



Direct Detection of Discharge Products in Lithium–Oxygen Batteries by Solid-State NMR Spectroscopy**

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The lithium oxygen (Li-O_2) or “lithium–air” battery is, in principle, a promising candidate for use as an energy storage system in electric vehicles. This is primarily due to its large theoretical specific energy of 3505 Wh kg^{-1} (an order of magnitude greater than that of a conventional lithium ion battery, LIB); this value is based on the reaction (in a non-aqueous electrolyte) of Li and O_2 to form lithium peroxide (Li_2O_2) and it includes the weight of the reactants.^[1] The development of the lithium–air battery is still, however, at an early stage with operating cells falling short of their promising potential.^[2,3] As such, essentially all parts of the battery have been studied, from the metal anode,^[4] the electrolyte,^[5–12] and the composite cathode accommodating the reaction between lithium and oxygen,^[13–18] to the design of various catalysts for both the discharge and charge reactions.^[1,19–21] Recent work has shown that one of the biggest challenges is the stability of the electrolyte.^[22–28] IR^[22,23] and Raman spectroscopy and X-ray diffraction (XRD)^[24] studies have shown that the use of a standard organic-carbonate-based LIB electrolyte leads

mainly to electrolyte decomposition with lithium carbonate being a major product. The decomposition is initiated by the reaction between the reactive reduced oxygen radical (the superoxide anion or LiO_2) and the carbonate group of the electrolyte.^[22,23] To date, the most success has been achieved with ether-derived electrolytes.^[7,12,24,25,29] Ethers support Li_2O_2 formation on the first discharge step; however, electrolyte decomposition occurs in subsequent cycles forming organic lithium salts and Li_2CO_3 .^[24,25] Furthermore, the results have brought into question the role of the nominal catalysts, and materials such as MnO_2 , thought originally to catalyze oxygen reduction, were in fact shown to enhance the electrolyte decomposition process.^[30] Thus it is becoming increasingly clear that careful characterization of the electrochemical products formed during cycling should accompany any optimization study.^[2] To this end, we demonstrate that solid-state NMR (ssNMR) spectroscopy, and in particular ^{17}O NMR spectroscopy, is a powerful tool with which to study the electrochemical products formed in these batteries. The ^{17}O NMR spectra provide clear signatures for the major discharge products, Li_2O_2 and lithium carbonate, making it possible to monitor the reaction products.

ssNMR spectroscopy has advantages over many other spectroscopic techniques in that it is sensitive to the entire bulk of the sample and is not limited by the size and degree of crystallinity of the particles formed during cycling. To date, only one study has employed high-field ^6Li magic-angle-spinning (MAS) ssNMR spectroscopy to differentiate the peroxide from carbonate products based on chemical shift alone.^[31] However, since Li bonding in most of its salts is highly ionic, the Li isotropic chemical shift of diamagnetic systems is a relatively insensitive measure of the Li environment.^[32] Here we utilize a combination of ^7Li and, for the first time in the study of this system, ^{17}O NMR spectroscopy, the latter being an extremely sensitive probe of the chemical environment. We demonstrate that ssNMR spectroscopy together with density functional theory (DFT) calculations of the relevant NMR parameters can unequivocally identify the main products (i.e., lithium carbonate and lithium peroxide) formed in the discharged batteries.

Lithium carbonate and lithium peroxide both contain three NMR-active quadrupolar nuclei, ^6Li (spin 1), ^7Li (spin 3/2), and ^{17}O (spin 5/2). ^7Li NMR spectra are straightforward to acquire owing to the high natural abundance (93 %) and gyromagnetic ratio of this nucleus. Unfortunately, the ^7Li chemical shifts of both compounds are essentially identical at 0 ppm. The quadrupolar coupling constant (C_Q), which is a measure of the interaction between the nuclear electric quadrupole moment and the electric field gradient at the

