LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-815006

Development of Operando Nuclear Magnetic Resonance Capabilities for Solid-State Battery Research

M. A. T. Marple

September 28, 2020

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Development of Operando NMR Capabilities for Solid-State Battery Research
Maxwell Marple (20-FS-12)
LLNL Tracking # LLNL-TR-815006

Abstract

Mechanistic information regarding solid-solid interfaces in solid-state batteries remains elusive as its observation requires a non-destructive *operando* technique. Such a technique does not currently exist. Solid-state nuclear magnetic resonance (NMR) is uniquely suited to address this challenge as it is sensitive to chemistry, structure, and dynamics and can measure buried interfaces. However solid-state NMR requires high speed spinning of the sample at the 'magic angle' (MAS) to obtain adequate resolution. The metallic current collectors in a battery are detrimental to spinning in magnetic fields as they generate eddy currents which prevent spinning and dampen the NMR signal. Furthermore, the spinning nature of the MAS NMR experiment requires a wireless means of charging for *operando* capabilities. These challenges were addressed in this research and *operando* MAS NMR enabled by optical wireless charging was demonstrated. By limiting the size of the metallic components, we were able to spin a sample holder with electrical leads and a solid-state battery up to a few kilohertz, fast enough for high-resolution NMR. We achieved wireless charging by attaching a photovoltaic cell to the head of the NMR rotor and used a laser to transmit power to the photovoltaic cell. Demonstration of the optical wireless charging was performed by polarizing a liquid electrolyte during an *operando* MAS NMR measurement. This novel capability is a transformative technique for investigating the mechanistic electrochemical processes in solid-state samples.

Background and Research Objectives

The transition to a carbon negative economy is driving an increased demand for better performing batteries for grid storage and transportation. Solid-state batteries (SSB) are an inherently safer and higher energy density alternative to current liquid electrolyte batteries; however, their performance is generally hindered by the formation of solid-solid interface (SSI) between the solid electrolyte and electrodes. Insight into the composition, structure, and kinetics of the SSI is exceptionally difficult to achieve with standard characterization techniques as it is nanometers thick, highly disordered, and it is buried deep within the electrochemical cell. Information regarding the SSI remains elusive as its influence requires a non-destructive *operando* technique to observe which does not currently exist.

State of the art characterization techniques for batteries are '*in situ*', where the battery is measured at various states of charge along the charge/discharge profile without destroying the integrity of the battery. While beneficial, *in situ* approaches can suffer from relaxation phenomena while not under bias during analytical measurements preventing insight into transient kinetics and metastable phase transformations. An *operando* approach, 'under working conditions', can simultaneously probe the battery with an analytical measurement and be charged/discharged at the same time. *Operando* measurements offer a wealth of otherwise inaccessible analytical data relative to *ex/in situ* measurements that can be used to develop a complete understanding of the electrochemical, physical, and chemical processes occurring within a functioning battery.

Operando and *in situ* techniques have been successfully implemented for liquid electrolyte batteries with a variety of analytical measurements: transmission electron microscopy (TEM), X-ray imaging and X-ray photoelectron spectroscopy, nuclear magnetic resonance (NMR), vibrational spectroscopy, and neutron reflectometry. (Boebinger et al. 2020) These techniques have been invaluable towards understanding reaction and degradation mechanisms of electrodes, improving their chemical stability, and cycle life. In comparison, *operando* and *in situ* techniques for SSB are still in their infancy and techniques tailored to observing the SSI are rare due to the buried nature of the interface and sample-limited nature of the interface. Entirely new techniques, methods, and cell designs are required to address these technical issues. The state of the art for investigating the SSI is with *in situ* TEM and XPS measurements however these techniques are surface sensitive and cannot probe the entire battery volume, adding complication to how representative the surface facing SSI is relative to a buried SSI. (Wynn et al. 2018)

