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

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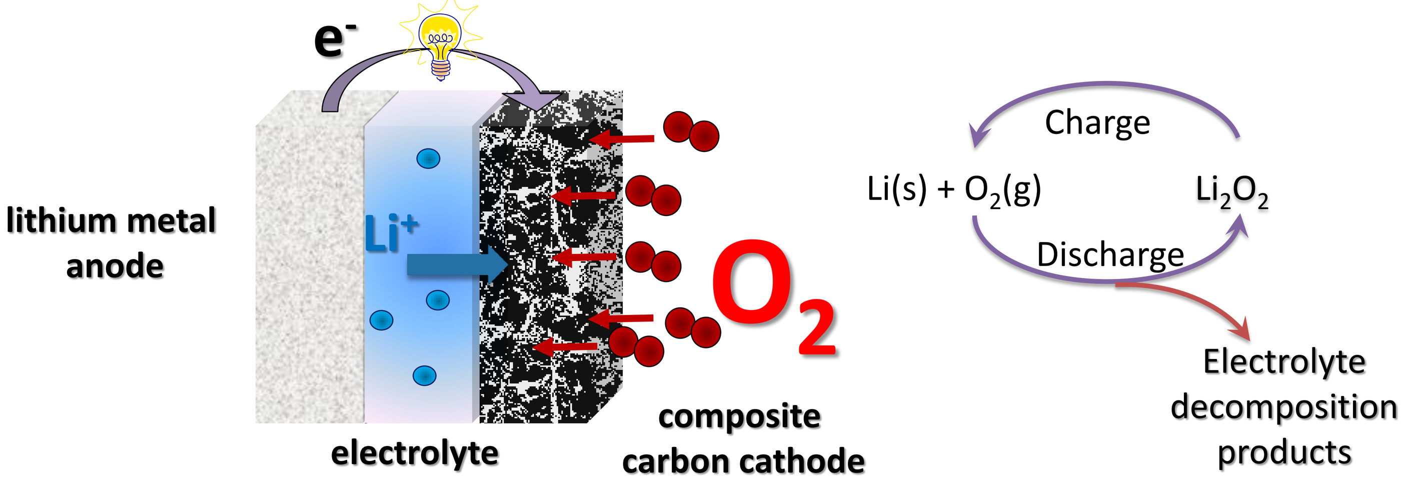
The Lithium-Oxygen battery

The lithium-oxygen battery is, in principle, a promising candidate for use as an energy storage system. Theoretically, it can store 3,505Whkg-[1] (approaching an order of magnitude more than a conventional lithium ion battery) based on the reaction (in a non-aqueous electrolyte) of Li and O_2 to form lithium peroxide (Li_2O_2) and including the weight of the reactants[1].



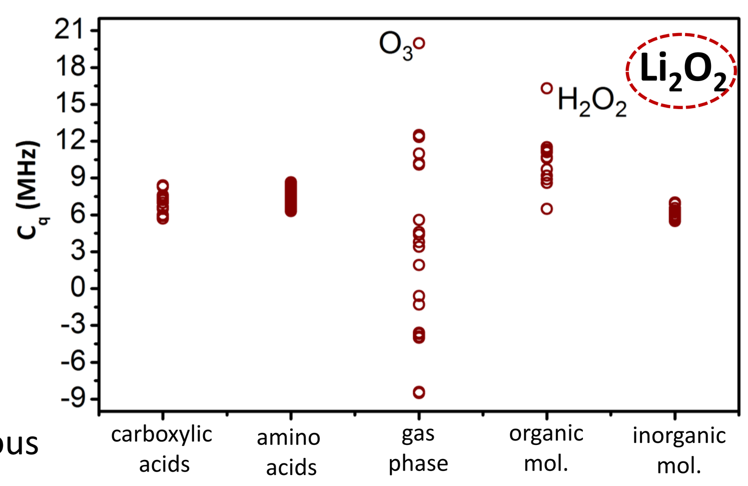
In practice the development of the battery is still at initial stages with operating cells falling short of their promising potential[2]. Among the challenges to be addressed are the identification of stable electrolyte systems, inert and porous cathode materials and efficient catalytic species. These can only be achieved with a careful analysis of the electrochemical products formed during the operation of the cell. Here we employ a multi-nuclear solid state NMR spectroscopy which enables us to monitor the evolution of these products during electrochemical cycling and gain insight into processes affecting capacity fading.