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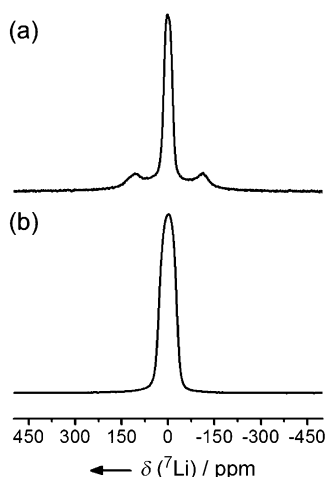


Figure 1. One-pulse static ^7Li NMR spectra of a) Li_2CO_3 and b) Li_2O_2 .

nucleus,^[33] does reflect the differences in the Li chemical environment in the two compounds. This can be appreciated from the very different ^7Li static NMR spectra of Li_2CO_3 and Li_2O_2 in Figure 1. The resonance of Li_2CO_3 has a typical quadrupole line shape, which can be fitted with a C_Q of 120 kHz and asymmetry parameter (η) of 0 (see the Supporting Information). The line shape of Li_2O_2 is distinct: it is relatively broad and does not display any obvious quadrupole features. As the linewidth is independent of the magnetic field strength, the broadening is attributed to homonuclear dipolar interactions between ^7Li nuclei and possibly dynamic effects.

^{17}O NMR spectra are nontrivial to acquire because of the low natural abundance of this nucleus (0.038 %). Thus, our first approach was to employ DFT calculations performed with the CASTEP code^[34,35] to estimate the relevant ^{17}O NMR parameters. These DFT calculations clearly showed that the ^{17}O parameters of the two model compounds were distinct; C_Q values of 7 and 18 MHz were obtained for the two carbonate oxygen sites and the single peroxide oxygen, respectively, the value for the peroxide being the largest value reported to date for an oxygen-containing solid.^[36] The large C_Q values pose severe experimental challenges on account of the resulting quadrupolar broadening.^[37] Nevertheless, we were still able to acquire natural-abundance spectra of the two salts by using very high magnetic fields (Figure 2). Despite the poor signal-to-noise ratio, the two salts can be clearly distinguished by their very different quadrupolar line shapes as predicted by the DFT calculations.

Based on the natural-abundance studies of the model compounds, we then investigated samples extracted from discharged cathodes. Two types of cells were compared, cell A with 1M LiPF_6 electrolyte in ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 (molar ratio) solution and cell B prepared with 1M bis(trifluoromethane)sulfonimide lithium (LiTFSI) electrolyte in dimethoxyethane (DME) solution (see the Experimental Section and representative electrochemical curves in the Supporting Information). The ^7Li NMR spectra of the two discharged cathodes (Figure 3)

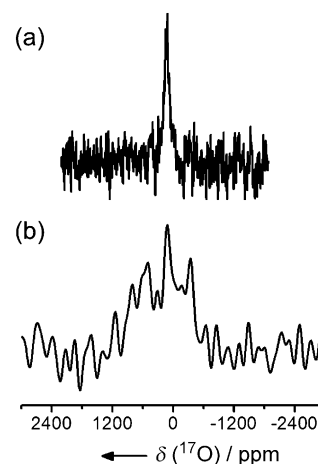


Figure 2. Natural-abundance static ^{17}O NMR spectra of a) Li_2CO_3 and b) Li_2O_2 acquired at 21.1 and 20 T, respectively.

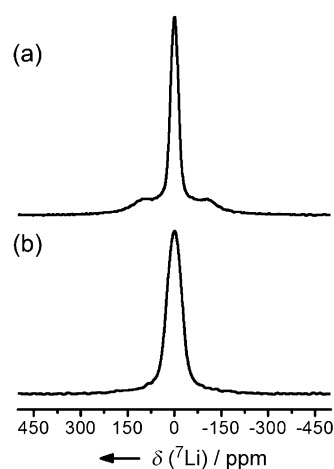


Figure 3. One-pulse static ^7Li NMR spectra of the discharged cathode from a) cell A and b) cell B.

show distinct line shapes characteristic of Li_2CO_3 (cell A) and Li_2O_2 (cell B) products. A slight broadening of the carbonate signal in cell A is ascribed to the amorphous or disordered nature of the discharged product and the presence of conductive carbon in the electrode.