Solid-state NMR spectroscopy is uniquely suited to address the challenge of probing buried interfaces as the NMR signal measured arises from the entirety of the sample. In addition, NMR is element selective, quantitative, and is sensitive to the materials structure and dynamics of mobile ions, including amorphous materials. The development of *operando* solid-state NMR will provide direct access to both the transient kinetics and structural mechanisms occurring under bias that will ultimately elucidate the influence of the SSI on battery performance. The merit of *operando* NMR capabilities has been demonstrated previously for liquid electrolyte batteries. The method was pioneered by Clare Grey's group at University of Cambridge (Pecher et al. 2017), wherein the NMR measurement is performed on a static liquid electrolyte battery that is housed within a polymer holder that the NMR coil is wrapped around and separate electrical leads with radiofrequency (RF) chokes are fed to a potentiostat outside the magnet. This *operando* method has been powerful for developing a mechanistic understanding of battery failure and degradation and provides insight for performance improvement. (Kitada et al. 2019; Lorie Lopez, Grandinetti, and Co 2019) This *operando* method for liquid electrolytes cannot be applied to solid-state batteries as solid materials have a local charge distributions, anisotropies, and couplings to neighboring nuclei that severely broaden NMR spectra compared to liquid-state spectra. Magic angle spinning (MAS) is used to improve spectral resolution for solid-state samples by physically spinning the sample within a rotor at high speeds, >5 kHz. MAS NMR is a requirement for obtaining high resolution line shapes of solid samples and a cornerstone of advanced two-dimensional NMR measurements.

Implementing *operando* NMR for solid-state batteries requires being able to perform magic angle spinning. This requirement carries many technical challenges that this research aims to address. The primary challenge arises from the metallic current collectors spinning rapidly within the NMR's high field magnet, on the order of 9 T. Moving any metallic component within a magnetic field will produce eddy currents. These eddy currents are detrimental to MAS NMR by producing a counter torque that prevents high speed spinning, excess heat generation, and attenuating the RF signal the NMR measurement acquires. The strength of the eddy current is proportional to the field strength, electrical conductivity of the metal, and the amount of metallic material within the rotor. An additional challenge for *operando* MAS NMR is developing a means to wirelessly charge and discharge the SSB while spinning. The ability to acquire advanced high-resolution *operando* MAS NMR spectra of solid-state batteries and the solid-solid interfaces formed during operation is critical for developing a deeper understanding of the connection between interfacial structure and dynamics and will lead to a breakthrough in advancing solid-state battery technology.

The objectives of this work are to test the feasibility of *operando* MAS NMR by (1) creating a rotor holder that both secures the battery for stable spinning while providing secure electrical contact, then (2) testing whether the battery can be charged wirelessly using a coupled laser and photovoltaic (PV) cell. An additional objective (3) arose during the progress of the project to develop a better understanding of the solid electrolyte used for this study as there is not any precedent for its short range structure and MAS NMR spectra which is needed to build a foundation upon to understand how it changes within the solid-state battery during operation. All objectives were met although demonstration of wireless charging was performed by polarizing a liquid electrolyte. A provisional patent was filed covering objectives 1 and 2, and a paper covering the results of objective 3 has been published.

Scientific Approach and Accomplishments

Objective 1

The first objective of the *operando* MAS development is to create a holder than both securely mounts the sample within the rotor while providing secure electrical contact to the PV cell and is amenable to high spinning speeds. Our approach revolves around a cylindrical battery design wherein a thin film solid-state battery is deposited around a cylindrical quartz substrate (Figure 1a). The use of a cylindrical geometry of the battery maximizes the interfacial area relative to a planar battery geometry thus increasing the NMR signal strength of the SSI and provides uniform density along the spinning axis enabling stable spinning conditions. The thin-film battery is composed of a platinum current collector, lithium cobalt oxide (LCO) as the cathode, amorphous lithium phosphorus oxynitride (LiPON) as the solid electrolyte, and copper as the anode current collector. This battery is chosen because its performance has been well characterized and its synthesis method is amenable to the cylindrical geometry. This cell design is deposited with radiofrequency sputtering as ‘anode-free’, during the initial charging stage Li metal deposits on Cu to form the anode. A cross section diagram in Figure 1a shows the thicknesses of each layer and shows that electrical contact can be made by touching the ends of the rod. The use of a thin-film microbattery leverages the limitations imposed by spinning metallic components by minimizing the thickness of the metallic current collectors to hundreds of nanometers thereby reducing the deleterious effects of eddy currents on spinning and RF signal shielding. Furthermore, the use of metallic current collectors ultimately limits the penetration depth of the RF field strength used to generate the NMR signal. The thin-film microbattery overcomes this issue as the total cell thickness (3 μm) is within the skin depth for ^{7}Li NMR signal at 9.4T (5.3 μm)(Bhattacharyya et al. 2010) while using copper current collectors, so all battery components are observable and the RF field strength within the battery is still 90%