Characterization by Solid state NMR

We have recently demonstrated how solid state NMR (ssNMR) spectroscopy, in particular of the ^{17}O nucleus, is a powerful tool in the investigation of the lithium-air battery as it allows a clear distinction between the main products formed in the cell – lithium peroxide and lithium carbonate[3].

The advantages of solid state NMR are:

- ✓ Allows a clear distinction between the main discharge products.
- ✓ Detects products formed in the bulk of the cathode as well as on the surface.
- ✓ Detects both crystalline and amorphous materials.



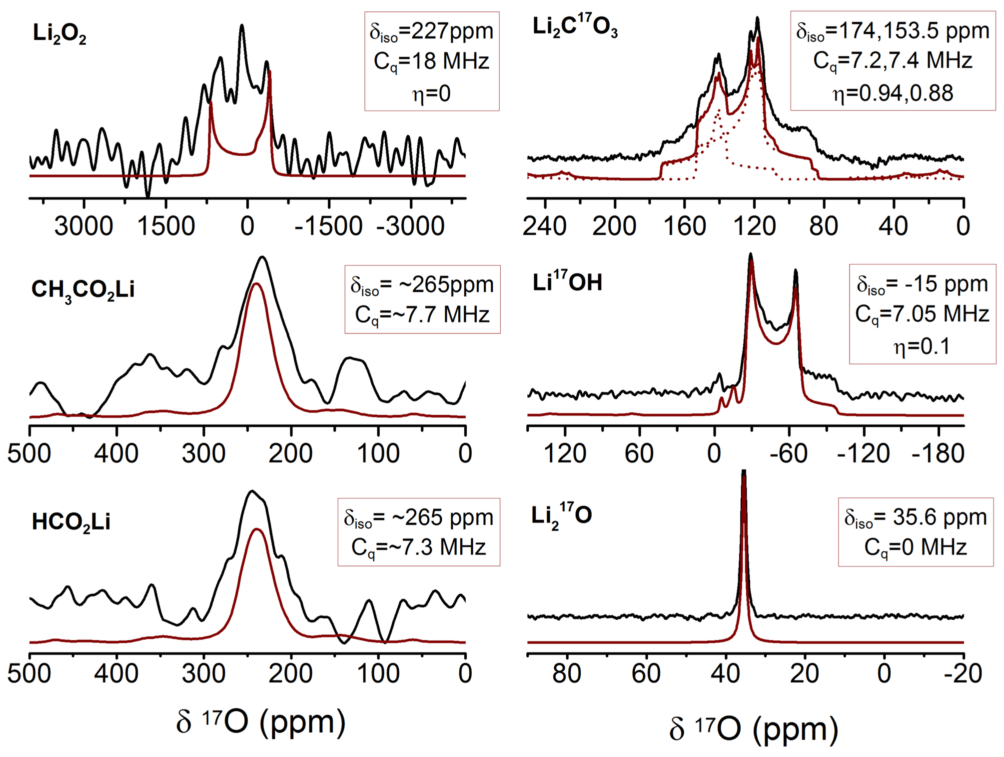
- ✓ ^{17}O (I=5/2) quadrupole coupling constant, C_q, is a sensitive probe to its chemical environment and can be used to uniquely identify the peroxide species.

[1] P.G. Bruce, S. A. Freunberger, L. J. Hardwick, J-M Tarascon, Nature Materials 2012, 11, 19.

