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# Investigation of the Conductivity in Li-Mn-O Thin Films

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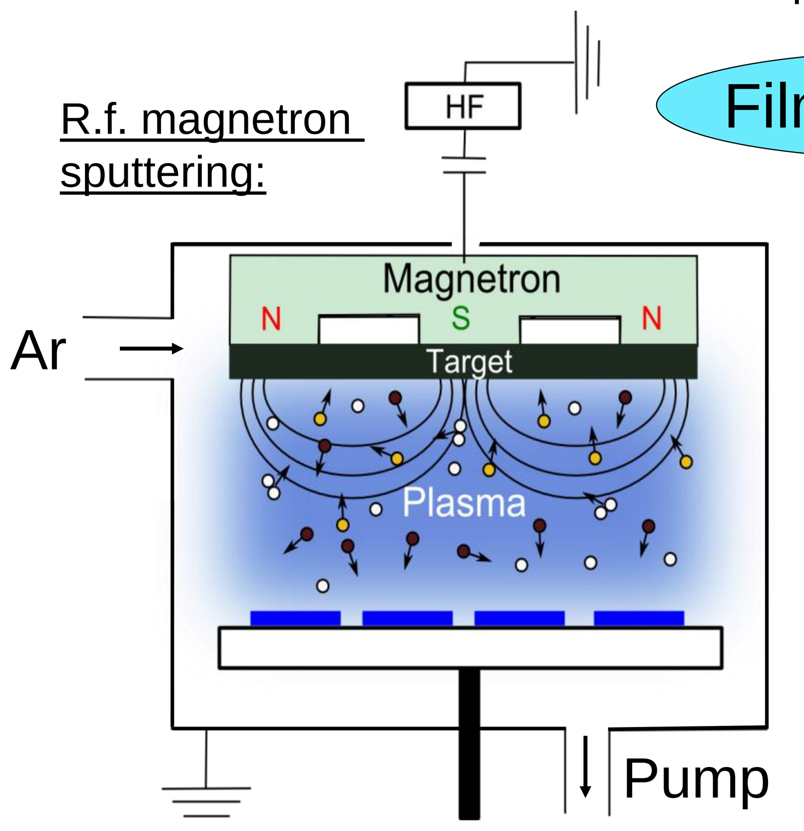
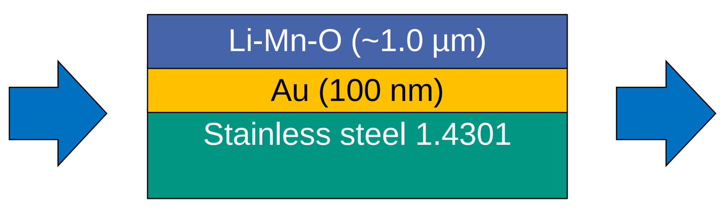
Today, lithium ion batteries (LIB) are high performance energy storage devices for portable consumer electronics like cellular phones or laptops. The development and investigation of cathode materials for lithium ion batteries plays an important role in gaining high electrical capacity and reversibility. One important intrinsic and physical criterion of an active cathode material is its lithium ion conductivity. This value limits the time scale on which lithium intercalation and deintercalation can be carried out, and therefore directly influences charging and discharging times of the devices by a consumer. Especially, for high power applications, which can only be realized by delivering a high amount of charges in a short period of time, it is mandatory to increase the conductivity. In this work, different lithium manganese oxide based thin film cathodes have been produced by r.f. magnetron sputtering. They are of potential interest in future thin film LIB applications.Further two techniques are presented to investigate both electrical and electrochemical behavior of these materials.