In view of the very small samples extracted from a typical battery cell (approximately 1 mg) the ^{17}O NMR spectra were acquired from cells cycled under an oxygen atmosphere consisting of 20% ^{17}O -enriched oxygen gas (the enrichment protocol is described in Supporting Information). Good agreement is obtained between the experimental ^{17}O MAS spectrum of the cell A cathode (Figure 4) and a simulation of the spectrum making use of the C_Q values extracted from the Li_2CO_3 DFT calculations, confirming that lithium carbonate is formed as the primary discharge product in cell A (EC/DMC). This observation is further supported by a ^{13}C chemical shift of roughly 170 ppm obtained for this sample (see the Supporting Information) obtained in a ^7Li -to- ^{13}C cross-polarization (CP) experiment,^[38] a method that is selective for ^{13}C spins close to lithium.

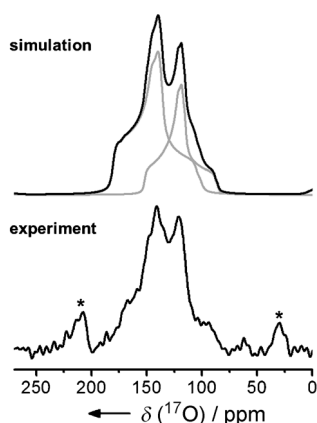


Figure 4. ^{17}O NMR spectra of the discharged cathode from cell A acquired at a MAS frequency of 20 kHz MAS at 20 T (bottom); asterisks label spinning side bands of the ZrO_2 rotor background signal. The simulated spectrum (top) was calculated using SPINE-VOLUTION^[39] for two oxygen sites with $\delta_{\text{iso}} = 152, 180$ ppm, $\delta_{\text{aniso}} = 225, 186$ ppm ($\eta_{\text{CS}} = 0.87, 0.5$), and $C_Q = 7.22, 7.98$ MHz ($\eta_Q = 0.9, 0.85$) with line broadening of 300 and 500 Hz and an intensity ratio of 1:2 respectively.

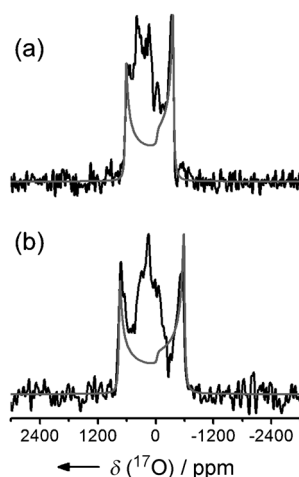


Figure 5. Static ^{17}O NMR spectra (black) of the discharged cathode from cell B acquired at a field strength of a) 20 T and b) 16.4 T. The experimental data (black) were simulated (gray lineshape) with a single oxygen site with $\delta_{\text{iso}} = 227$ ppm, $\delta_{\text{aniso}} = -375$ ppm ($\eta_{\text{CS}} = 0$), and $C_Q = 18$ MHz ($\eta_Q = 0$). See the Supporting Information for additional details concerning the fit.