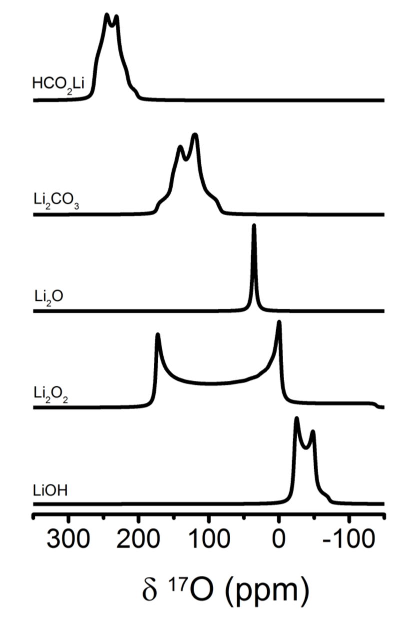
[2] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, The Journal of Physical Chemistry Letters 2010, 1, 2193. L. J. Hardwick, P.G. Bruce, Current Opinion in Solid State and Materials Science 2012, 16, 178.

[3] M. Leskes, N.E. Drewett, L.J. Hardwick, P. G. Bruce, G. R. Goward, C. P. Grey, Angewandte Chemie International Edition 2012, 24, 2880.

Library of possible electrochemical products

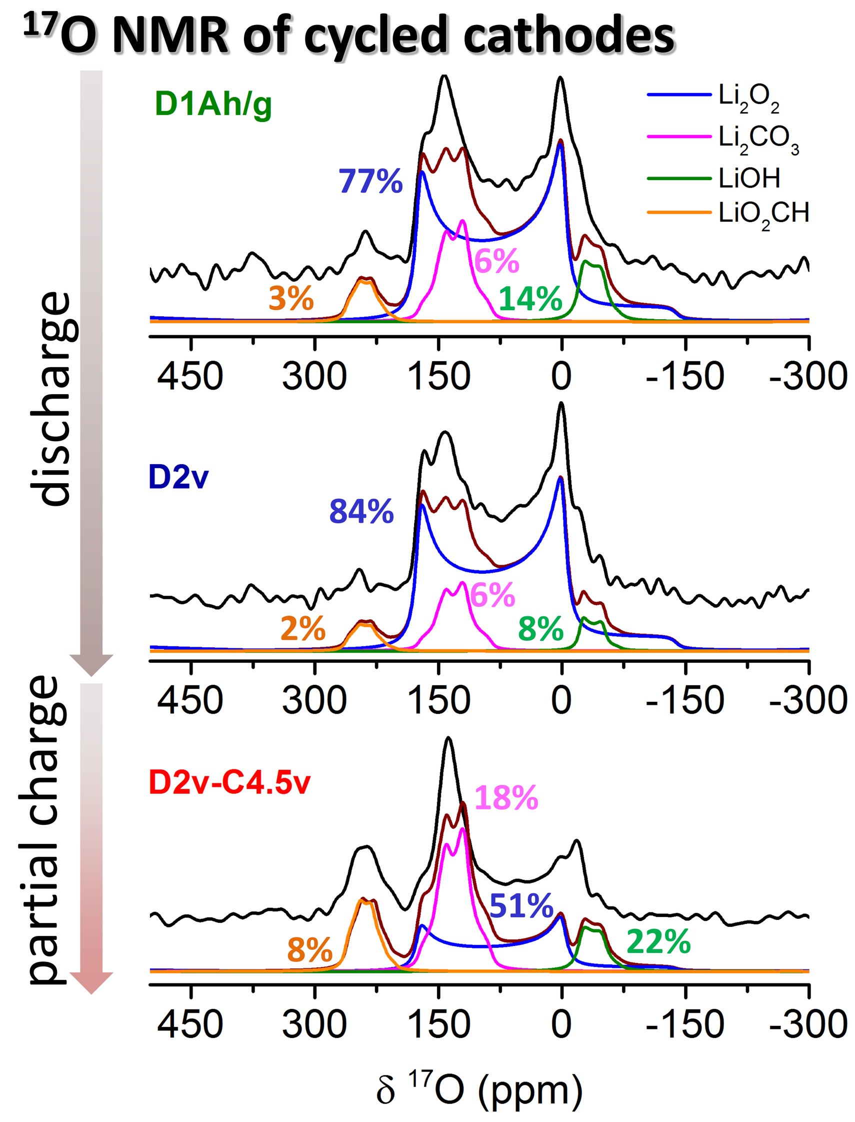


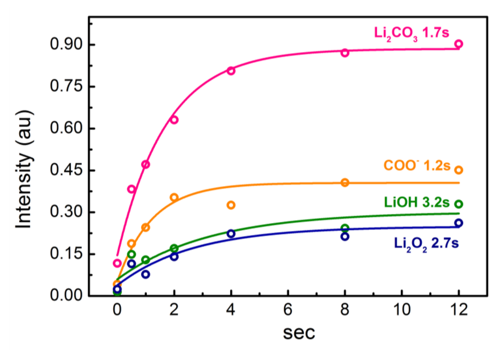