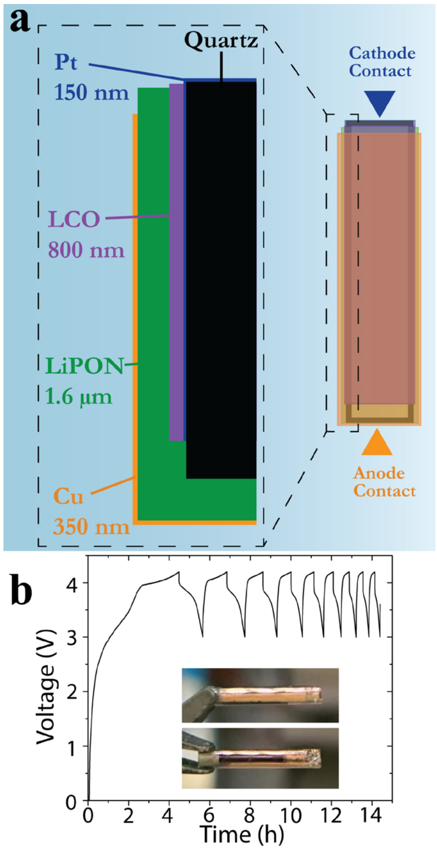

Figure 1. a. Schematic of the cylindrical solid-state battery. A cross-section shows the layer thicknesses and layering positions. b. Charge cycling profile of the thin-film battery, charged with 1 μA between 3V to 4.2V. Inset shows the thin-film battery with patterned Cu sections to boost RF permeability. The dark region is exposed LiPON.

of that outside the copper current collector. The cylindrical SSB was created by our collaborators in Shirley Meng's group at University of California San Diego. A charge cycling profile is shown in Figure 1b, the battery can be cycled between 3V and 4.2V for over 9 cycles with distinguishable voltage plateau using a current of 1 μA. However, there is capacity loss observed with each cycle as there is no capping layer covering the cell leading to gradual oxidization of Li metal at the anode. Furthermore, in testing the NMR acquisition of the cylindrical battery, it was found a monolithic coating of Cu around the battery significantly attenuated the signal strength. To limit this attenuation and increase the RF permeability into the battery, Cu was deposited as two stripes leaving two exposed sections of LiPON (Figure 1b inset). This suggests future designs for solid-state batteries for *operando* MAS NMR need to have the outermost metallic current collector composed of a less conductive material (like carbon) or use a patterned current collector like a mesh to allow RF through.

A model of the SSB holder and cylindrical SSB is shown in Figure 2a with colored solid lines indicating the position of the electrical leads. The top and bottom of the holder have recessed holes sized to firmly grasp on a 1.6 mm diameter rod ensuring it is aligned along the central axis of the rotor. The electrical leads make contact with the ends of the cylinder once it is seated in the top and bottom holders. Furthermore, the electrical leads are threaded outside the top holder for external electrochemical contact, making this design amenable to *in situ* experiments as well. The top holder has two holes for the optoelectrical element 'hat' to slot into, this 'hat' has either a photovoltaic or photoresistor attached to the top for either wireless charging or discharging and is intended to be interchangeable depending on the experimental conditions required. Figure 2b shows the manufactured holders with a glass rod in position of the cylindrical battery. Figure 2c shows the complete assembly with the cylindrical battery, once the battery is secured it can be easily loaded within the rotor by pushing down; Figure 2d shows the loaded rotor ready for *operando* or *in situ* MAS NMR measurements.

Various materials were tested for the electrical leads to determine their impact on

