polymorph of metallic Sn in the atomic-layer-deposition synthesis. The results of a [7]Li study of the electrochemical cycle will also be presented. Changing ratios of lithium:tin in the metallic alloys at the nanoparticle cores are observed via the [7]Li chemical shifts as the reduction potential is altered, and the formation of $Li^+C_n^-$ is also observed at low potentials with respect to metallic Li.

References: [1] J.B. Goodenough, Y. Kim *Chemistry of Materials* **22** (2009) 587-603. [2] D. Wang, X. Li, J. Yang, J. Wang, D. Geng, R. Li, M. Cai, T.-K. Sham and X. Sun. *Submitted.*

Alkaline-Earth Metal Solid-State NMR Study of Mg, Ca, and Sr Complexes in Organic Molecular Environments

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Some of the least studied NMR-active nuclei in the Periodic Table are the quadrupolar alkaline-earth metals (^{25}Mg, ^{43}Ca, and ^{87}Sr). This is either due to their low natural abundances (0.145% for ^{43}Ca) or their large quadrupole moments (305 mb for ^{87}Sr). Furthermore, studies of these metals in organic complexes are rather rare because there is a larger dilution factor of the nuclei present compared to most inorganic materials [1,2]. Therefore, NMR experiments at standard magnetic fields are often challenging or unfeasible. This is unfortunate given the importance of these metals in biological and materials applications. The 21.1 T instrument at the National Ultrahigh-Field NMR Facility for Solids has made this study possible for a systematic series of metal aryl carboxylates (benzoate and salicylate ligands). We have extracted electric field gradient (EFG) tensor parameters and chemicals shifts from a large range of compounds and these data are correlated to their crystal structures. For example, in the case of the Mg^{2+} complexes, the quadrupolar coupling constant, C_Q, is related to distortions in the octahedron formed by the oxygen atoms in the first coordination sphere of the metal.   We have also observed ligand-binding to Ca^{2+} *via* a nitrogen atom; this environment is distinguishable from that consisting solely Ca$-$O bonds in the ^{43}Ca NMR spectrum due to the changes in the ^{43}Ca EFG and chemical shift tensor parameters. Preliminary ^{87}Sr data demonstrate that the value of $C_Q(^{87}$Sr$)$ is sensitive to changes in the coordination number at the metal centre. All of these experimental findings are corroborated using gauge-including projector-augmented-wave density functional theory (GIPAW DFT) calculations based on the crystal structures.

References: [1] J.C.C. Freitas and M.E. Smith, *Ann. Rep. NMR Spectrosc.***75** (2012) 25-114. [2] D. Laurencin and M.E. Smith, *Prog. Nucl. Magn. Reson. Spectrosc.* **68** (2013) 1-40.

^{2}H NMR study of the insertion of the myristoyl group of neuroral calcium sensor proteins in lipid bilayers

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Neuronal calcium sensor (NCS) proteins consist of four domains called EF-Hand, which include two α-helices bridged by a Ca^{2+}-chelation loop with a highly conserved sequence. These proteins are acylated at the N-terminal and at low calcium concentration, the myristoyl group is sequestered into a hydrophobic

cavity. The binding of one to four Ca^{2+} leads to the extrusion of the myristoyl (known as the calcium-myristoyl switch) and the exposure of many hydrophobic residues allowing the protein to move from a cytosolic form to a membrane bound form. This property has an important biological function in the visual phototransduction cascade.

To determine the insertion of the recoverin myristoyl group into different model membranes, recoverin acylated with a perdeuterated myristoyl group was prepared to obtain ^2H solid-state NMR spectra of the myristoyl group in membranes. Samples were prepared at a lipid-to-protein molar ratio of 200:1, corresponding to one deuterated myristoyl group for 400 undeuterated lipid fatty acyl chains. Experiments were first performed at Université Laval using the 400 MHz spectrometer but the signal-to-noise ratio was insufficient. The results obtained at 900 MHz indicate a preferential interaction of the myristoyl group with monounsaturated membranes. In addition, the results confirm the extrusion and membrane insertion of the myristoyl group in the presence of calcium and therefore, the existence of a calcium myristoyl switch. These results bring significant insights into the mechanism of action of recoverin.

Lipids in motion: Lateral diffusion of lipids in bilayers measured via ^{31}P CODEX

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The anisotropic lateral diffusion of lipids is an inherent feature of biological membranes and is essential to many of its functions. Label-free NMR methods for determining lateral diffusion coefficients include static ^1H pulsed field gradient (PFG) NMR diffusion experiments on magnetically aligned bicelles or physically aligned lipid bilayers, and magic angle spinning (MAS) ^1H PFG NMR on spherical lipid bilayer vesicles. Static 1D or 2D ^{31}P NMR exchange experiments on spherical lipid bilayers can also be used to measure lateral diffusion. In all of these methods, resolution of different phospholipids is somewhat limited. We have demonstrated that the MAS Center-band Only Detection of Exchange (CODEX) [1] experiment can be used to determine the lateral diffusion coefficient of phospholipids in large unilamellar vesicles (LUVs) [2]. Using ^{31}P CODEX, the diffusion coefficients of as many as five different phospholipid species have been determined simultaneously. Furthermore, lateral diffusion coefficients can be determined in both the liquid-crystalline and the gel phase. This permits an analysis of liquid-ordered and liquid-disordered domains. We anticipate that this approach will prove useful in exploring phenomenon such as lipid rafts, and lipid-protein and protein-protein interactions.

References: [1] E.R. deAzevedo, W.-G. Hu, T.J. Bonagamba, K. Schmidt-Rohr, *J. Am. Chem. Soc.* **121** (1999) 8411–8412. [2] Q. Saleem, A. Lai, H.H. Morales, P.M. Macdonald, *Chem. Phys. Lipids* **165** (2012) 721–730.

Lock, gradients and inverse detection - from high-resolution to solid-state NMR

Martine Monette

Bruker Ltd., Milton, Ontario, Canada

Bruker has recently introduced a new solids probe optimized for ^1H detection. The probe is suitable for 2D and 3D correlation experiments on ^{13}C and ^{15}N labeled samples. The new design includes a lock channel and a gradient at the magic angle. Typical technical data will be presented, as well as recent results on microcrystalline SH3 protein.