Detecting the ^{17}O spectral signature of various lithium-oxygen compounds at high magnetic fields allows us to identify them when they are formed in the battery .



Fitting the second-order quadrupole line shape we can determine the NMR parameters and simulate the spectra at the same conditions (magnetic field and magic angle spinning frequency). The various species are clearly distinguishable by their ^{17}O spectra.

^{17}O NMR of cycled cathodes



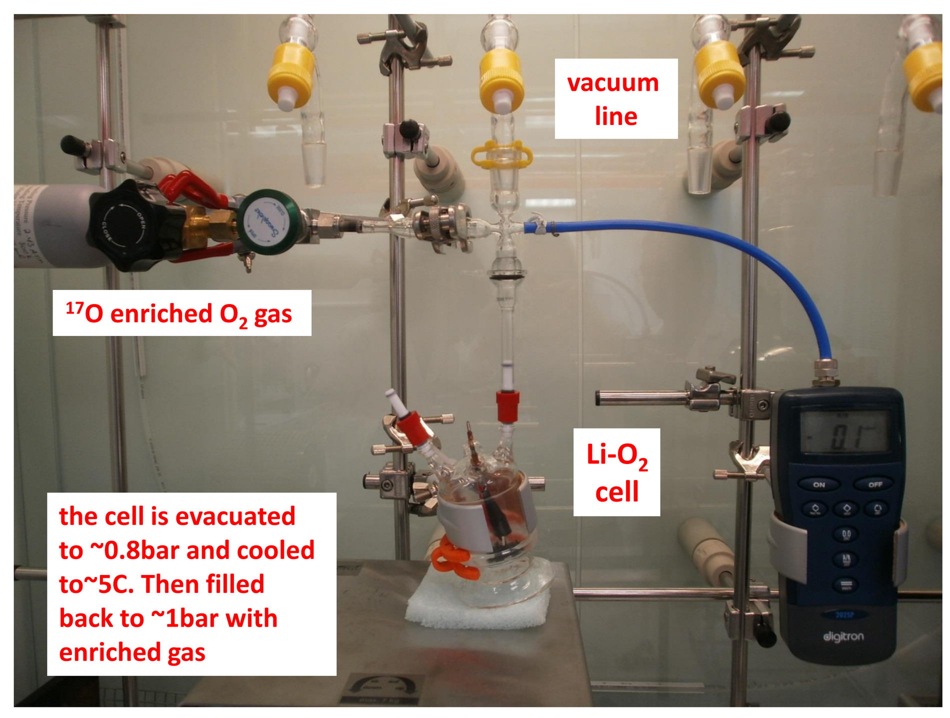


Taking into account the relaxation of the different species in order to get more quantitative analysis

