A simplified model for O_2 transport and reduction kinetics in porous cathodes of Li-O cells

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Introduction

Todays Li-O cells suffer a number of inconveniences. However, their investigation is justified by the very high theoretical energy density of the Li-O – system. Performance determining processes are mainly oxygen transport and reaction kinetics. This work is comprised of two main parts to approach these issues:

1) A cell **design approach** to **actively enrich the electrolyte** with O_2 and find out about possible **differences**/improvements **compared to passive O_2 supply**. The idea is to improve the performance by increasing the O_2 concentration in the electrolyte. For this purpose a 2-mode cell was constructed allowing for the supply of O_2 to the cathode in two ways. Either exchanging an inert gas (e.g. Ar) for O_2 above the cathode (classic way = passive mode) or using a 2-channel curly structure to push oxygen directly into the cathode (active mode).

2) Development of a **simplified model** to quantitatively describe measured discharge curves. The model allows isolated study of the most important processes influencing the cell performance. Its behaviour is governed by a **small set of parameters** that correlate to physical quantities.

Model scope

Included:
- Absorption of O_2
- Diffusive transport of O_2
- Kinetics of O_2 reduction reaction
- Passivation of the active cathode surface (BET)
- SOC-effect on O_2 transport (pore clogging)

Not included:
- All aspects of Li – transport
- Thermodynamics
- Recharging

Model equations / Model sketch

Assumed discharge reaction path: $O_2 + e^- \rightarrow O_2^-$ | $Li^+ + O_2^- \rightarrow LiO_2$ | $2LiO_2 \rightarrow Li_2O_2 + O_2$

slowest reaction → rate determining

follow up reactions are fast and not considered in model equations

O_2 - Transport / Consumption:

$$\frac{\partial}{\partial t}\frac{c_{O_2}(x,t)}{v_{elyt}(x,t)} = \frac{\partial}{\partial x}\left(D_{eff}(x)\cdot\frac{\partial}{\partial x}\frac{c_{O_2}(x,t)}{v_{elyt}(x,t)}\right) - \frac{1}{2}\cdot k_1\cdot\sigma(x,t)\cdot\frac{c_{O_2}(x,t)}{v_{elyt}(x,t)}$$

Li_2O_2 – Production:

$$\frac{\partial}{\partial t}\frac{c_{Li_2O_2}(x,t)}{v_{elyt}(x,t)} = \frac{1}{2}\cdot k_1\cdot\sigma(x,t)\cdot\frac{c_{O_2}(x,t)}{v_{elyt}(x,t)}$$

Li_2O_2 – concentration → volume fraction

$$v_{Li_2O_2} = \frac{M_{Li_2O_2}}{\rho_{Li_2O_2}}\cdot c_{Li_2O_2} \implies \frac{\partial}{\partial t}v_{elyt}(x,t) = -\frac{\partial}{\partial t}v_{Li_2O_2}(x,t) = -\frac{M_{Li_2O_2}}{\rho_{Li_2O_2}}\cdot\frac{\partial}{\partial t}c_{Li_2O_2}(x,t)$$

Active surface:

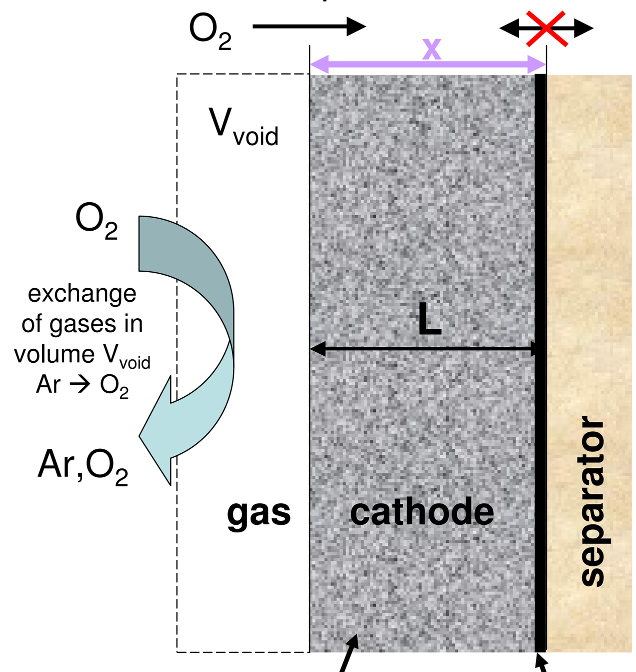
$$\sigma(x,t) = \sigma_0(x) - \sigma_{passivated}(x,t) = \sigma_0(x) - \frac{M_{Li_2O_2}}{\rho_{Li_2O_2}\cdot d}\cdot c_{Li_2O_2}(x,t)$$