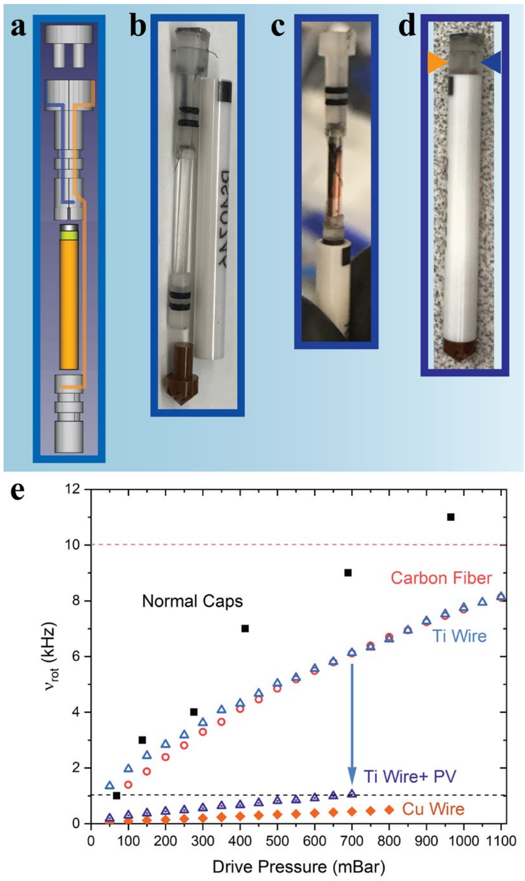

Figure 2. Development of the solid-state battery rotor holder for a 4 mm pencil-style rotor. a. 3D model of the components, from top to bottom, the removable optoelectrical element 'hat' for mounting a photovoltaic cell, the holder contains electrical leads (blue and orange solid lines) and a recessed hole that holds the cylindrical battery, solid-state cylindrical battery, bottom holder fixes the position of the battery along the central axis. Divots in the top and bottom holder are positions for o-rings. b. Constructed holder with a glass rod in place of the cylindrical battery. Electrical leads are thin titanium wire that are threaded through the holder and secured with epoxy. Beside the holder assembly is the magic angle spinning (MAS) rotor and drive cap. c. The holder mounted with the cylindrical battery. d. Whole assembly sealed within the MAS rotor. Electrical connection for *in situ* electrochemical measurements can be made by contact with the titanium wire threaded outside the holder, indicated by the position of the two triangles. e. Comparison of different materials for electrical leads and the influence on spinning speed (ν_{rot}).

spinning speed (Figure 2e). Spinning a rotor is accomplished by applying drive pressure to the rotor within a stator however the presence of metallic components will generate a braking torque to counteract this spinning. An ideal spinning speed is 10 kHz for producing high resolution line shapes. Using copper wire as the electrical leads limits spinning to under 500 Hz. Higher spinning speeds are obtained by using either carbon fiber or thin (75 μm) titanium wire which have orders of magnitude less electrical conductivity compared to copper and allows for a max spinning speed of 8 kHz. Attaching the PV cell to the rotor assembly decreased the maximum spinning speed to 1 kHz due to the aluminum contacts on the cell. The maximum spinning speed of the rotor assembly can be increased by removing the Al contacts. While there is room for improving the rotor design to further maximize spinning speeds, we successfully created a rotor battery holder that can be spun at high speeds (≥ 1 kHz) and used for either *in situ* or *operando* MAS NMR measurements.

Objective 2

Our approach for enabling *operando* MAS NMR is by optical wireless power transmission, where a high-power laser is focused on a PV cell to produce a constant potential and current source to the battery in the rotor. This technology is advantageous for *operando* MAS NMR because the high energy light source will not interfere with the magnetic fields or RF used to measure the NMR signal. The PV cell used is a commercially available specialty vertical multi-junction PV cell which can generate a high voltage (~8 V) while maintaining a small footprint (a 3 mm by 3 mm square, Figure 3a). The laser is directed from an external laser source outside the magnet into the NMR probe by an optical fiber. The end of the fiber is directed to the PV cell by a right-angle prism contained within a mount that is fixed to the MAS stator (Figure 3a). The laser source used for this study was a variable power 15 mW 660 nm laser, which produced up to 8 μA photocurrent and 6 V photovoltage in the PV cell while not spinning in the NMR magnet (Figure 3b). The output photovoltage and photocurrent can be increased by using a higher power laser source and optimizing the beam shape to uniformly illuminate the PV cell. It was found the output photovoltage and photocurrent of the PV cell depend on the magnetic field (Figure 3b). While inside the magnet, the photovoltage is decreased slightly while the photocurrent is ~70% of the value when placed below the magnet where a there is drastically lower magnetic field. The decrease of the photocurrent is dependent on orientation of the p-n junction relative to the magnetic field and is a result of a Lorentz force acting upon charge carriers. (Fathabadi 2020) As such the output photocurrent while spinning during an *operando* MAS measurement could be further