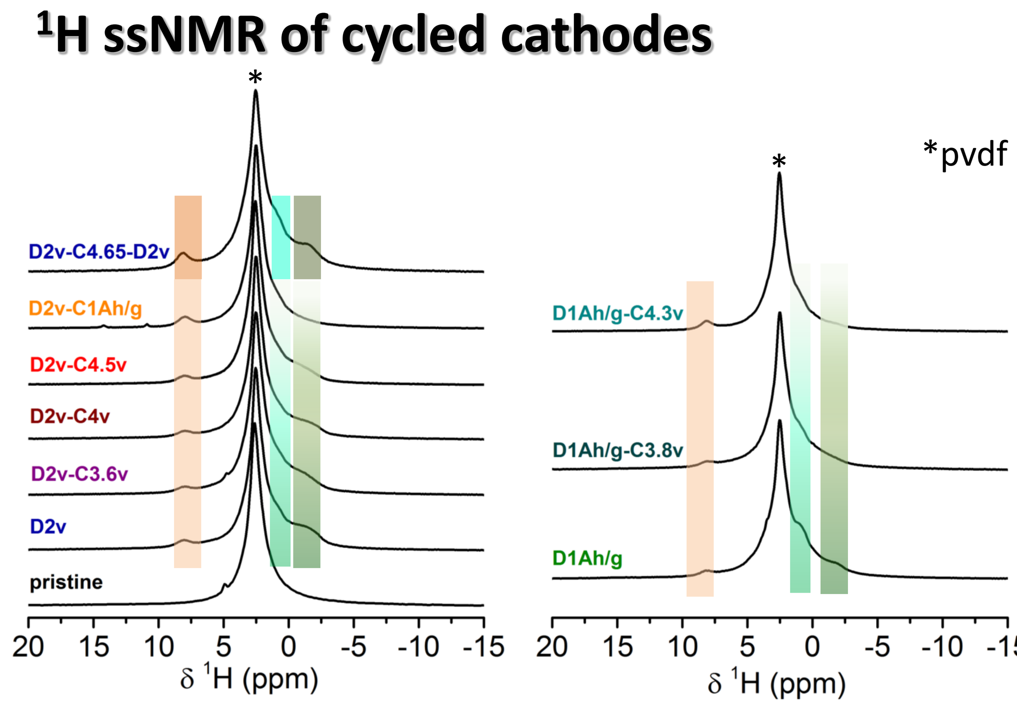
$$I(d_1) = I_0(1 - e^{-\frac{d_1}{T_1}})$$

^{17}O enrichment of the products

Cycling the battery with ^{17}O enriched oxygen atmosphere results in isotope enrichment of the products which can be identified and monitored during the cycle.