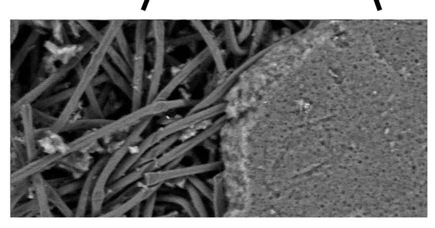
Measured quantity: $j(t) = k\cdot F\cdot\int_0^L \sigma(x,t)\cdot\frac{c_{O_2}(x,t)}{v_{elyt}(x,t)}\cdot dx$

Quantities:
c .. concentration
v .. volume fraction
k .. heterog. rate coefficient of ORR
σ .. volume specific BET – surface
D_{eff} .. effective diffusion coefficient
d .. maximum layer thickness of Li_2O_2

Sublabels:
O_2 .. oxygen
Li_2O_2 .. lithium peroxide
elyt .. electrolyte

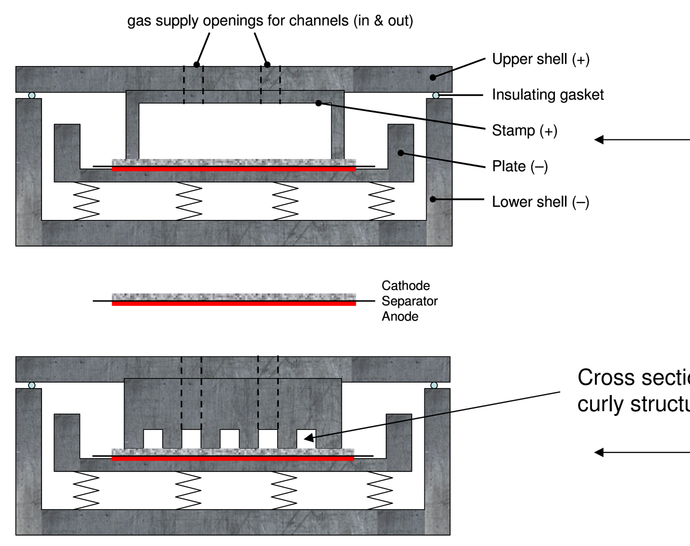
Application of model:
Unknown parameters are systematically varied until a suitable fit curve is obtained (refinement)

