

Monitoring the Electrochemical Processes in the Lithium-Oxygen Battery by Solid State NMR Spectroscopy

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The lithium-air battery is, in principle, a promising candidate for use as an energy storage system. Theoretically, it can store up to $3,505 \text{ Wh kg}^{-1}$ (approaching an order of magnitude more than a conventional lithium ion battery) based on the reaction (in non-aqueous electrolytes) of lithium and oxygen to form lithium peroxide and including the weight of the reactants¹. In practice the development of the battery is still at initial stages with operating cells falling short of their promising potential². Among the challenges to be addressed are the identification of stable electrolyte systems, inert and porous cathode materials and efficient catalytic species. These can only be achieved with a careful analysis of the electrochemical products formed during the operation of the cell.

We have recently demonstrated how solid state NMR (ssNMR) spectroscopy, in particular of the ^{17}O isotope, is a powerful tool in the investigation of this system as it allows a clear distinction between the main products formed in the cell – lithium peroxide and lithium carbonate³. The advantages of ssNMR over other physical characterization techniques, such as infra-red, powder x-ray diffraction and Raman spectroscopy, is its sensitivity to the entire bulk of the cathode material and the detection of both crystalline and amorphous products.

Here we extend this method further and employ a multi nuclear NMR approach which enables us to monitor the evolution of these products during electrochemical cycling and gain insight into processes affecting capacity fading. The ^{17}O NMR signatures of several possible products (Fig. 1) demonstrate these can be clearly identified and their evolution can be monitored in cathodes extracted from cells at various state of charge (Fig. 2). While lithium peroxide is the predominant product in the 1st discharge in 1,2-dimethoxyethane (DME) based electrolytes, it reacts with the carbon cathode surface to form carbonate during the charging process. ^{13}C ssNMR provides evidence for carbonate formation on the surface of the carbon cathode which is removed at high charging voltages in the first cycle but accumulates at later cycles.

Small amounts of lithium hydroxide and formate are also detected in discharged cathodes and while the hydroxide formation is reversible, the formate persists and accumulates in the cathode upon further cycling.

Our results indicate that the rechargeability of the battery is limited by both the electrolyte and the carbon cathode stability. Furthermore they demonstrate the utility of ssNMR spectroscopy in directly detecting product formation and decomposition within the battery, a necessary step in the assessment of new electrolytes, catalysts and cathode materials for the development of a viable lithium-oxygen battery. The extension of this approach towards in-situ NMR studies of operating cells will also be discussed.

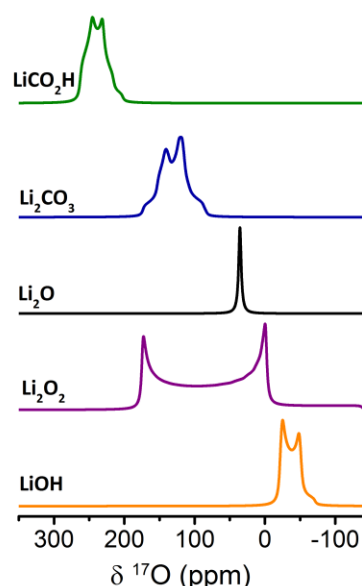


Figure 1. A library of ^{17}O magic angle spinning NMR spectra of possible electrochemical products.

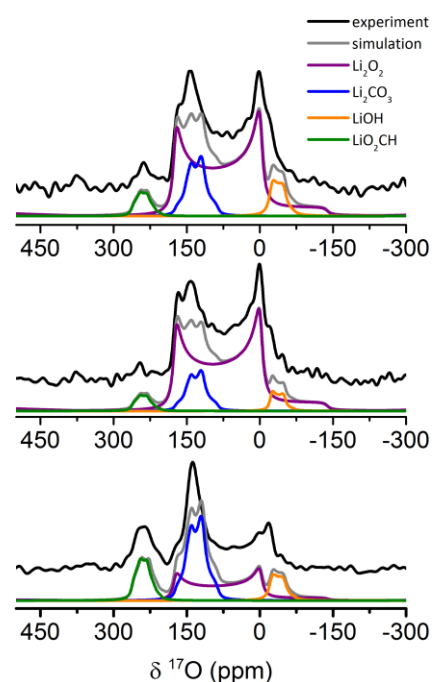


Figure 2. ^{17}O Magic angle spinning NMR spectra (black) of cathodes that were discharged to 1000mAh/g (top), 2000mAh/g (center) and charged to 4.5 V (bottom). Lithium peroxide was identified as the main discharge product (purple) as well as decomposition products such as lithium hydroxide (yellow), carbonate (blue) and formate (green).

¹ P.G. Bruce, S. A. Freunberger, L. J. Hardwick, J-M Tarascon, *Nat. Mater.* (2012), 11, 19.

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