

The Role of Metal Catalysts in the Electrochemistry of the Lithium-Air Battery – a Solid State NMR Study

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Li-Air batteries, based on their high theoretical specific energy are an extremely attractive technology for electrical storage devices. However, there are a number of scientific and technical challenges that must first be overcome if the promise of Li-Air batteries is to become a reality¹. A critical challenge is the slow kinetics of the electrochemical oxygen reduction and oxygen evolution reactions (ORR and OER respectively), which give rise to poor reversibility, high overpotentials and low energy efficiency. A variety of catalysts have been investigated in order to lower these overpotentials and improve the energy efficiency ranging from carbonaceous materials to metal particles². α -MnO₂ has been extensively studied and has shown to have a high energy storage capacity. Recently, studies have shown the ability of metal nanoparticles as catalysts: where Au is the most active for ORR and Pt is the most active for OER³. Although these catalysts appear to be catalysing the Li-Air reaction from the electrochemistry, seen by a lowering of the overpotentials, a thorough study and identification of the products formed during cycling needs to be employed.

Solid state NMR (ssNMR) is a powerful tool to investigate the Li-Air system as it allows for clear identification of the desired product formed in the battery – lithium peroxide, as well as electrolyte and electrode decomposition products; lithium carbonate, lithium formate, lithium acetate and lithium hydroxide⁴. ssNMR has many advantages over conventional characterisation techniques as it is sensitive to the entire bulk of the sample and can be used to detect both crystalline and amorphous samples.

Here we use ssNMR to identify the main products formed during the 1st cycle when precious metal catalysts are used with a carbon cathode in an ether based electrolyte. We identified mainly decomposition products during 1st cycle, implying that the catalysts are not catalysing the Li-Air reaction but are in fact, aiding decomposition, most likely from the solvent.

Our results indicate that the use of catalysts in the Li-Air system is not necessarily straightforward and can lead to decomposition instead of catalysing the formation of lithium peroxide. Further careful study, using ssNMR should be used in order to understand the role of the catalyst in the Li-Air system and to evaluate whether any catalysis can occur with the non-soluble products formed.

¹ Bruce PG, Freunberger SA, Hardwick LJ, Tarascon JM, Nat Mater. 2011, 11, 19-29

² Cheng F, Chen J, Nat Chem. 2012, 4, 962-963

³ Lu YC, Gasteiger HA, Crumlin E, McGuire R, Shao-Horn Y, J. ElectroChem, Soc. 2010, 167, A1016-A1025

⁴ Leskes M, Drewett NE, Hardwick LJ, Bruce PG, Goward GR, Grey CP, Angew. Chem. Int. Ed, 2012, 51, 8560-8563