

Stability of Fluorinated Solvents in Li-O₂ Batteries

Jasim Uddin,^a Vyacheslav S. Bryantsev,^a Vincent Giordani,^a Wesley Walker,^a Michel Armand,^b Gregory V. Chase,^a Dan Addison^a

^aLiox Power Inc.
129 N. Hill Ave., Ste. 103, Pasadena, CA 91106, USA

^bCIC Energigune, Alava Technology Park, Albert Einstein, 4801510 MIÑANO Álava, Spain

Electrolyte instability in aprotic Li-O₂ batteries is a significant technical problem that must be solved in order for this technology to acquire practical significance. Many solvents and salts have been investigated, but still no electrolyte system has been demonstrated that is sufficiently stable toward both Li metal and the O₂ electrode during deep cycling over practically relevant time scales.

There is growing recognition that galvanostatic cycling alone does not establish the stability of a solvent in Li-O₂ batteries. For example, one recent publication¹ demonstrates galvanostatic cycling with high cycle numbers in cells containing tetraethylene glycol dimethyl ether, although other groups^{2,3,4,5} have provided rigorous evidence based on electrochemical mass spectrometry, NMR and other techniques that this solvent, along with ethers, carbonates, esters and lactones generally, undergo decomposition in the O₂ electrode. Solvents with superior stability with respect to the O₂ electrode include nitriles and amides^{6,7} although instability with negative electrode materials makes their use problematic.

Selective fluorination is a design strategy that could potentially improve critical solvent properties such as SEI stability, O₂ transport and oxidative stability. This talk describes the design, synthesis and testing of selectively fluorinated amides, sulfamides and sulfones for Li-O₂ batteries. Both experimental and computational methods are employed to characterize relevant properties of novel synthesized solvents from among these classes, including DFT calculations, quantitative electrochemical mass spectrometry and electrochemical impedance spectroscopy. Improvements in Li metal stability for acetamide solvents through selective fluorination will be discussed in detail.

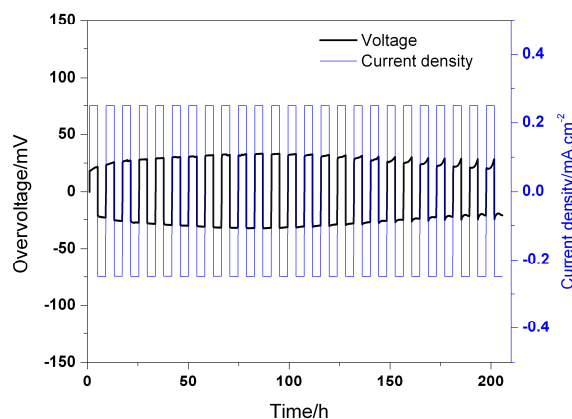


Figure 1. Galvanostatic cycling in symmetric Li cells containing 0.5M LiTFSI in dimethyltrifluoroacetamide (DMTFA) at 0.25 mA/cm².

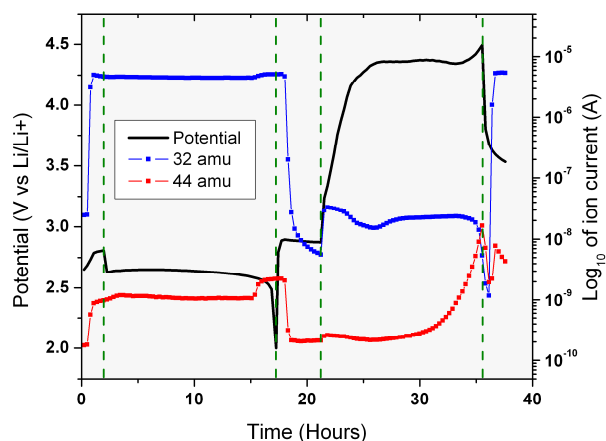


Fig. 2. Li-O₂ cell cycling at 0.1 mA/cm² with *in situ* electrochemical mass spectrometry. Cell contains 0.5M LiTFSI in dimethyltrifluorobutyramide (DMTFBA).

References:

1. H-G. Jung., J. Hassoun, J-B. Park, Y-K. Sun, B. Scrosati, *Nature Chemistry*, **4**, 579 (2012).
2. S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bard, P. G. Bruce, *Angew. Chem. Int. Ed.*, **50**, 8609 (2011).
3. B. D. McCloskey, D. S. Bethune, R. M. Shelby, G. Girishkumar, A. C. Luntz, *J. Phys. Chem. Lett.* **2**, 1161 (2011).
4. V. S. Bryantsev, F. Faglioni, *J. Phys. Chem. A*, **116**, 7128 (2012).
5. K. R. Ryan, L. Trahey, B. J. Ingram, A. K. Burrell, *J. Phys. Chem. C*, **116**, 19724 (2012).
6. Y. Chen, S. A. Freunberger, Z. Peng, F. Barde, P. G. Bruce, *J. Am. Chem. Soc.*, **134**, 7952 (2012).
7. V.S. Bryantsev, J. Uddin, V. Giordani, W. Walker, D. Addison, G. V. Chase, *J. Electrochem. Soc.* **160** (1), A160 (2013).