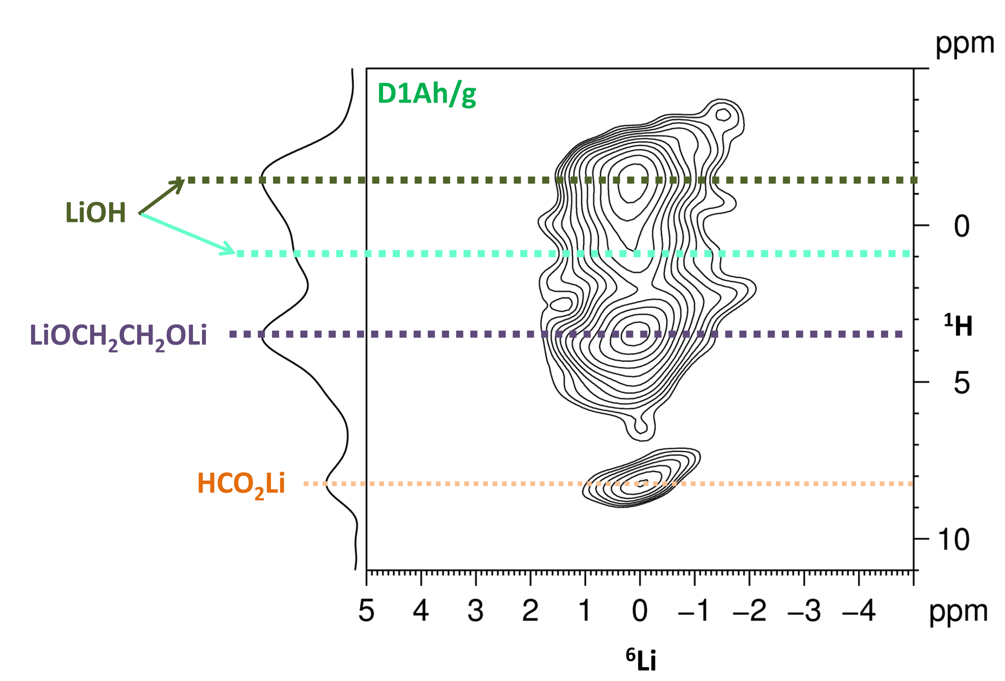


^1H ssNMR of cycled cathodes

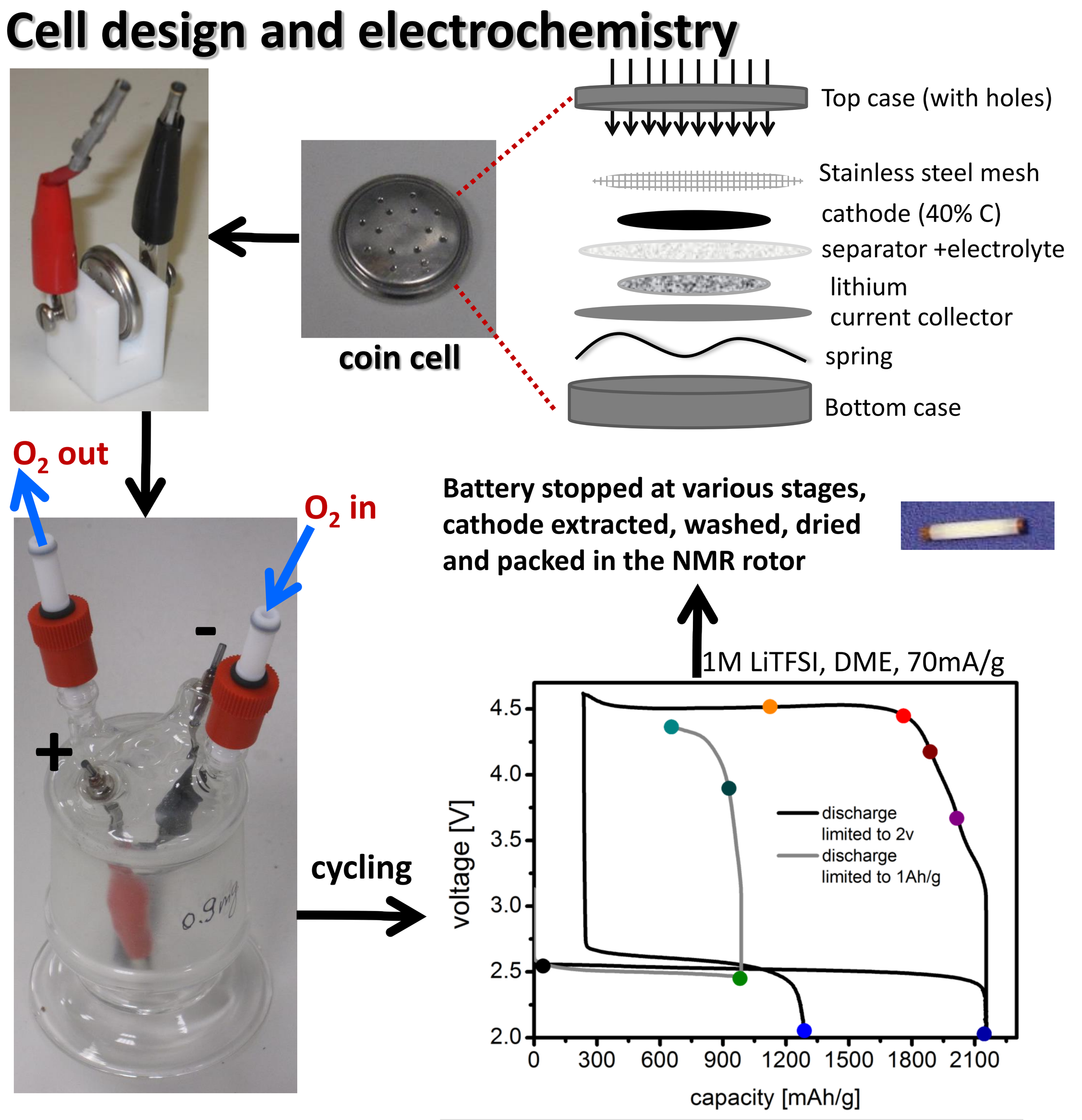


^1H spectra are used to monitor the evolution of lithium hydroxide and formate.