## Film Synthesis



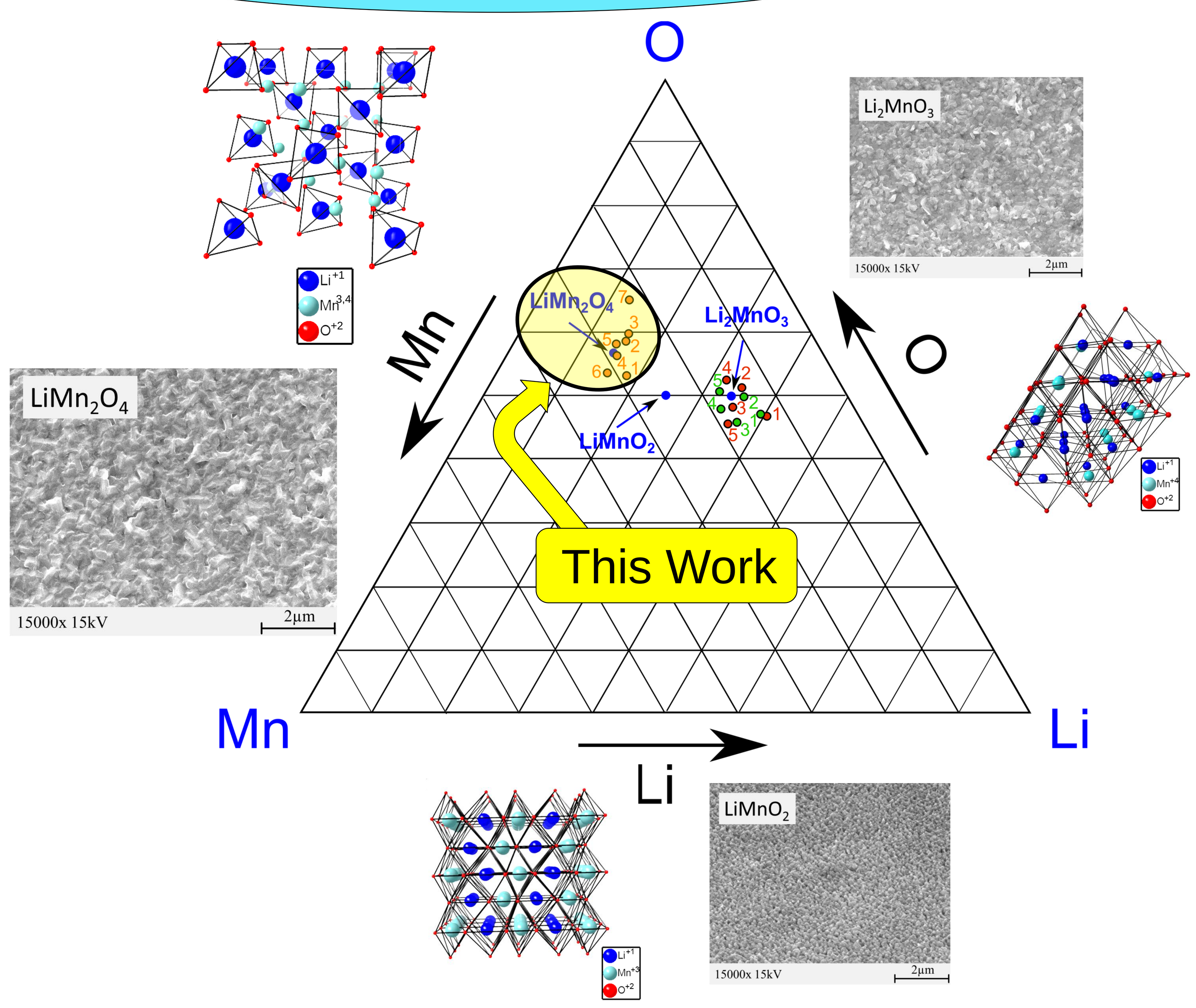

Studied synthesis parameters:

- Argon working gas pressure: 0.5 Pa - 16 Pa
- Target power: 50 W - 150 W
- Thermal annealing atmosphere: Air, Vakuum
- Thermal annealing temperature: 300 °C – 700 °C
- Target materials: $LiMn_2O_4$, $Li_2MnO_2$



