

^{139}La NMR studies in lanthanum oxides and battery materials

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Lanthanum containing materials have made their way into the realm of lithium battery materials, with many lithium ion conducting oxides containing lanthanum. Although ^{139}La solid-state NMR has been performed on many materials for structural analysis, this technique is not routinely used [1-5]. This is due to the large quadrupole coupling seen for ^{139}La in many lanthanum materials [2, 5].

The application of ^{139}La NMR to battery materials is a novel strategy for structural elucidation of these complex materials. In many cases multiple lanthanum sites are present, which can make deconvolution of NMR spectra challenging. For this reason, it is useful to study other lanthanum oxide materials, making note of chemical shifts, δ_{iso} , and quadrupole parameters such as the quadrupolar coupling, C_Q , and asymmetry parameter, η . We have begun to study some common lanthanum oxides, as well as some lanthanum containing battery materials.

LaAlO_3 is a simple oxide material, in which there is only one crystallographically unique lanthanum site, which lies on a highly symmetric site. Simulations were performed in DMFit software [6]. Figure 1 shows the static and MAS ^{139}La NMR spectra of LaAlO_3 .

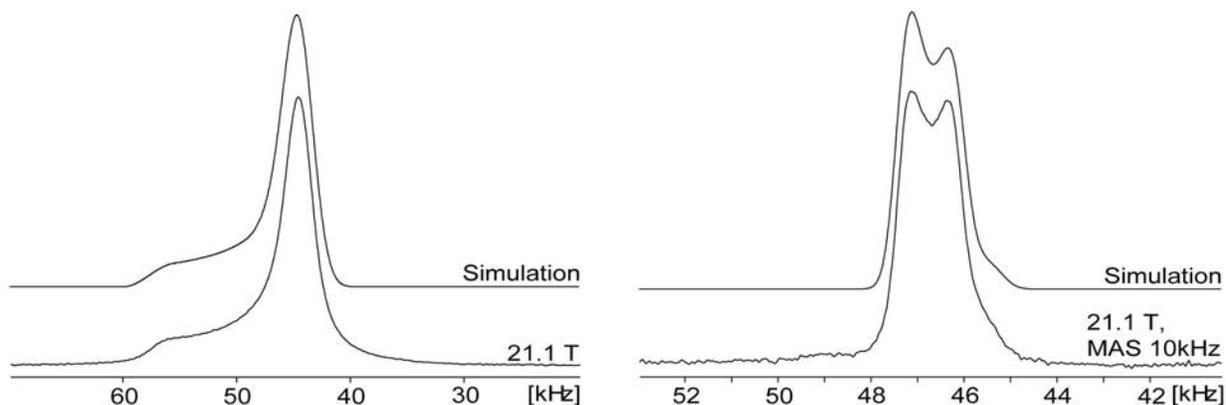


Figure 1: Static (left) and 10 kHz MAS (right) ^{139}La NMR spectra collected at 21.1 T. Simulations were performed for each spectrum in DMFit, and the quadrupolar parameters were in agreement: $C_Q = 7.0 \text{ MHz} \pm 0.4 \text{ MHz}$, $\eta_Q = 0.0 \pm 0.2$, and $\delta_{\text{iso}} = 375 \text{ ppm} \pm 1 \text{ ppm}$. These spectra were collected using a single pulse experiment.

Other lanthanum oxides proved to be more difficult to study, with challenging ^{139}La NMR spectra. Figure 2a shows the ^{139}La spectrum of La_2NiO_4 . The spectrum of this diamagnetic material was collected using a WURST-QCPMG pulse sequence, and gave surprisingly poor signal to noise [7]. The lack of resolution of singularities in this spectrum made simulation very difficult, even though there is only a single lanthanum site.

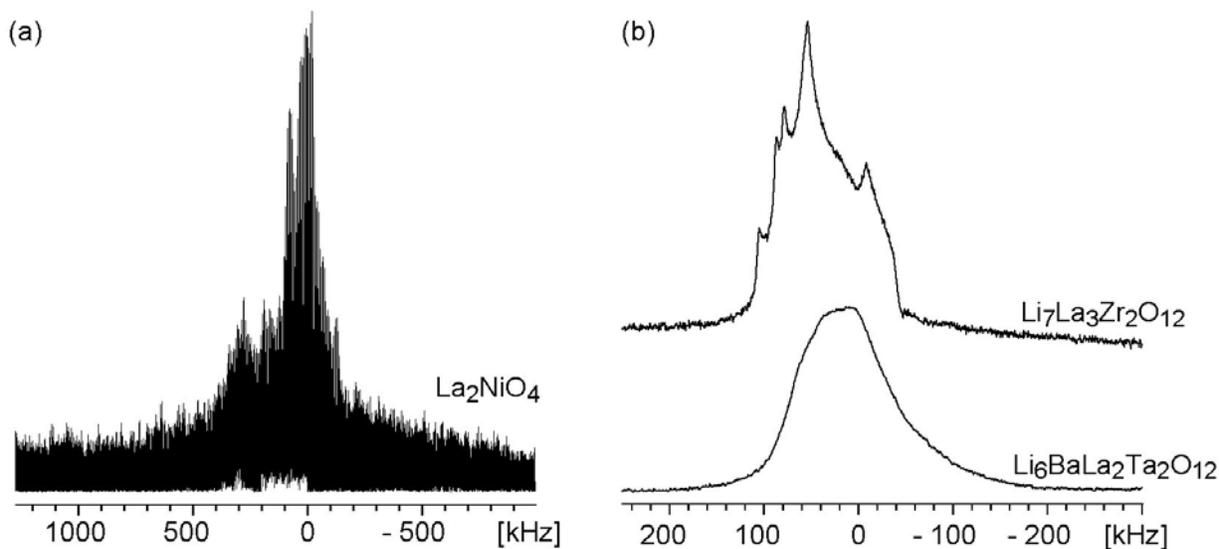


Figure 2: (a) ^{139}La static NMR spectrum of La_2NiO_4 . The spectrum was collected through stepwise collection using the WURST-QCPMG pulse sequence [7, 8]. (b) ^{139}La static NMR spectra of potential lithium battery materials $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$. The spectra were collected using a WURST-echo pulse sequence.

Other challenging lanthanum materials include many of the battery materials. Figure 2b shows the ^{139}La spectra of two potential battery materials, $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. These are potential electrolyte materials, and are diamagnetic in nature. Interestingly they have very different NMR spectra. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ has two crystallographically unique lanthanum sites. This can be clearly seen in the very detailed ^{139}La NMR spectrum. Unfortunately distinguishing between these sites is quite challenging, and is still a work in progress. The ^{139}La NMR spectrum of $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ is, in contrast, void of any visible singularities. This featureless line shape with tapering to low frequency is characteristic of a distribution of quadrupole parameters that result from atomic level disorder in the material [5]. Disorder is common in lithium ion conductors, and this spectrum is reminiscent of the ^{139}La NMR spectrum of another known lithium ion conductor, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ [5].

The collection of ^{139}La NMR spectra shown here shows the versatility and sensitivity of the ^{139}La nucleus to its environment. Although collection, and simulation of these spectra can be challenging, the technique is a useful tool for the analysis of lanthanum containing battery materials.

References

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