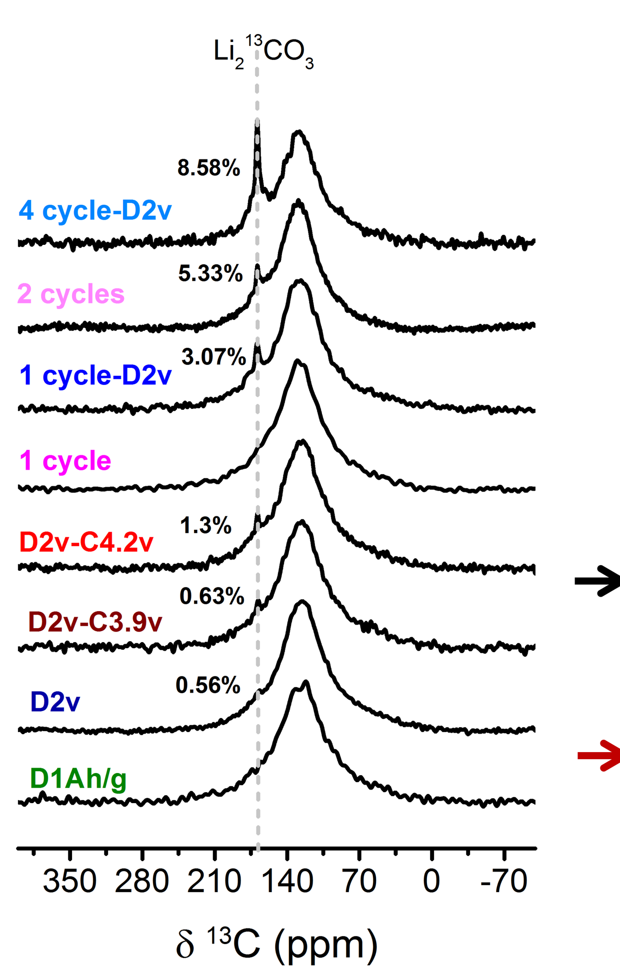
^1H-^6Li 2D correlations aid in filtering the pvdf signal and identifying a fragment of the DME formed at initial discharge.



