

## Palladium Nanoparticles as Catalysts for Li-O<sub>2</sub> Battery Cathodes

Hugh Geaney,<sup>1,2</sup> Gillian Collins,<sup>1,2,3</sup> Colm Glynn,<sup>1,2</sup>  
Justin D. Holmes<sup>1,2,3</sup>, and Colm O'Dwyer<sup>1,2</sup>

<sup>1</sup> Department of Chemistry, University College  
Cork, Cork, Ireland

<sup>2</sup> Micro & Nanoelectronics Centre, Tyndall  
National Institute, Lee Maltings, Cork, Ireland

<sup>3</sup> Centre for Research on Adaptive Nanostructures  
and Nanodevices (CRANN), Trinity College  
Dublin, Dublin 2, Ireland

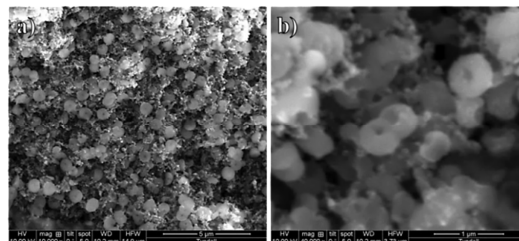
The Li-O<sub>2</sub> battery system is an excellent candidate for use in electric vehicles due to its exceptionally high theoretical capacity.(1) This system depends on the reversible production and decomposition of Li<sub>2</sub>O<sub>2</sub> at the cathode upon discharge and charge respectively. However, Li-O<sub>2</sub> batteries are still at fledgling status due to several performance hurdles which must be overcome if they are to become viable systems over practical lifetimes (e.g. >300 charge/discharge cycles). Results to date show that pure carbon cathodes exhibit excellent initial capacities which rapidly diminish due to the formation of unwanted by-products such as Li<sub>2</sub>CO<sub>3</sub> on the cathode.(2) These products cannot be easily decomposed and ultimately cause a reduction in battery capacity in successive cycles. The possible sources of byproduct formation are three-fold: i. due to reaction of the Li<sub>2</sub>O<sub>2</sub> with CO<sub>2</sub> or H<sub>2</sub>O in air. ii. decomposition of the electrolyte, and iii. decomposition of the carbon support. To circumvent the issue of reactions with CO<sub>2</sub> and moisture, the majority of Li-O<sub>2</sub> tests to date have been conducted in pure O<sub>2</sub> environments. Focus on alleviating the other performance issues have centred primarily on the identification of stable electrolyte systems and the use of catalysts which are specific to oxygen reduction/evolution.

Initial research Li-O<sub>2</sub> battery research involved the use of carbonate based electrolytes which are prevalent in Li-ion technology. However, these electrolytes are not suitable for rechargeable Li-O<sub>2</sub> cells as they lead to Li<sub>2</sub>CO<sub>3</sub> formation caused by electrochemical decomposition. Recent efforts have turned to the use of more stable electrolytes including room temperature ionic liquids and a variety of organic compounds (glymes, DMSO, various ethers etc.). Within these recently examined electrolytes, sulfolane is an attractive, low cost candidate that is stable to 4.5 V, ensuring its compatibility with Li-O<sub>2</sub> operating voltage windows.(3)

Various noble metals (e.g. Pt(4)) and metal oxides (e.g. MnO<sub>2</sub>(5)) have been investigated as bifunctional catalysts aimed at improving the rate behaviour and capacity retention for Li-O<sub>2</sub> cells. Despite being the most efficient oxygen

reduction catalyst known, Pd has not been widely studied for Li-O<sub>2</sub> applications.(6) Furthermore, comparison of the morphology and composition of charged and discharged Li-O<sub>2</sub> cathodes with and without the presence of catalysts has not been widely studied and is of crucial importance if rechargeable systems are to be realized.

In this work, we have examined the use of Pd nanoparticles as catalysts for Li-O<sub>2</sub> battery cathodes. Undergoing investigations have focused on galvanostatic charge/discharge measurements on various cathodes with Pd nanoparticle catalysts of various sizes and loadings on Super P carbon supports. Direct electrochemical and compositional comparisons with pure Super P carbon cathodes allowed the effect of Pd catalyst nanoparticles to be probed. By conducting these analyses using a sulfolane based electrolyte, it was possible for Li<sub>2</sub>O<sub>2</sub> to be produced as the sole discharge product which is key to a rechargeable system. Fig. 1 show such characteristic toroid shaped Li<sub>2</sub>O<sub>2</sub> particles formed densely across the carbon cathode after discharge. Using scanning electron microscopy, X-ray diffraction and Raman spectroscopy, we also detail the effect of Pd nanoparticle catalysts on the galvanostatic response and characteristics of product formation in charged and discharged cathodes. This research highlights Pd nanoparticles as effective catalysts for Li-O<sub>2</sub> battery cathodes towards higher rate, rechargeable Li-O<sub>2</sub> battery systems.



**Figure 1.** SEM images of Li<sub>2</sub>O<sub>2</sub> particles formed upon discharge.

### References

- [1] Z. Peng, S. A. Freunberger, Y. Chen and P. G. Bruce, *Science* **337**, 563 (2012).
- [2] M. M. Ottakam Thotiyl, S. A. Freunberger, Z. Peng and P. G. Bruce, *J. Am. Chem. Soc.* **135**, 494 (2013).
- [3] D. Xu, Z.-l. Wang, J.-j. Xu, L.-l. Zhang, L.-m. Wang and X.-b. Zhang, *Chem. Commun.* **48**, 11674 (2012).
- [4] J. Zhang, G. Chen, M. An and P. Wang, *Int. J. Electrochem. Sci.* **7**, 11957 (2012).
- [5] T. T. Truong, Y. Liu, Y. Ren, L. Trahey and Y. Sun, *ACS Nano*, **6**, 8067 (2012).
- [6] A. K. Thapa and T. Ishihara, *J. Power Sources*, **196**, 7016 (2011).