"Oxygen transport in porous cathodes of Li-O cells: A simplified model approach"

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The Lithium-Oxygen battery is currently an intensively studied system because of its very high theoretical energy density.

Most Li-O cells use pure Lithium as the negative electrode (anode) since it is light and thus supports a high energy density. The positive electrode (cathode) of Li-O cells often consists of a porous and electrically conducting medium soaked with electrolyte. As cathode materials often carbon is chosen as it is very abundant, cheap, easy to synthesize (with high specific surface) and versatile.

During operation Oxygen is absorbed into the electrolyte from the gas phase. Discharging takes places on the cathode/electrolyte interface. The discharge reaction yields Li_2O or Li_2O_2 as reaction products. Both, Li_2O and Li_2O_2, can be oxidized to retain Li and Oxygen respectively. However, the potential to oxidize Li_2O is high enough to cause side reactions and decompose the electrolyte and/or electrode material. Additionally there is a very low efficiency caused by a large overpotential upon both charge and discharge. Li_2O_2 is the desired reaction product because of its lower oxidation potential. Still proper catalysts need to be found to increase the efficiency.

The system, although first published in 1996 by Abraham and Jiang is in an initial state of research. To exploit its benefits a number of issues have to be addressed.

Oxygen transport and oxygen reduction kinetics are considered among the most pressing issues of today's Li-O – cells. Several classes of cathode structures (micro- and meso porous) as well as materials including catalysers have been investigated already, but yet without a success substantial enough to commercialize the Li-O system. Exceptions like nano-porous Au-cathodes[1] show in principle the viability of the Li-O-cells but are cost inefficient. To improve bottleneck processes of the cells usually a large number of experiments and analysis has to be done. Depending on the electrochemical system, electrochemical methods such as cyclic voltammetry can be hard to interpret. The Li-O - system is such a case, because the discharge reaction involves kinetically slow electron transfer steps followed by faster chemical reactions. This fact requires a computer approach to interpret measured data.

Computer model can help to understanding the measured data more deeply, but an arbitrary number of parameters can be used which can blur the view on important mechanisms and their interactions. Here a simplified, 1-dimensional computer model will be presented. It facilitates the interpretation of data generated by a certain electrochemical method. The model covers the most crucial aspects of Li-O - cells upon discharge, including O_2-absorption from gas phase, diffusive O_2 - transport and O_2-reduction kinetics as well as passivation of the active cathode BET surface and pore clogging by reaction products. By accepting a certain inaccuracy of the model, the number of unknown and/or difficult to measure parameters is kept to a minimum, leaving only the absorption coefficient α, the effective O_2 diffusion constant D_{eff} and the heterogeneous rate coefficient of the oxygen reduction reaction k_1 as free parameters. Other parameters like the BET surface, porosity or the passivation layer thickness can be measured by straight forward methods. Aspects of the Li-transport are disregarded completely as the Lithium concentration in the electrolyte is several orders of magnitude above the oxygen concentration. (depending on the electrolyte)

Chronoamperometry is used as the experimental method to generate the data that can be interpreted by means of the model. The computer model simulates a one-time discharge at constant potential and calculates a current transient curve which is compared to measured curves. Since in experiment discharging is done at constant potentials, the heterogeneous rate coefficient k_1 can really be regarded as a constant. Its dependency on the potential is elucidated by performing several discharges at different constant potentials. The model predicts the discharge curves well enough to retain a Tafel like behaviour of k_1. Discharging at different temperatures allows for the calculation of the activation energy of the ORR.

A measured curve with a simulated curve is shown on picture 1. The measured curve was obtained by applying a fixed potential that should discharge the cell. Purging the cell with oxygen causes a non-zero current, which is recorded over time. Passivation leads to current fading.
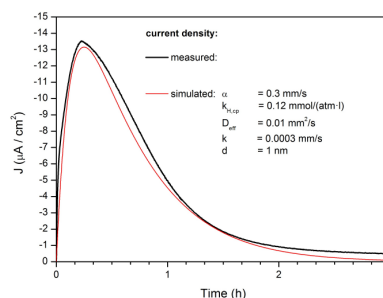
Picture 1: Discharge at const. potential (current fading starts at t ≈ 20min)

Parameters obtained by this simple model might be considered as starting values for more sophisticated simulation software such as DENIS by Bessler et al.[2]

Gas diffusion cathodes with an optional micro porous layer as well as in house synthesized CNT on steel meshs serve as cathode materials to validate the model.

The parameter k_1 capsules aspects of the electron transfer step. (Accordingly $D_{eff} \rightarrow O_2$ transport and $\alpha \rightarrow O_2$ absorption) The model applied here helps gaining general understanding of the system as a whole. Deviations from measured data must be clarified by means of other more complex models, where especially the correlation to the parameters of the simple model will be enlightening.

[1] Science 337(6094) 563-566 (AUG 2012) A Reversible and Higher-Rate Li-O₂ Battery (Peng, Freunberger, Chen, Bruce)

[2] J. Electrochem. Soc. 159(9) A1528-42 (2012) A Flexible Framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells (Neidhardt, Fronczek, Jahnke, Danner, Horstmann, Bessler)