Determination of lithium diffusion coefficients in commercial electrodes by impedance modelling

Michael Weiss[1*], Jörg Illig[1], Jan Philipp Schmidt[1], Moses Ender[1], André Weber[1], Ellen Ivers-Tiffée[1,2]

[1]Institut für Werkstoffe der Elektrotechnik (IWE),
Karlsruhe Institute of Technology (KIT),
D-76131 Karlsruhe, Germany
[2]DFG Center for Functional Nanostructures (CFN),
Karlsruhe Institute of Technology (KIT),
76131 Karlsruhe, Germany

* Corresponding author: Tel.: +4972160848795
E-mail: m.weiss@kit.edu

Lithium-ion batteries are most promising as energy storage system in mobile applications, where high energy as well as high power density is necessary.
To be able to stress such batteries with high currents fast diffusion processes are required. A measure for the diffusivity is the diffusion coefficient.
PITT and GITT are established methods to determine diffusion coefficients, measuring current respectively voltage relaxations for some minutes after corresponding pulses and analysed according to [1] [2].
In this contribution, we introduce a method which also excites the cell by a current pulse, however the voltage relaxation behaviour is recorded for several hours and subsequently analysed by Fourier transformation according to [3]. This impedance data set contains all polarisation processes, and necessitates the subtraction of the differential capacity [4]. Figure 1 shows a Nyquist plot of the resulting impedance spectrum spanning over a frequency range from MHz down to µHz. The frequency range of interest for determining the diffusion coefficient is indicated by a bracket. Is characteristic shape is best represented by a Finite Length Warburg element. CNLS-fit defines model parameters [5]. Using the relation between the Warburg time constant and the effective diffusion length, which is determined by FIB tomography 3D electrode reconstruction (Figure 2) and subsequent the diffusion coefficient is calculated [6].
In our study we investigate commercial cathodes like $LiFePO_4$, $LiCoO_2$ and NMC in experimental test cell housings with a three electrodes setup. Lithium metal is used as counter electrode whereas $Li_4Ti_5O_{12}$ is applied as reference electrode to clearly separate the single electrode's contribution.
Diffusion coefficients and diffusivity of the cathode materials are presented and will be compared with those determined by PITT and GITT.
The advantage of this method is the determination of the diffusion coefficient without being limited to Fickian diffusion, which is the fundamental assumption of PITT and GITT.

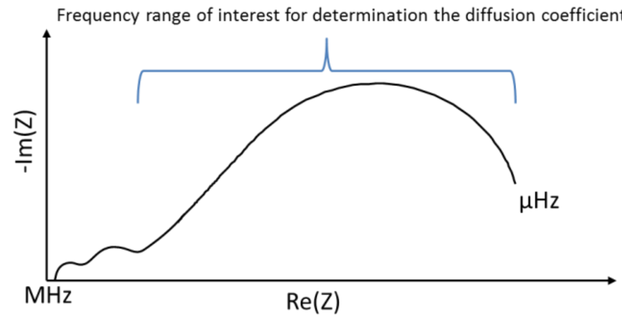

Figure 1: exemplary measured impedance spectrum post processed by subtracting the differential capacity

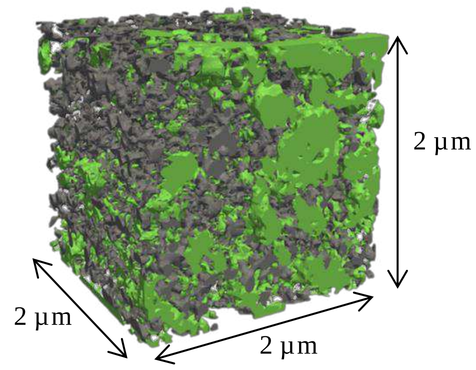

Figure 2: micro structure reconstructions of a $LiFePO_4$ cathode

References

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