

## Reaction and Transport in Gas Diffusion Electrodes of Li-O<sub>2</sub> batteries: Experiments and Modeling

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Lithium-oxygen (Li-O<sub>2</sub>) batteries are a potential alternative to conventional combustion technologies in the mobility sector. Two possible solvent systems are in the focus of extensive research at the moment. Namely, systems with aprotic and aqueous electrolyte [1].

Major challenges in the development of Li-O<sub>2</sub> systems arise from the formation of solid discharge products. In the cathode of aprotic Li-O<sub>2</sub> batteries Li<sub>2</sub>O<sub>2</sub> is formed during discharge. Li<sub>2</sub>O<sub>2</sub> has a low electric conductivity [2] and passivates active surfaces. Additionally it may block pore space and hamper the transport of reactants [3]. In the case of a low solubility and diffusivity of O<sub>2</sub> in the liquid electrolyte, e.g. ionic liquids, this becomes an important capacity and power limitation.

Aqueous electrolytes offer an interesting alternative as gas diffusion electrodes (GDEs) allow to overcome O<sub>2</sub> transport limitations. During discharge the solid reaction product LiOH·H<sub>2</sub>O precipitates at concentrations above the solubility limit ( $c_s=5.3$  mol/l). This causes capacity limitations due to restricted mass transport similar to the aprotic case. A main challenge is to find a stable protective layer for the Li metal electrode. Li reacts vigorously with water which causes major security risks and makes experimental studies on a full cell a difficult task. Therefore, the system is an ideal candidate to be studied in numerical simulations.

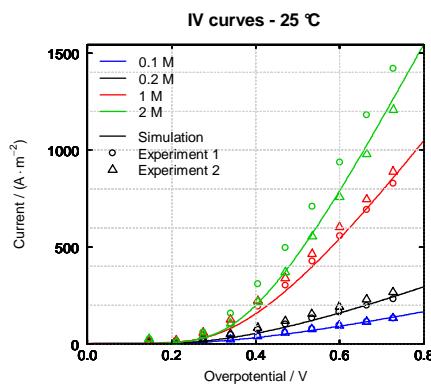


Figure 1: IV curves in LiOH solution. Symbols: half-cell experiments; solid lines: numerical simulations.

Here we present a detailed numerical modeling and experimental validation study of aqueous Li-O<sub>2</sub> cells. The simulations are based on a 1D multi-phase modeling framework presented previously [4]. The framework is capable of describing the formation and transport of multiple gaseous, liquid and solid phases in aqueous and aprotic Li-O<sub>2</sub> batteries. We model capillary-pressure driven transport of the aqueous electrolyte in the GDE [5]. The parameters stem from in-house half-cell experiments and from the literature. Cyclic voltammograms (Figure 1) and electrochemical impedance spectra (Figure 2) were measured with a three-electrode setup in LiOH solutions. Our transport and reaction model was successfully validated over a wide range of temperatures and concentrations (Figure 1 and 2).

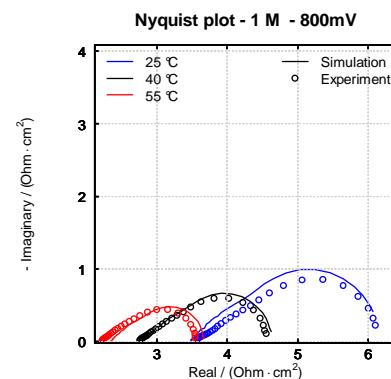


Figure 2: Nyquist plots of impedance spectra measured in 1 M LiOH solution at a polarization of 800 mV vs. RHE.

Precipitation of solid LiOH·H<sub>2</sub>O is modeled via the classical theory of nucleation and growth. LiOH·H<sub>2</sub>O can either form heterogeneously on the surface or homogeneously on nucleation centers in the bulk of the solution. This gives rise to several possible electrode and cell designs which offer an improved battery capacity. We evaluate and optimize different cell design concepts, including flooded electrode, gas diffusion electrode, porous separator, and bulk separator, under various operation conditions (Figure 3).

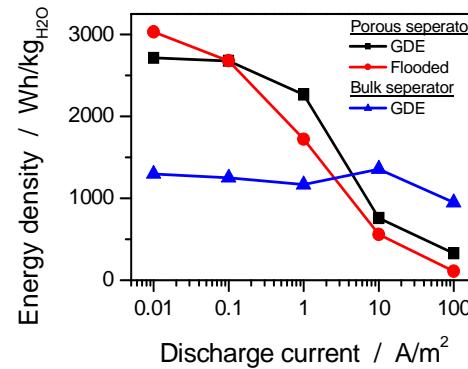


Figure 3: Energy density for different cell configurations of Li-O<sub>2</sub> batteries with aqueous electrolyte. The optimal configuration depends on the operating conditions.

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