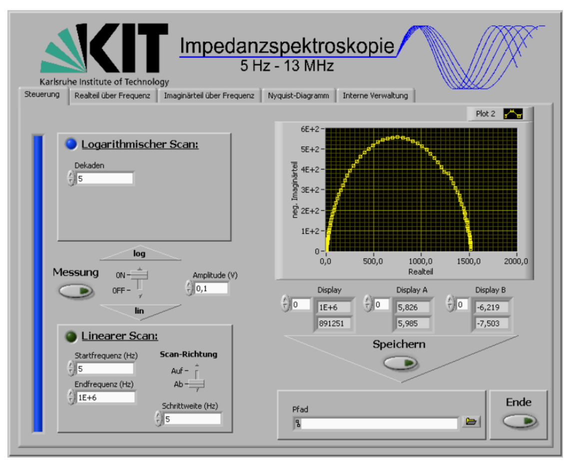

It was possible to synthesize three different cathode materials, which are of potential interest in future thin film lithium ion battery applications.

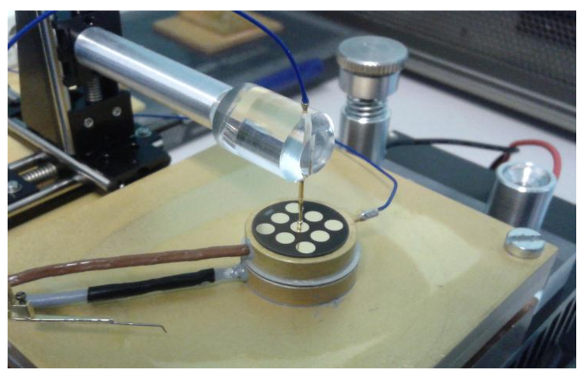
## Composition & Microstructure



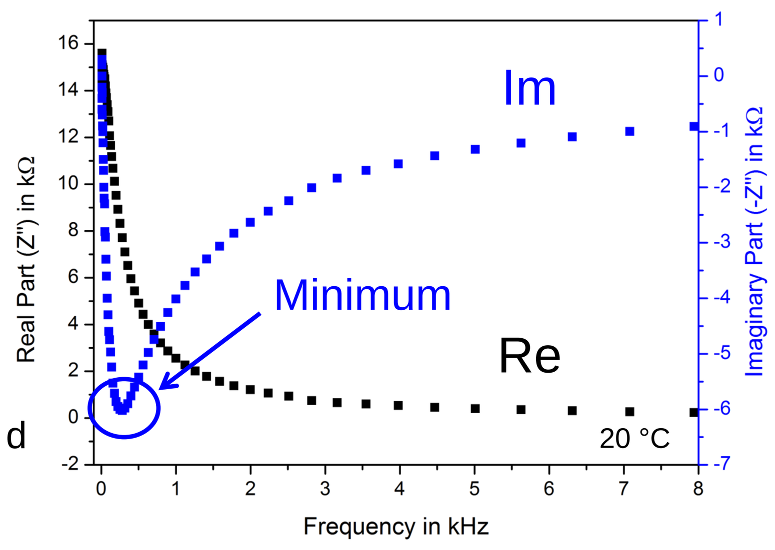

## Electrical Characterization

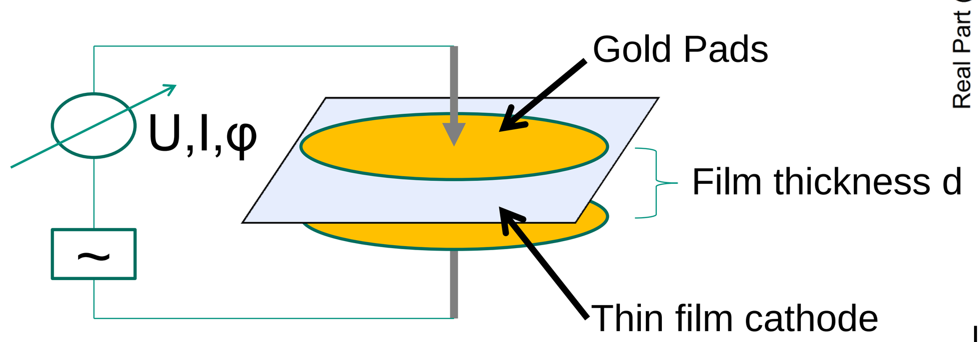
With AC-impedance spectroscopy it is possible to investigate the conductivity $\sigma_{dc}$ of LIB thin film materials. Therefore in this work, an impedance test device was build up in combination with a Labview based analyze software.
As a model system $c$-$LiMn_2O_4$ was chosen in this paper.