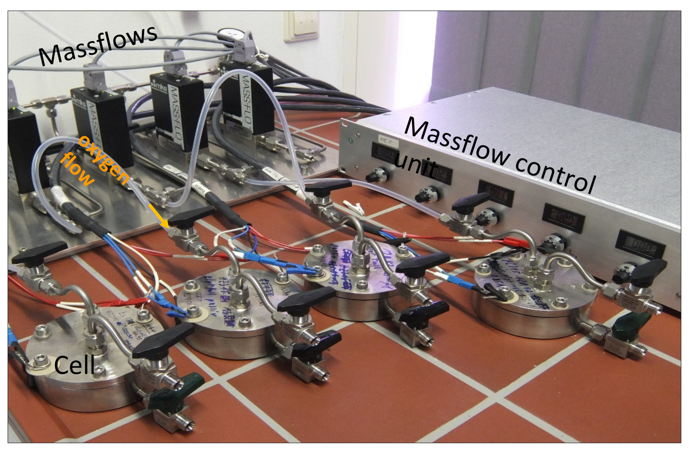




GDL MPL
REM of cathode material

Cell design





Device in Laboratory

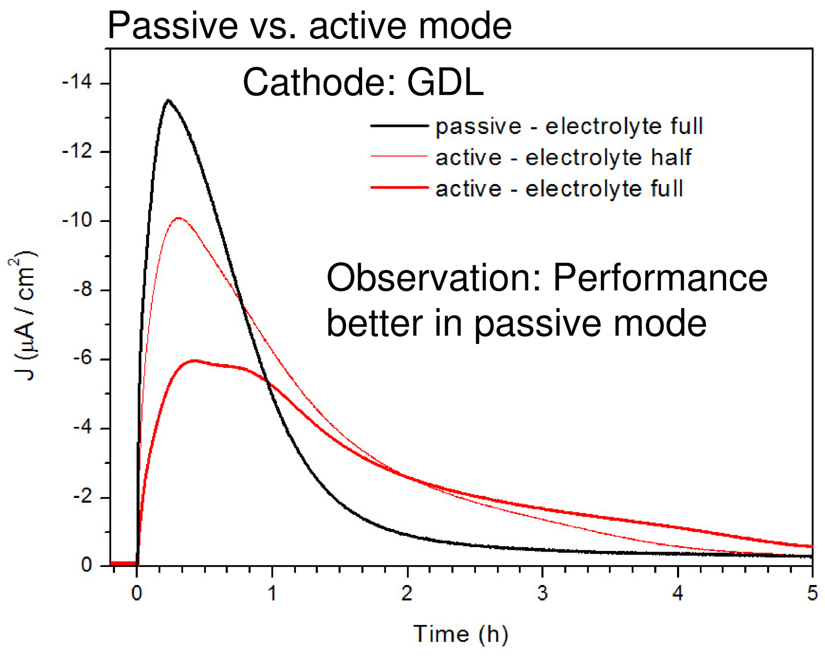
GDL Cathode Material: Freudenberg H2315

Results: Passive vs. Active

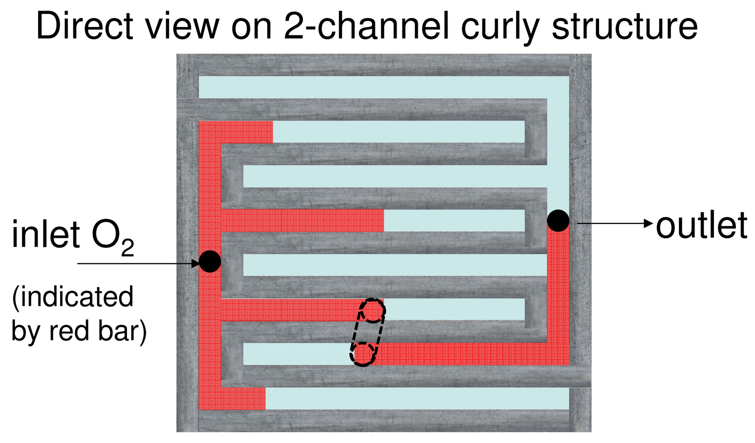
Measurement method: Chronoamperometry

- Potential is applied at which cell should get discharged
  → without O_2: initial decaying current (not shown)
- After initial current decayed: O_2 supply is started

Passive vs. active mode



Direct view on 2-channel curly structure



- Plateau – Rayleigh instability:
  → Electrolyte is displaced first at one certain location
- Build up of a shortcut for oxygen flow
  → Pressure drop in inlet channel
  → Decreased O_2 supply

Materials

Anode:
- Lithium (Chemetal)

Cathode:
- Gas-diffusion layer – GDL (250µm) H2315 (Freudenberg)
- GDL-Material: carbon fibers (Ø ≈ 10µm) - nonwoven fabric
  vol. spec. surface: σ ≈ 2,6·10⁵ m²/m³
- Micro-porous layer – MPL (~30µm) H2315 C4 (Freudenberg)
- MPL-Material: carbon black, PTFE binder
  vol. spec. surface: σ ≈ 4,8·10⁷ m²/m³

Electrolyte:
- 0.25M LiTFSI in PP13TFSI (ionic liquid)