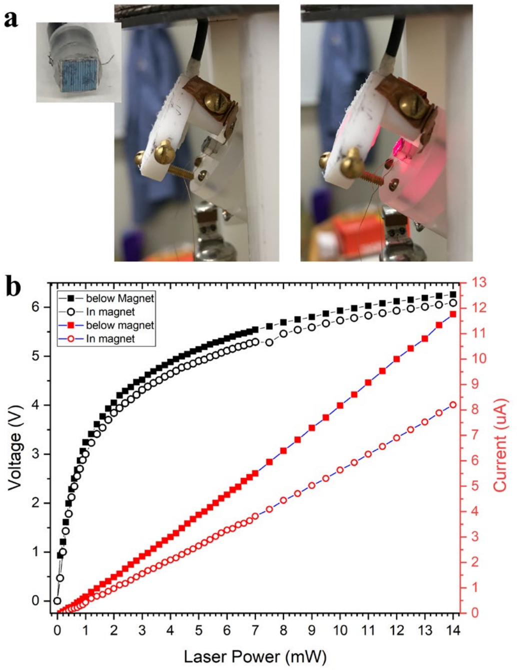

Figure 3. a. Left, a photograph on the vertical multi-junction photovoltaic cell fixed on the end of the rotor assembly. The output of the fiber optic beam goes through a right-angle prism within the mount. The mount is shown with the laser off (middle) and on (right). b. The open circuit voltage and short-circuit current of the photovoltaic cell inside and outside the magnet. There is diminished photocurrent generated while inside the 9.4T magnet.

diminished from similar Lorentz force interactions or eddy current effects within the circuit. The efficiency of the photocurrent and photovoltage while spinning ultimately dictates if the *operando* MAS NMR technique is feasible and can only be tested by carrying out an *operando* MAS NMR measurement. The SSB battery depicted in Figure 1 was mounted into the holder (Figure 2) and its open circuit voltage was checked to verify electrical continuity for preliminary *in situ* MAS NMR experiments. The SSB was spun up to 2 kHz for NMR optimization and check periodically to verify electrical continuity was maintained throughout. However, after spinning the SSB beyond 5 kHz there was not a measurable open circuit voltage implying a loss of electrical continuity. Before this a spectrum of the ^{7}Li MAS NMR on the discharged battery was collected (Figure 5). After dismantling within an argon glovebox it was discovered a loose wire touched the thin film battery during spinning causing the film to be removed and the limited timeframe of the project prevented further *operando* and *in situ* testing of the SSB. These results were promising and further tests with the SSB will be explored later.

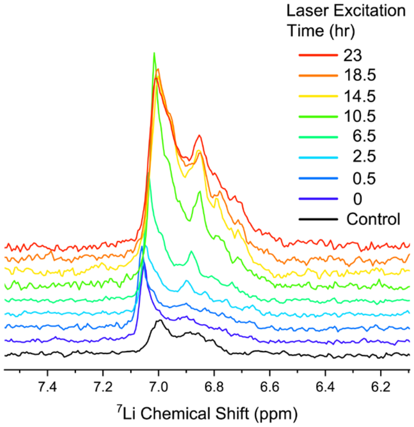

Figure 4. ^{7}Li *Operando* MAS spectra of electrochemical decomposition of $LiPF_6$. The sideband shows the gradual broadening and intensity increase reflecting changes in the electronic structure around the nucleus while charging. The A 660 nm, 14mW laser is used for optical wireless power transmission.