By these measurements an alternating sinusoidal voltage with an amplitude of $V_{ss}$=100 mV at different frequencies is applied to a small capacitor, which consists of two gold pads with a diameter of 3 mm. The thin film cathode is placed between these two collectors as a dielectric medium.



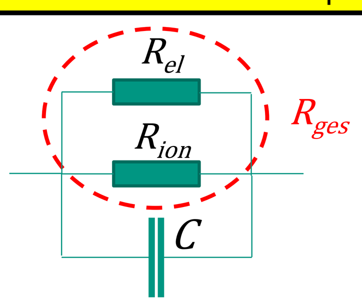

In the case of a system with a capacity like behavior, the imaginary part has a minimum in the frequency range between 10 Hz and 1 MHz. This leads to a semicircle in the Nyquist diagram.

Equivalent circuit:

$$\hat{Z}(\omega) = Z'(\omega) + iZ''(\omega) \qquad \hat{\sigma}(\omega) = \frac{d}{\hat{Z}(\omega)\cdot S}$$

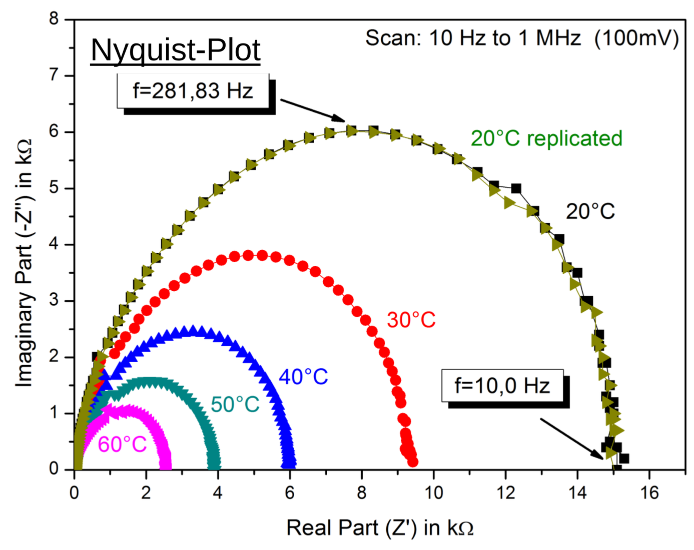
$$\sigma'(\omega) = \frac{d}{S}\cdot\frac{Z'}{|\hat{Z}|^2} \qquad \sigma''(\omega) = -\frac{d}{S}\cdot\frac{Z''}{|\hat{Z}|^2}$$

