The Rechargeable Aprotic Li and Na-O_2 Batteries

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Interest in the rechargeable Li and Na-O_2 batteries is driven by their high theoretical specific energy, Li-O_2 (3500 $Whkg^{-1}$) and Na-O_2 (1108 $Whkg^{-1}$). [1-6] However, a number of challenges face the realization of practical devices. Such challenges demand an understanding of the reactions and processes in the cell, especially at the electrodes. [4,7-10] In the case of the Li-O_2 cell, the main focus has been on the reaction at the cathode:

$$O_2 + 2\,e^- + 2\,Li^+ = Li_2O_2$$

This simple reaction belies several complex problems. Li_2O_2, is an insulating solid, if it grows on the electrode surface it can only do so to a thickness of approx. 6 to 7 nm. [11] The resulting passivation leads to low rates and low capacities. If Li_2O_2 grows from solution, passivation is avoided, leading to high rates and capacities. The solvent donor number is an important factor in controlling which pathway, surface film or solution growth, occurs. Low donor number ethers promote surface films while high donor number solvents result in solution growth. Unfortunately, high donor number solvents are more susceptible to decomposition by the reactive O_2^- nucleophile (the intermediate in the O_2/Li_2O_2 reaction is LiO_2). We show that using redox mediator molecules to shuttle electrons between the electrode surface and solution, Li_2O_2 can be formed and decomposed in solution even in a low donor number solvent like ethers, Fig. 1. As a result, rates and capacities of several mA and mAh cm^{-2} respectively are observed. This also avoids the LiO_2 intermediate in solution, reducing solvent decomposition and halving the discharge overpotential. Furthermore, by avoiding contact between Li_2O_2 and the carbon cathode the stability of the later is improved.

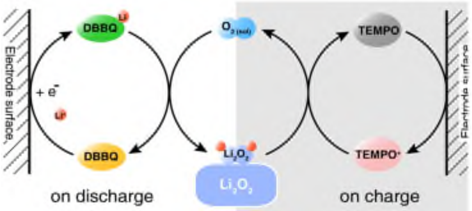

Figure 1: Schematics of positive electrode reactions on discharge and charge in the presence of dual mediators.

Although ethers, if used in conjunction with mediators, exhibit improved solvent stability, they do not solve the problem. The decomposition of the electrolyte solution in Li-O_2 cells will be discussed in the context of the mechanism of Li_2O_2 formation and decomposition.

Ultimately the Li-O_2 cell must operate in air. The effect of H_2O in the gas stream and hence in the electrolyte solution on the mechanism of O_2/Li_2O_2 and the effect on cell performance are important. The influence of H_2O on the O_2 reduction mechanism will be considered.

Turning to Na-O_2, the product at the cathode is NaO_2, which limits the capacity compared with Na_2O_2, but as NaO_2 is soluble it leads to better intrinsic rechareability. The factors that govern the growth of NaO_2, especially the influence of the electrolyte solvent on film vs particle growth from solution, will be considered.

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