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 3.0505Wh/kg \(^{-1}\) (approaching an order of magnitude more than a conventional lithium-ion battery) based on the reaction (in a non-aqueous electrolyte) of \(\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_3 \) forming lithium peroxide \((\text{Li}_2\text{O}_3)\) 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. \(^1\) Among the challenges to be addressed are the identification of stable electrolyte systems, inert and porous cathode materials and efficient catalytic species. This 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 those 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 \(^{17}\text{O}\) 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 lithium. \(^2\)

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.
- \(^{17}\text{O}\) (\(\approx\text{S}^{-2}\)) quadrupole coupling constant, \(C_{\text{Q}}\) is a sensitive probe to its chemical environment and can be used to uniquely identify the peroxide species.

Library of possible electrochemical products

Detected at the \(^{17}\text{O}\) 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 \(^{17}\text{O}\) spectra.

Cell design and electrochemistry

In the cell design, various electrodes, cathodes, electrolytes were used. Each electrode was made of materials known to be inert to the aqueous electrolyte. The cathode was made of 

\(\text{LiOH} \quad \text{Li}_2\text{O}_3 \quad \text{Li}_2\text{O}_3\text{H}_{\text{2}} \quad \text{LiOH} \quad \text{Li}_2\text{O}_3\text{H}_{\text{2}}\)

Conclusions

- Lithium peroxide is the main discharge product in the initial cycle in DMF accompanied by non-negligible electrolyte decomposition forming lithium hydroxide and carbonate 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 blocking layer.
- 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.

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References


Note: The rest of the text contains detailed scientific information and figures related to the lithium-oxygen battery and its characterization using solid-state NMR spectroscopy. The image includes diagrams and chemical reactions, which are important for understanding the paper's content.