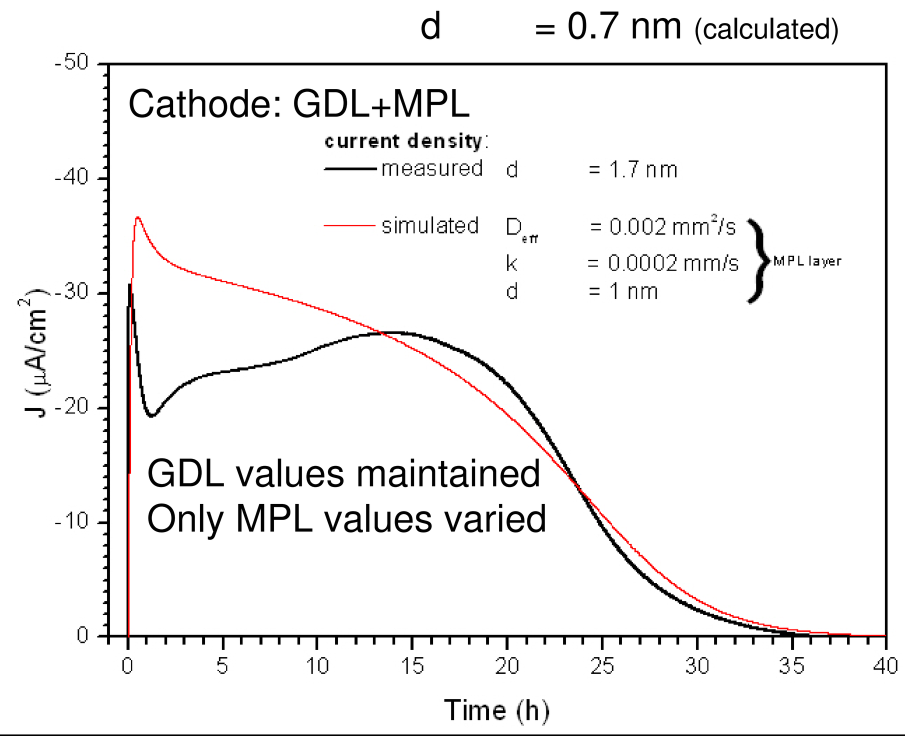
Comparable Values for D_{eff}:

DMSO:	$1.67\cdot10^{-9}$ m²/s
MeCN:	$4.64\cdot10^{-10}$ m²/s
DME:	$1.22\cdot10^{-9}$ m²/s

Laoire 2010,J. Phys. Chem. 114, 9178-9186

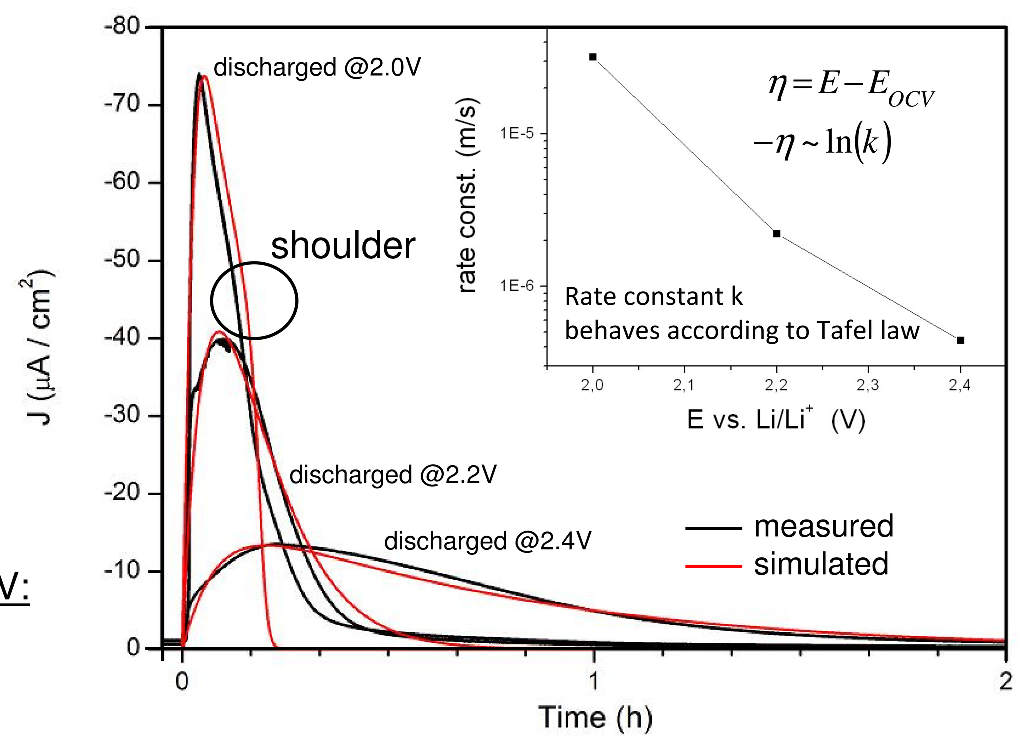
Fit values found for GDL discharge at 2.4V:

α	= 1 mm/s
$k_{H,cp}$	= 0.07 mol/(m³·atm)
D_{eff}	= $1\cdot10^{-8}$ m²/s
k_1	= 0.00044 mm/s
d	= 0.55 nm (fit value)
d	= 0.7 nm (calculated)

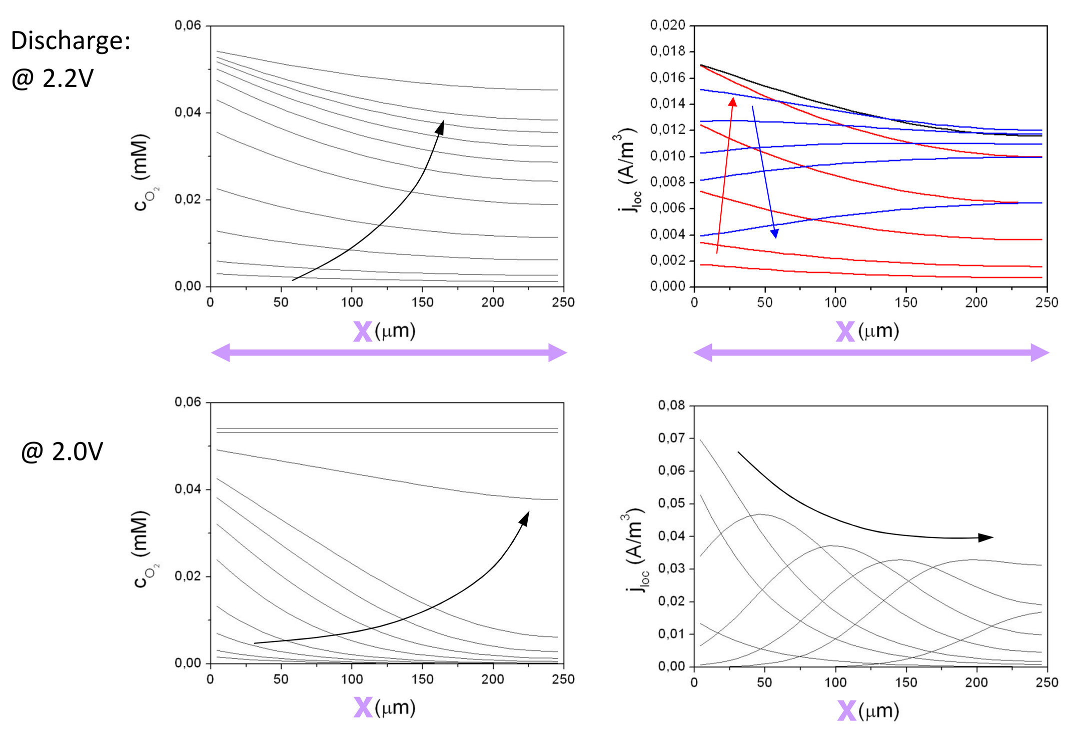


Simulation (for passive mode)

Cathode: GDL only
Model „predicts" measured curves by changing k



O_2 – concentration: Current density distribution:



Conclusions

- Active mode has contrary effect → no performance improvement over passive mode
- Simple mathematical model covers basics of chronoamperometry method
  - crucial parameters correspond to physical quantities
  - fitting possible (but requires long time or fast computing)
- Shoulder at high rate discharge (2.0V) indicates transition from rate- to diffusion limited behaviour
  - O_2 is consumed faster than it is transported across the cathode depth
- Better overall understanding of inner working
  - Variation of single parameters to identify perfomance limiting quantities
  - Find redundant quantities (e.g. to save material → cost)

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