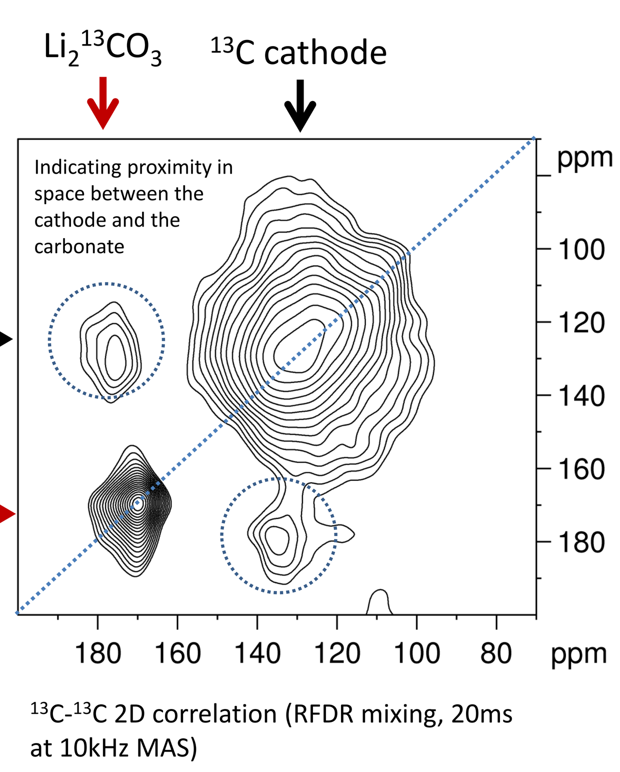
Cell design and electrochemistry



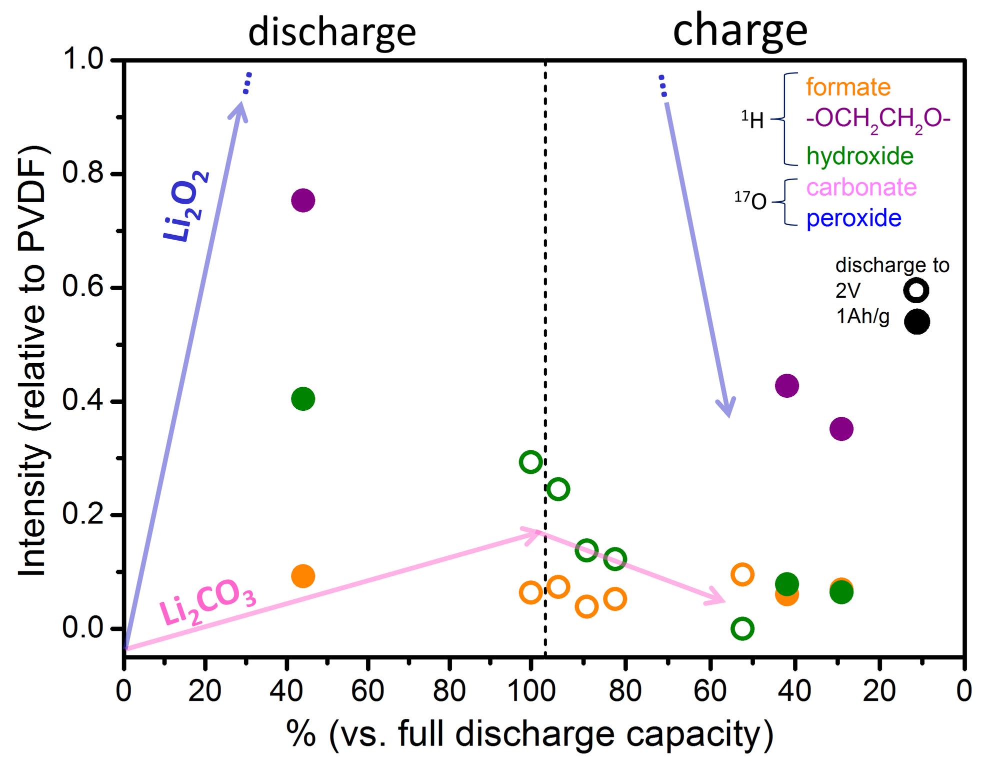
^{13}C ssNMR of cycled isotope enriched cathodes



The cathode reacts with lithium peroxide upon charging forming lithium carbonate. From the second cycle carbonate accumulates on the surface.



^{13}C-^{13}C 2D correlation (RFDR mixing, 20ms at 10kHz MAS)



Conclusions

- Lithium peroxide is the main discharge product in the initial cycle in DME accompanied by non-negligible electrolyte decomposition forming lithium hydroxide, carbonate and formate.
- Upon charge significant amounts of lithium peroxide decompose below 4.5V.
- While the hydroxide decomposes upon charging, formate accumulates on the cathode surface.
- The carbon cathode, though inert during the first discharge, is unstable in the presence of peroxide at higher voltages forming a layer of carbonate that blocks the surface.
- Limiting the capacity to 1000mAh/g results in similar distribution of products with a slight decrease in the charge potential, possibly due to a thinner insulating layer of products.
- We have demonstrated that a multinuclear solid state NMR approach is a powerful method for directly detecting product formation and decomposition within the cathode, a necessary step in the evaluation of new electrolytes, catalysts and cathode materials for the development of a viable lithium-air battery.

Acknowledgments

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