Final Publishable Summary Report

In recent years the lithium-air battery has emerged as potential energy storage device for electric vehicles. Theoretically it can store very high specific energy, 3505 Whkg^{-1} (in non-aqueous electrolytes), a ten time increase in energy compared to commercial lithium-ion batteries. However, the battery is still at development stages and in order to fulfil its potential several scientific and technological challenges must be addressed. One of the main challenges is the identification of stable electrolyte and cathode materials. The high energy offered by the system is based on the reversible reaction between lithium and oxygen to form lithium peroxide. The process involves formation of very reactive intermediate superoxide species and the product itself, lithium peroxide, is highly oxidizing. Thus the efficiency of the system and its reversibility are at stake due to side reactions between these products and the components of the electrolyte and electrodes. Therefore in order to develop a viable system these side reactions must be identified and controlled.

The goal of this research project was to develop and employ a solid state nuclear magnetic resonance (ssNMR) based approach that will allow identifying critical processes in the cell: distinguishing reversible formation of lithium peroxide from parasitic side reactions products and how their occurrence depends on the various system components (electrolyte, cathode and catalysts).

The first objective was the development of ex-situ NMR methodology that will allow distinguishing the desired discharge product, lithium peroxide, from parasitic side reactions products as well as monitoring their formation along the electrochemical cycle. ^{7}Li NMR was shown to be a straight forward tool for screening systems that were mostly forming peroxide from those that are sensitive to decomposition resulting in formation of lithium carbonate and lithium hydroxide. A more detailed analysis was obtained based on ^{17}O ssNMR. A spectral library of possible electrochemical products was assembled and used to identify and monitor the various products in operating cells in a reliable way. In combination with ^{1}H NMR we were able to identify the decomposition products formed in various electrolyte systems and suggest mechanisms for their formation. To fulfil this objective we have developed a protocol for assembling the lithium-oxygen cells, cycling and disassembling that will allow controlling the cells atmosphere (for isotope enrichment) as well as for minimal interference with the products formed within the electrode.

We have employed this approach to distinguish relatively stable electrolytes (based on ether solvents) from reactive electrolytes (carbonate based solvents) used with carbon electrodes. Since carbon electrodes often result in inefficient cycling due to the high voltage required to charge the cell

compared to the voltage of its discharge, we have investigated the source of this voltage increase by using ^{13}C enriched carbon electrodes which allowed us to identify processes related to cathode reactivity. Lithium carbonate was identified as the main product of electrode decomposition and it was found to form mostly upon charge as a result of oxidation of the carbon by the peroxide formed on discharge. The carbonate coating formed on the electrode surface and its accumulation upon extended cycling lead to the increase in over potential of the charge process.

The cycling inefficiency using carbon based electrodes indicates that alternative electrode materials must be identified. While precious metal catalysts and transition metal oxides often have a positive effect on the electrochemical performance mostly by reducing the charge over-potential, their exact role in the electrochemical cycle is yet to be determined. Employing ssNMR we have found that although they seem to improve the cycling efficiency, the apparent decrease in charge potential is associated with significant electrolyte decomposition processes resulting in formation of mostly lithium hydroxide.

Our results indicate that the reversibility of the lithium-oxygen system and its cycle life are limited by both the electrolyte and electrode stability. Even though some electrolyte solvents are mostly stable, the formation of very small amounts of side products results in increased charge over-potential leading to even more side reactions upon charge. At these elevated potentials the carbon electrode is not stable in the presence of lithium peroxide forming lithium carbonate which coats its surface. Catalytic species added for lowering the over-potential should be carefully considered as they can cause increased decomposition reactions.

We have developed an NMR based methodology which is advantageous compared to other analytical tools due to its high chemical specificity which allows distinguishing the products formed in the working cells. Furthermore, it can detect a wide range of products, independent of their degree of crystallinity or order and whether they are formed in the bulk or on the surface of the electrode. We expect this approach to be beneficial in the assessment of new electrolytes, catalysts and cathode materials for the development of a viable lithium-air battery.