An alternative means of testing the *operando* MAS NMR is by electrochemically decomposing the liquid electrolyte $LiPF_6$ with the photocurrent. $LiPF_6$ is a major component in a common liquid electrolyte mixture (1.2 M LiPF6 in a 3:7 weight percent mixture of ethylene carbonate and ethyl methyl carbonate) for lithium-ion batteries and electrochemically decomposes into HF, POF_3 and LiF above 4.4 V. (Solchenbach et al. 2018) The electrochemical decomposition can be monitored in *operando* by detecting the ^{19}F, ^{7}Li, and ^{31}P MAS NMR signals, where decomposition products will be revealed as new peaks that increase in intensity with time. The rotor holder was modified to have extended Ti wires submerged into the liquid electrolyte for generating a bias in the liquid. The *operando* experiment was carried out over 23 hours while spinning at 588 Hz using a laser power of 14 mW. A control spectrum was also collected to account for any degradation not caused by the *operando* experiment; this was the $LiPF_6$ liquid electrolyte loaded into the same rotor and left outside the magnet without a PV cell for the same time period. The *operando* experiment results in broadening of the ^{7}Li line shape and an increase of the spinning side band intensity to the control (Figure 4). These changes indicate the chemical identity of the species are not drastically changing, as that would result in a new chemical shift, but the broadening indicates the spin-spin relaxation time (T_2) of the Li ions gradually shortens with *operando* time. The intensity of the spinning sidebands arises from first order quadrupolar, dipolar, and chemical shift anisotropy interactions; these interactions are more sensitive to the electronic structure around the nucleus. After the *operando* NMR measurement, the open circuit voltage of the control and the *operando* sample were taken and found to be 0.02 V and 2 V, respectively. This is proof that the *operando* MAS NMR technique works, as charge is being accumulated and stored within the electrolyte. However, the input photovoltage was not high enough to drive electrochemical decomposition, corroborated by the lack of a new peak for HF in the ^{19}F spectra (not shown). The accumulation of charge during the MAS measurement implies the electrolyte was polarized and the changes observed in the ^{7}Li spectra were due to forming an electric double layer at the Ti wire electrodes. These results indicate the photovoltage during the *operando* measurement was below 4.4 V. This lower photovoltage could be result of the limited divergence of the beam size over the short distance between the fiber and PV cell. It found during testing of the PV cell performance that the entire PV cell needs to be uniformly illuminated to reach higher photovoltages. This issue can be resolved by using a divergence lens to expand the beam size and the photocurrent can be increased by using a higher power laser source. A provisional patent application has been filed in FY20 on the *operando* MAS NMR experimental setup described here.

Objective 3

During the project it was found that there was a surprising lack of knowledge on the structure of the amorphous solid-electrolyte LiPON used for the cylindrical battery. An investigation of the structure of LiPON with experimental ^{31}P and ^{7}Li MAS NMR complimented by ab initio and first principle calculations was performed to lay the foundation of understanding the SSI in this battery system by elucidating the structure of the solid electrolyte before it is in contact with electrodes. We resolved the structure of LiPON and found to be composed isolated phosphate monomers with N incorporated in both apical and as bridging sites in phosphate dimers (Figure 5a). These structural results suggest LiPON's stability with lithium metal is a result of its glassy character. These results were published in Angewandte Chemie (Marple et al. 2020) and further strengthened our collaborative ties with Prof. Shirley Meng at University of California San Diego. Preliminary results of the ^{7}Li MAS NMR spectra of the cylindrical battery are compared to LiPON (Figure 5b). The ^{7}Li NMR spectrum of LiPON shows a single Lorentzian line shape due to the rapid motion of Li ions at room temperature. In comparison, the cylindrical SSB in the discharged state has a narrow peak agreement with LiPON however there is a broad component underneath, composed of $LiCoO_2$ and Li_2O. Further investigation of the *in situ*/*operando* ^{7}Li NMR on the cylindrical battery was impeded by sample limitations and complications with laboratory access due to Covid-19 shutdowns. These preliminary results are promising and will be explored at a later date to further elucidate the structural and chemical influence of the SSI.

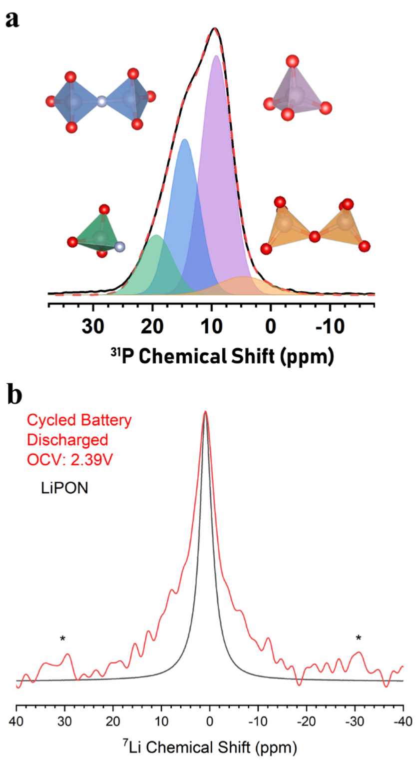

Figure 5. a. ^{31}P NMR of LiPON solid electrolyte. Deconvolution shows the four constituent phosphorus units making up the amorphous structure. O atoms are in red and N are white. b. 7Li NMR spectrum of LiPON and the discharged thin-film solid-state battery, Pt/$LiCoO_2$/LiPON/Cu. The broad component seen in the battery is due to $LiCoO_2$ and Li_2O.