The static ^{17}O NMR spectra of a sample from cathode B acquired at two magnetic field strengths (Figure 5) can be fit well by utilizing the same ^{17}O parameters, when both the quadrupole and chemical shift anisotropy parameters are taken into account, the latter also being significant at these high fields.^[40] The large C_Q value used in the fit, 18 MHz, is very close to that calculated by DFT (18.6 MHz) and is far larger than any other ^{17}O moment reported in the literature for organic or inorganic solid compounds,^[36] including organic ethers, acids, aldehydes, and ketones. The ^{17}O peroxide species, which gives rise to a resonance with a very large separation between the two line shape singularities at the

edges, has a unique ssNMR signature and is clearly the main product formed during the first discharge with a DME electrolyte. The additional intensity in the spectrum is partly due to the background signal from the zirconia rotor ($\delta_{\text{iso}} \approx 380$ ppm) and possibly some electrolyte decomposition products. In order to resolve these additional signals we have acquired the high-resolution ^{17}O NMR spectrum from another discharged cathode from cell B (Figure 6b), by

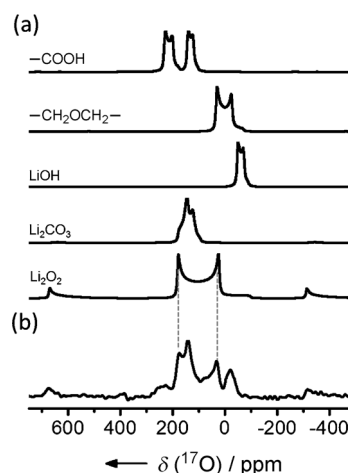


Figure 6. a) Simulated ^{17}O MAS NMR spectra of the possible oxygen sites in the discharge products formed in cell B (for details on the simulation parameters see the Supporting Information) compared with b) the experimental spectrum of a discharged cathode from cell B acquired at a field of 21.1 T and 60 kHz MAS.

using ultrafast MAS which narrows the quadrupolar line shape and removes the broadening caused by chemical shift anisotropy.^[41] A comparison between this MAS spectrum and the simulated ^{17}O spectra of several possible decomposition products (Figure 6a) again indicates that the main product is lithium peroxide, but there are additional contributions from lithium carbonate ($\delta_{\text{iso}} \approx 160$ ppm), lithium hydroxide ($\delta_{\text{iso}} \approx -40$ ppm), and carboxylate groups, which are expected to resonate in the region of 200 ppm (additional details of the simulations and assignment are given in the Supporting Information). No signal is seen in the ^7Li -to- ^{13}C cross-polarization experiment, suggesting that the lithiated carbonates/carboxylates are minor products.

In conclusion, we have shown that ^7Li and ^{17}O ssNMR spectroscopy is a valuable tool for the study of electrochemical products formed during the operation of Li- O_2 batteries. Experimental and DFT studies show that the main products have distinct NMR signatures. Future studies will make use of ultrafast MAS (above 60 kHz) and multiple-quantum MAS (MQMAS)^[42] techniques to help separate the large C_Q line shape of the peroxide from those of the various decomposition products, and are expected to enhance the capability of this approach for assigning different lithium and oxygen species. Monitoring the formation and decomposition of electrochemical products is a crucial step in the design and optimization of a rechargeable Li- O_2 battery and the results

presented here demonstrate the utility of ssNMR spectroscopy to help determine the viability of new cell reactions, electrolytes, solutions, etc. based on the direct detection of the bulk, solid-phase reaction products.

Experimental Section

Li_2CO_3 and Li_2O_2 were purchased from Sigma–Aldrich and used without further purification. The peroxide was stored and packed in the NMR rotor in an argon glove box. Oxygen cathodes were prepared from a mixture of Super P Li (Timcal) and PVDF with weight ratios of 40:60 following the published procedure for porous cathodes (see the Supporting Information). Li–O_2 cells were assembled in an argon glove box in either Swagelok-type or coin cells, modified to allow gas entrance on the cathode side. The assembled cells were sealed in a glass chamber with two valves used to flush the cells with either natural-abundance or 20% ^{17}O -enriched oxygen gas. Electrochemical measurements were carried out with an Arbin cycler. Following cycling, cells were disassembled in the glove box and the cathodes were washed twice with acetonitrile and dried under vacuum.

NMR measurements were performed on 16.4 T Bruker Avance III 700, 20 T Bruker Avance III 850, and 21.1 T Bruker Avance II 900 NMR spectrometers.

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