$$\frac{1}{Z} = \frac{1}{R_{ion}} + \frac{1}{R_{el}} + i\omega C$$

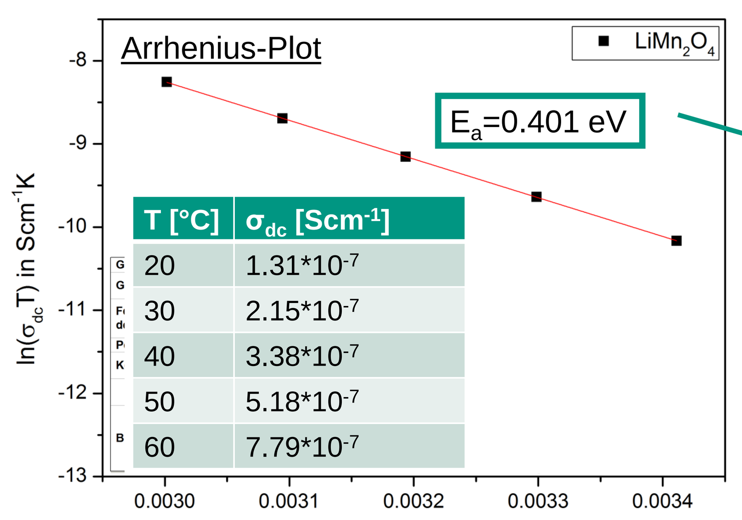



$$\sigma''(\omega) = \omega\cdot C\cdot\frac{d}{S}$$

$$\sigma'(\omega \approx 0) = \sigma_{dc} = \frac{d}{S}\cdot\frac{R_{el}+R_{ion}}{R_{el}R_{ion}} = \frac{d}{S}\cdot\frac{1}{R_{ges}}$$




Nyquist plot: From the intersection with the end of the semicircle at small frequencies (10 Hz) and the real part axis of the Nyquist-plot, it is possible to calculate the specific conductivity of the thin film.




| T [°C] | $\sigma_{dc}$ [$Scm^{-1}$] |
|---|---|
| 20 | $1.31*10^{-7}$ |
| 30 | $2.15*10^{-7}$ |
| 40 | $3.38*10^{-7}$ |
| 50 | $5.18*10^{-7}$ |
| 60 | $7.79*10^{-7}$ |

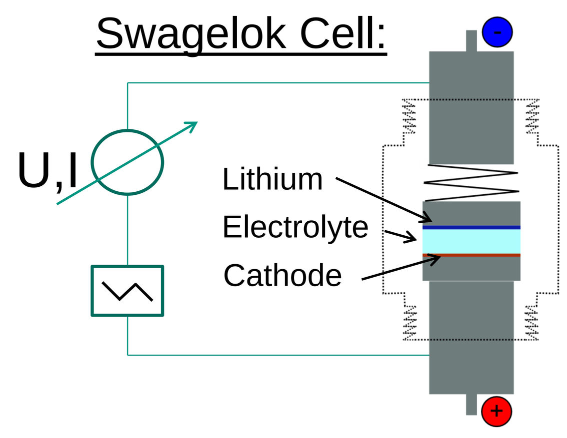
Table 1

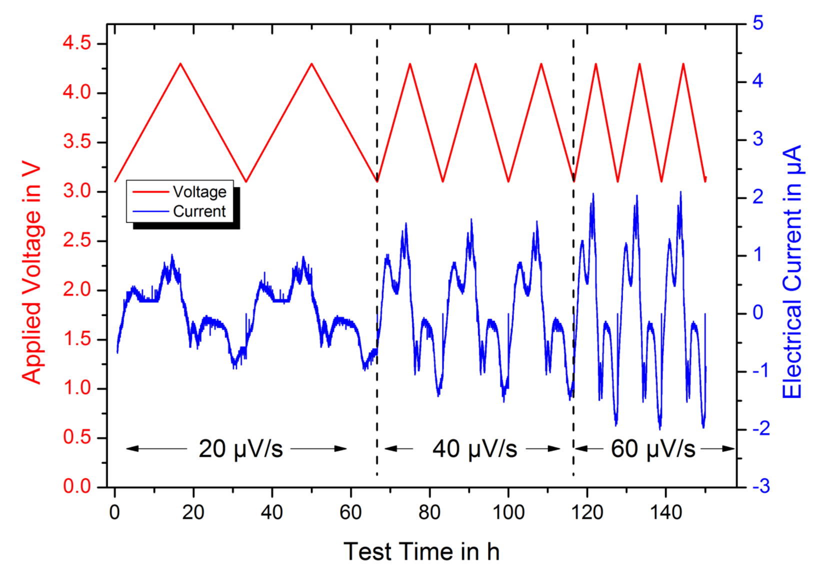
| $E_a$ (eV) | Literature |
|---|---|
| 0.44 / 0.42 | Iguchi, J.A. Phys. 2002; Vol. 91 |
| 0.3 - 0.5 | Molenda, Solid. S. Ion. 1999; Vol. 123 |
| 0.42 | Hussain, Ionics 2007; Vol. 13 |
| 0.4 - 0.45 | Guan, S.S. Ionics 1998; Vol. 110 |

