

On the challenge of developing rechargeable Li–Air Batteries: is it real?

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Lithium-oxygen systems seem to be the most promising rechargeable Li batteries in terms of energy density. We see a lot of publications and citations on this topic. Not too many publications indicate the instability of the electrolyte solutions used in Li-O₂ cells. The common assumption proposes that the main problem may be oxidation of the solvents during charging. In fact the discharge processes may be even more problematic. The superoxide and peroxide anions thus formed are very active moieties, especially in the presence of the highly electrophilic Li ions in solution phase. The highly nucleophilic peroxide and super-oxide thus formed can attack most of relevant polar aprotic solvents and irreversibly change the solutions composition. Some experts in the field argue that solvents decomposition in Li-O₂ cells happens only in small percentages (and initial cycling) similar to what actually happens in commercial lithium ion batteries. However, in lithium-oxygen systems, decomposition continues also after the initial cycles and it is more intensive because of the unique nature of the nucleophilic lithium oxides thus formed. The instability of the carbonate solvents has been already clearly shown. It can be said that even when good results are exhibited with Li-oxygen cells, it does not mean that the cells actually work by well-known mechanisms of oxygen reduction and oxidation. There is a lack of agreement among people working in the field on the stability of polyether solvents as some publications show reasonable cycling with Triglyme/TFSI while others indicate the formation of side products related to solvent decomposition. The motivation to find more durable solvents lead to the exploration of new options, including DMSO, amides, sulfones and ionic liquids. In recent publications lithium-oxygen cells with DMSO based solutions could show more 100 cycles (by limiting the capacity). The experimental details related to this presentation are presented in references 1 and 2. Figure 1 shows voltammetric and EQCM response of three Li salt solutions based on PC, DMSO and triglyme solvents. There are some similarities in their electrochemical behavior: the reduction broad peak between 2.7 to 2V can be associated with O₂⁻ and O₂⁻² formation. The OER of these systems is still unclear and there is no full accepted mechanisms. Despite some electrochemical similarities, the EQCM response show different trends. The EQCM response of mass and current changes in Triglyme or DMSO with 1M LiTFSI shows a relatively reasonable fitting between them. During the cathodic scan, mass is accumulate on the electrode, and when the potential is swept back (anodically) we observe that all the mass is removed from the electrode surface. This correlates well with the reversibility of lithium oxide formation and dissolution in the polyether and DMSO electrolytes solutions. In the carbonate based solution, the mass change is not reversible and the mass continue to accumulate even during the anodic scan. This linear mass change can be attributed to the continuous reaction of PC with the oxides due to its electrophilic nature.

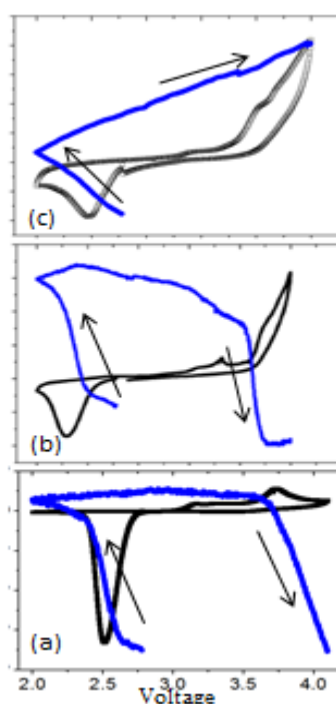


Fig 1. Cyclic voltammetry (black) and EQCM response (blue) of (a) DMSO/LiTFSI 1 M gold WE (b) triglyme/LiTFSI 1 M Pt WE (c) PC/LiTFSI 1 M Pt WE in oxygen atmospheres.

One might conclude from such studies that DMSO or polyether systems can work in a reversible mode. However, the post mortem analysis of Li-O₂ cells based on DMSO or polyether solutions exhibit a wide spectrum of irreversible side products formation due to solution decomposition and carbon corrosion.

A good example for ORR products analysis in Triglyme/LiTFSI was carried out by “matrix-assisted laser desorption/ionization” (MALDI) mass spectrometry. The mode of ionization was set for positive voltage and the resulting fragments are positively charged. The m/z values of the major MALDI fragments measured from the discharged electrodes in Triglyme/LiTFSI are listed in figure 2. Looking at the various fragments, it becomes clear that they can be readily associated with degradation of the solvent and to its reaction with lithium peroxide. All aspects of possible R&D of Li-O₂ batteries will be thoroughly discussed in the presentation.

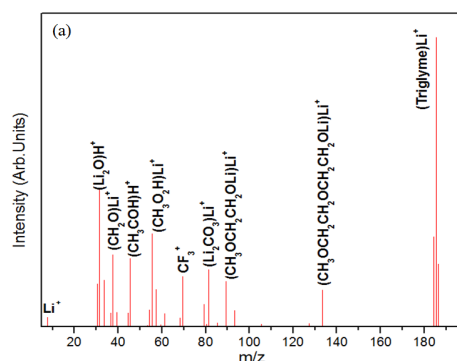


Fig 2 . MALDI response of an activated carbon electrode discharged to 2 V in triglyme/LiTFSI solution.

References

- (1) Etacheri, V. et Al, *Journal of Materials Chemistry A* **2013**, *1*, 5021-5030
- (2) Sharon, D. et Al, *The Journal of Physical Chemistry Letters* **2013**, *4*, 127–131.