

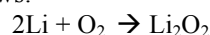
## A Multinuclear Solid State NMR Study of Potential Electrolytes for the Li-Air Battery

Z.E.M. Reeve<sup>1</sup>, Michal Leskes<sup>2</sup> and Clare P. Grey<sup>2</sup> G. R. Goward<sup>1\*</sup>,

<sup>1</sup> Department of Chemistry and Brockhouse Institute for Materials Research, McMaster University, 1280 Main St. W. Hamilton, ON, L8S 4M1 Canada

<sup>2</sup> Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge UK, CB2 1EW

Recent developments in battery technology have been driven by the need for high energy density batteries suitable for automotive applications. In recent years the Li-Air batteries has received a considerable amount of attention as the theoretical energy density is equivalent to that of gasoline [1]. The reversible Li-Air battery has the potential to revolutionize energy storage for hybrid and electric vehicles. The high theoretical energy density is associated with Li<sub>2</sub>O<sub>2</sub> formation upon discharge with a non-aqueous electrolyte[2]. The governing discharge reaction is as follows:



where O<sub>2</sub> is accessed from the environment. O<sub>2</sub> enters the battery through the porous cathode and is reduced to O<sub>2</sub><sup>-</sup> the nucleophilic superoxide species. Upon charging Li<sub>2</sub>O<sub>2</sub> is decomposed[2].

Currently the high theoretical energy density has not been realized as there are many experimental challenges associated with the Li-Air battery, such as: the electrolyte stability, dendrite formation at the Li metal anode, fading capacity upon multiple cycling and the cathodes sensitivity to CO<sub>2</sub> and H<sub>2</sub>O [1, 2]. The electrolyte stability is a fundamental problem that greatly impacts that battery performance.

Several non-aqueous electrolytes including; alkyl carbonates (propylene carbonate), ethers (tetraglyme and 1,3-dioxolane) and dimethylformamide [3-5] have been investigated for the Li-Air battery where electrolyte decomposition has been observed in all cases. The electrolytes are being consumed via a nucleophilic attack by the superoxide species at the electrophilic region of the electrolyte [3-5].

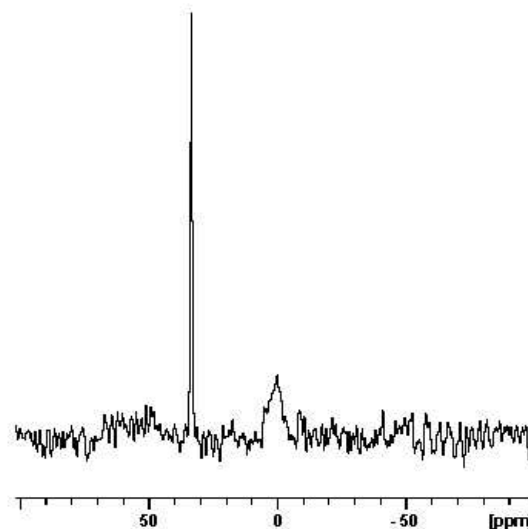
Phosphorous ionic liquids (PILs) are a promising class of electrolytes, whose stability will be determined by solid-state NMR (ssNMR). PILs have many features that make them desirable electrolytes; thermal and electrochemical stability, hydrophobic, low volatility and non-flammable [6].

<sup>7</sup>Li and <sup>17</sup>O ssNMR have been used as a selective technique to determine and distinguish the discharge species found in the Li-Air battery [7]. The electrolyte stability can indirectly be determined through the analysis of the discharge species. The presence of species other than Li<sub>2</sub>O<sub>2</sub> indicate that electrolyte decomposition has occurred. The PILs selected will be studied by <sup>31</sup>P and <sup>7</sup>Li and <sup>17</sup>O ssNMR. <sup>31</sup>P ssNMR allows for the direct determination of the electrolyte stability. If the PIL was stable, given the ideal electrochemistry, then the only expected <sup>31</sup>P NMR peak would correspond to the unreacted PIL electrolyte. Observations of other peaks

would indicate electrolyte decomposition.

Bulky PIL electrolytes are investigated here, to probe their robustness in functioning Li-Air cells. It was hypothesized that the electrophilic regions of the electrolyte would be protected from nucleophilic attack by steric hindrance. Figure 1, a preliminary <sup>31</sup>P NMR spectrum of a discharged cathode, tentatively indicates electrolyte decomposition has occurred, as the PIL electrolyte is observed at 33ppm, in addition to a unknown species at 0ppm. The unknown phosphorous species is likely the results of electrolyte decomposition. Alternative PILs will also be studied. The <sup>31</sup>P spectra of the relevant PILs will be compared to determine if a trend exist between the PIL structure and the amount of electrolyte decomposition.

Additionally, <sup>7</sup>Li and <sup>17</sup>O NMR is used to determine the identity of the species formed during discharge.



**Figure 1-** <sup>31</sup>P Solid-state NMR spectrum of a discharged cathode, where both the PIL electrolyte and electrolyte decomposition products are observed.

Investigations of electrolyte stability remains a key building block in the development of viable Li-Air technologies, and solid-state NMR offers excellent sensitivity for nucleus-specific evaluation of PIL electrolytes.

### References

1. Girishkumar, G., Journal of Physical Chemistry Letters 2010. **1**(14): p. 2193-2203.
2. BrucePeter, G., et al., Nat Mater, 2012. **11**(02): p. 172-172.
3. Bruce, P., G., et al., Angewandte Chemie, 2011. **50**: p. 8609-8613.
4. Freunberger, S.A., et al., Journal of the American Chemical Society, 2011. **133**(20): p. 8040-8047.
5. Chen, Y., et al., Journal of the American Chemical Society, 2012. **134**(18): p. 7952-7957.
6. Sugiya, K.T.a.M., Electrochemistry Communications, 2007. **9**: p. 2353-2358.
7. Leskes, M., et al., Angewandte Chemie International Edition, 2012. **51**(34): p. 8560-8563.