Impact on Mission

The *operando* MAS NMR capability is entirely new characterization technique for investigating energy materials and is unique to LLNL. The technique can be applied more broadly to investigate not only batteries but any material under bias including performing *operando* electroplating, hydrogen splitting, electrochemical reduction and oxidization of materials. This new capability is synergistic with LLNL's Energy Materials strategic plan and addresses major experimental needs of LLNL's Energy and Climate Security focus area.

Conclusion

We have demonstrated the feasibility of *operando* MAS NMR through optical wireless power transmission. The results of this demonstration will be complied as a publication to be submitted to a high impact journal (*Nature Materials*) along with additional results on the cylindrical solid-state battery. The technique can be improved and expanded upon by continued development. The collaboration with Dr. Shirley Meng at UC San Diego will be further strengthened through continued development of the cylindrical battery and performing investigations of the Li/LiPON interface. Funding opportunities to apply the *operando* MAS NMR method to other solid-state battery systems created by additive manufacturing will be pursued through an Emerging Research LDRD or through EERE.

References

Bhattacharyya, R., et al. 2010. "In Situ NMR Observation of the Formation of Metallic Lithium Microstructures in Lithium Batteries." *Nature Materials* 9 (6): 504–10. https://doi.org/10.1038/nmat2764.

Boebinger, M. G., et al. 2020. "Understanding Transformations in Battery Materials Using in Situ and Operando Experiments: Progress and Outlook." *ACS Energy Letters* 5 (1): 335–45. https://doi.org/10.1021/acsenergylett.9b02514.

Fathabadi, Hassan. 2020. "Magnetic Field Effect on Silicon Based Solar Cells." *Materials Chemistry and Physics* 244 (April): 122684. https://doi.org/10.1016/j.matchemphys.2020.122684.

Kitada, K., et al. 2019. "Unraveling the Reaction Mechanisms of SiO Anodes for Li-Ion Batteries by Combining *in Situ* ^{7}Li and *Ex Situ* ^{7}Li/^{29}Si Solid-State NMR Spectroscopy." *Journal of the American Chemical Society* 141 (17): 7014–27. https://doi.org/10.1021/jacs.9b01589.

Lorie Lopez, J. L., et al. 2019. "Phase Transformations and Capacity Fade Mechanism in Li_x Sn Nanoparticle Electrodes Revealed by Operando ^{7}Li NMR." *Journal of Materials Chemistry A* 7 (17): 10781–94. https://doi.org/10.1039/C9TA03345A.

Marple, M.A.T., et al. 2020. "Local Structure of Glassy Lithium Phosphorus Oxynitride Thin Films: A Combined experimental and Ab Initio Approach." *Angewandte Chemie International Edition*, August, anie.202009501. https://doi.org/10.1002/anie.202009501.

Pecher, O., et al. 2017. "Materials' Methods: NMR in Battery Research." *Chemistry of Materials* 29 (1): 213–42. https://doi.org/10.1021/acs.chemmater.6b03183.

Solchenbach, S., et al. 2018. "Quantification of PF_5 and POF_3 from Side Reactions of $LiPF_6$ in Li-Ion Batteries." *Journal of The Electrochemical Society* 165 (13): A3022–28. https://doi.org/10.1149/2.0481813jes.

Wynn, T.A., et al. 2018. “*In Situ* and *Operando* Probing of Solid–Solid Interfaces in Electrochemical Devices.” *MRS Bulletin* 43 (10): 768–74. https://doi.org/10.1557/mrs.2018.235.

Publications and Presentations

Marple, M.A.T., et al. 2020 “Local structure of glassy lithium phosphorous oxynitride thin films: a combined experimental and *ab initio* approach.” *Angewandte Chemie International Edition*, August. https://doi.org/10.1002/anie.202009501. LLNL-JRNL-810272

Marple, Maxwell. 2020. “Operando solid-state nuclear magnetic resonance spectroscopy specialized rotor insert for probing materials and devices under electrical bias.” US Provisional Patent Application 62961332, filed January 15, 2020.

Notes to the Editors

- Any instance of “7Li”, “31P”, or “19F” should have the respective number superscript.
- Any instance of a number proceeding a letter in a chemical formula or within should be subscript, for example the 6 in LiPF6.
- Ex situ, in situ, and operando should be in italics.
- The Greek letter mu, μ, is used in the unit micrometer μm and microamp μA