All measurements in this work were carried out temperature-dependently between 20 °C and 60 °C. This allows the determination of the activation energy $E_a$ of the ionic hopping mechanism because the lithium hopping is temperature activated.

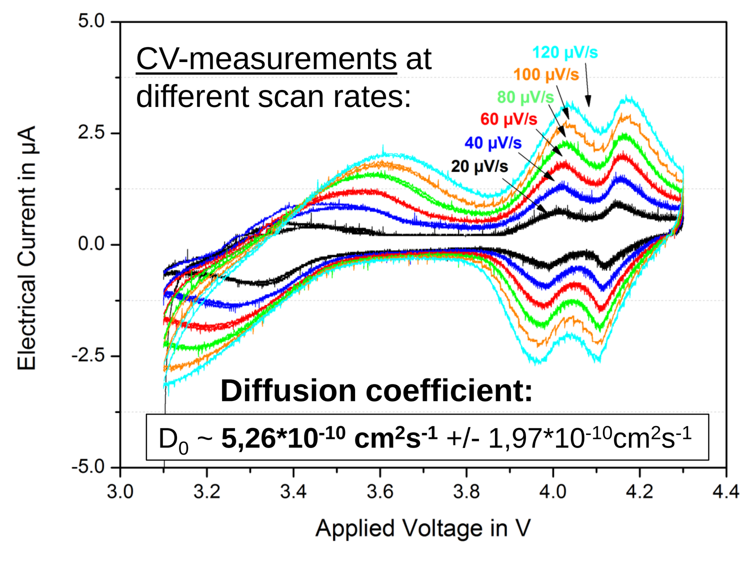
## Electrochemical Characterization

Potentiostatic cyclic voltammetry (CV) measurements have been carried out, in order to investigate the lithium diffusion behavior during electrochemical cycling. The electrochemical measurements were realized by using pure metallic lithium as anode in so called Swagelok cells. As a separator a glass fiber filter and as an electrolyte $LiPF_6$ (1M) in EC/DMC (1:1) was used.




During the measurement a triangle shaped voltage ramp is applied to the cell. The current is measured simultaneously.




In the Randles-Sevcik-Equation the peak current of different redox reactions depends on the square route of the scan rate of the applied voltage ramp. So it is possible to determine the lithium diffusion coefficient $D_0$ of the active material by sweeping voltage ramps with different scan rates.

$$I_p = 0{,}446nFA\left(\frac{nF}{RT}\right)^{1/2}\upsilon^{1/2}D_0^{\ 1/2}C_0$$ Randles-Sevcik-Equation

$$i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_0}{(\pi t)^{1/2}}$$ Cottrell Equation

## Conclusion:

In this work three different cathode materials (cubic-$LiMn_2O_4$, monoclinic-$Li_2MnO_3$ and orthorhombic-$LiMnO_2$) were prepared by radio frequency magnetron sputtering, which are all of potential interest for future all solid state thin film battery applications. Two different characterization methods were build up to investigate the electrical and electrochemical properties of this materials. First measurements were carried out at a $c$-$LiMn_2O_4$ model system and showed a good agreement with determined values from existing literature. Now all requirements were met to investigate different thin film cathode materials with respect to their electrical and electrochemical behavior. Future work aims at the determination of the intrinsic physical properties of $o$-$LiMnO_2$ and $m$-$Li_2MnO_3$, and the separation of the electronic and ionic part of the conductivities. This separation is a challenge which could be solved by introducing different electronic or ionic blocking electrodes between the gold pads and the thin film cathodes.



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