

Elucidating the origins of limited rechargeability in Li-O₂ batteries

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Nonaqueous Li-air batteries suffer from rechargeability limitations associated with both electrode and electrolyte instabilities.¹⁻⁸ These instabilities could arise from various possible reasons, including thermal chemistry of Li₂O₂ with the solvent or electrode during discharge, or Li₂O₂-induced parasitic electrochemistry with cell components during charging. However, the ability to quantify contributions to efficiency losses occurring during either discharge or charge remains elusive. This presentation will highlight our current efforts to quantify Li₂O₂ formation during discharge and Li₂O₂ oxidation during charge. This analysis is combined with quantitative measurements of O₂ consumption and evolution using DEMS, thus allowing us to more completely understand the parasitic processes that lead to limited Li-O₂ cell rechargeability.

1. McCloskey, B. D.; Bethune, D. S.; Shelby, R. M.; Mori, T.; Scheffler, R.; Speidel, A.; Sherwood, M.; Luntz, A. C. Limitations in rechargeability of Li-O₂ batteries and possible origins. *J. Phys. Chem. Lett.* **2012**, 3043-3047.
2. McCloskey, B. D.; Speidel, A.; Scheffler, R.; Miller, D. C.; Viswanathan, V.; Hummelshøj, J. S.; Nørskov, J. K.; Luntz, A. C. Twin problems of interfacial carbonate formation in nonaqueous Li-O₂ batteries. *J. Phys. Chem. Lett.* **2012**, 3 (8), 997-1001.
3. Ottakam Thotiyil, M. M.; Freunberger, S. A.; Peng, Z.; Bruce, P. G. The carbon electrode in non-aqueous Li-O₂ cells. *J. Am. Chem. Soc.* **2012**.
4. Gallant, B. M.; Mitchell, R. R.; Kwabi, D. G.; Zhou, J.; Zuin, L.; Thompson, C. V.; Shao-Horn, Y. Chemical and morphological changes of Li-O₂ battery electrodes upon cycling. *J. Phys. Chem. C* **2012**, 116 (39), 20800-20805.
5. McCloskey, B. D.; Scheffler, R.; Speidel, A.; Girishkumar, G.; Luntz, A. C. On the mechanism of nonaqueous Li-O₂ electrochemistry on C and its kinetic overpotentials: some implications for Li-air batteries. *J. Phys. Chem. C* **2012**, 116 (45), 23897-23905.
6. Bryantsev, V. S.; Giordani, V.; Walker, W.; Blanco, M.; Zecevic, S.; Sasaki, K.; Uddin, J.; Addison, D.; Chase, G. V. Predicting solvent stability in aprotic electrolyte Li-air batteries: nucleophilic substitution by the superoxide anion radical (O₂^{•-}). *J. Phys. Chem. A* **2011**, 115 (44), 12399-12409.
7. Veith, G. M.; Nanda, J.; Delmau, L. H.; Dudney, N. J. Influence of lithium salts on the discharge chemistry of Li-air cells. *J. Phys. Chem. Lett.* **2012**, 3 (10), 1242-1247.
8. Younesi, R.; Hahlin, M.; Treskow, M.; Scheers, J.; Johansson, P.; Edström, K. Ether based electrolyte, LiB(CN)₄ salt and binder degradation in the Li-O₂ battery studied by hard X-ray photoelectron spectroscopy (HAXPES). *J. Phys. Chem. C* **2012**, 116 (35), 18597-18604.