Analysis of Electrolytes for Lithium Ion Batteries Using Solid State NMR Methods

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The development of novel electrolyte materials for lithium ion batteries has been the focus of much research in recent years.[1] Solid state electrolytes offer stability against attack by electrodes, and promise to sustain a higher operating voltage window, allowing the design of batteries with higher power output.[2]

Solid state NMR provides a unique and powerful tool to examine the mobility of lithium ions in these highly conductive electrolyte materials.[3] With the ability to focus on the mobile species alone, this tool facilitates the study of ionic hopping in a microscopic setting, avoiding grain boundary effects.

The solid state electrolyte $Li_6BaLa_2Ta_2O_{12}$ has a garnet-like structure, and is known to have one of the highest ionic conductivities of this class of materials, at 4 x 10^{-5} S/cm.[4] Previous studies focusing on conductivity and reactivity have been performed using bulk conductivity measurements, and powder X-ray diffraction.[5] In this work, these materials have been studied using solid state NMR techniques to assess ionic motion as a function of temperature, independent of grain boundary resistance.

Rotational Echo Double Resonance (REDOR) NMR is a heteronuclear technique capable of measuring the dipolar coupling between a pair of nuclei. This experiment is traditionally used to determine distances between an isolated pair of nuclei.[6] However, this technique can also been used to study ion mobility in materials, since dipolar coupling changes as a function of ion exchange.[7] We have utilized the fact that lithium has two NMR active isotopes, ^{6}Li and ^{7}Li, which are distributed throughout the crystallographic Li sites in lithium electrolyte materials. By measuring the changes in the dipolar coupling as a function of temperature we can assess the lithium dynamics in these materials.

For the first time, we have used $^{6}Li\{^{7}Li\}$-REDOR to study temperature dependent ionic motion in solid state electrolyte materials. Here the experiment produces a buildup curve, with a slope that is dependent on the dipolar coupling between ^{6}Li and ^{7}Li. Examination of this slope as a function of temperature, shown in ***Figure 1***, allows us to study the temperature dependent dynamics in lithium ion conductors.

A comparison has been made between the electrolytes, $Li_6BaLa_2Ta_2O_{12}$, and $Li_6BaLa_2Nb_2O_{12}$ to study the variation of ion mobility as a function of temperature. We have found that although similar ionic conductivities and activation energies have been reported for these materials in bulk conductivity measurements, the response of the NMR experiments to changes in temperature indicates different activation energy for lithium ion hopping in these two materials. The deviation from previous studies is due to the effect of grain boundary resistance, and other bulk effects, which dominate the ionic conductivity.

This study highlights the overwhelming effect of bulk contributions. Moreover, these results point to the necessity to further understand the significance of bulk contributions, and cater material preparation to minimize these effects.

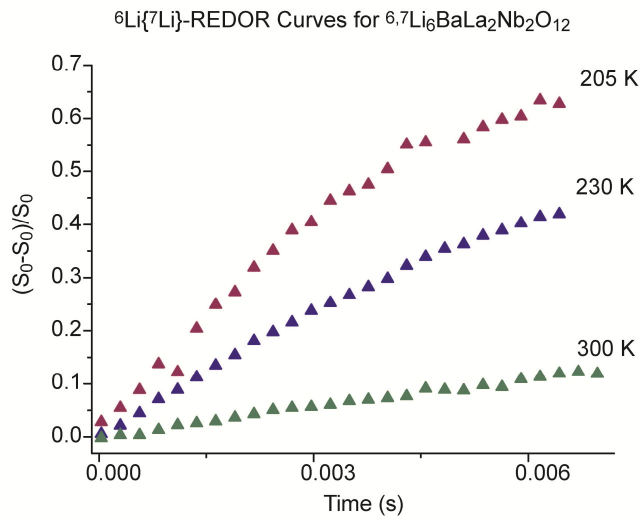

Figure 1. $^{6}Li\{^{7}Li\}$-REDOR curves for $^{6,7}Li_6BaLa_2Nb_2O_{12}$ at 205, 230, and 300 K. Different slopes indicate different ionic hopping rates.

References

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