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Abstract

Electrochemical impedance spectroscopy for lithium ion batteries has recently gained increasing attention due to its ability of non-invasive evaluation of important electrochemical parameters. Commonly used three-electrode test cells, however, proved unreliable due to asymmetric current line distributions, causing severe distortions of impedance spectra. Finite element method (FEM) simulations can visualize these current lines at different frequencies and simulate impedance spectra at given geometries. By applying FEM simulations to a recently developed coaxial impedance test cell, limiting conditions for reliable impedance measurements could be identified. Using a reference electrode in coaxial position yields sufficiently reliable results as long as the electrode misalignment is small compared to the electrolyte thickness and edge effects are prevented.

1 Introduction

The recent impetus in lithium ion battery research requires a manifold of methods for the analysis of materials, electrodes and electrochemical reactions. Since batteries are rather inaccessible electrochemical systems, non-invasive techniques for in-situ analysis are highly required. Electrochemical impedance spectroscopy (EIS) utilizes the frequency dependent current response of an electrochemical system following a sinusoidal voltage perturbation (or vice versa) to separate physico-chemical processes via their specific relaxation time constants in time domains from 10^{-5} to 10^{3} s.

Electrochemical impedance spectra of two-electrode systems can be easily recorded. These spectra are, however, a sum of the impedance of anode and cathode likewise and not suitable for evaluation and quantification of any reaction mechanism or limitation apart from the electrolyte resistance. Three-electrode systems including a reference electrode are therefore needed to analyse each electrode independently [1]. EIS of three-electrode systems, however, is neither easy to perform nor easy to interpret. First the reference electrode needs to act like a spectator observing a single point in the current line distribution between working and counter electrode without interfering with the aforementioned. Second, the geometry of the used test cell needs to guarantee a frequency-independent distribution of current lines. In other words, the reference electrode should be positioned in such a way that it observes always the same equipotential surface at each frequency, so that changes in the current response can be solely attributed to the voltage perturbation (or vice versa) [2–4].

While these requirements have long been addressed for aqueous electrolytes, it is of special importance for electrolytes with low conductivities and thin geometries such as in solid electrolytes or fuel cells [5–9]. Some cell geometries have been developed for reliable experiments, but even less are suitable for very thin electrolytes as needed in batteries. Among the possible solutions are i) lithium micro-reference electrodes [10,11], ii) reference electrodes located behind the working electrode [12] or iii) the use of symmetric two-electrode cells [13]. These solutions, however, are not convenient for repeated impedance analysis, since they are complicated to assemble or do not allow for regular charge/discharge cycling. To overcome these limitations, we developed a new, easy to assemble, three-electrode test cell with coaxially oriented reference electrodes and tested it using LFP electrodes as model system [14]. It proved to yield reliable results. Scaling effects were successfully removed and inductive loops in the high-frequency domain were limited to above 50 kHz. Nevertheless, it remained

an open question, in how far EIS in this system is still limited by the given geometry and accuracy of electrode alignment.

Finite Element Method (FEM) simulation is a numerical technique to approximately solve partial differential equations in a three-dimensional space by breaking down the space in a finite number of elements. It has been previously used to visualize current distributions during EIS for fuel cells and was recently applied to understand distortions in commonly used Swagelok three-electrode cells [15]. The advantage of FEM is that it can help avoiding numerous electrochemical experiments by systematically changing relevant parameters once a sufficiently accurate model has been identified. It may help revealing experimental weaknesses of specific cell designs, which are otherwise not accessible, since parameters such as charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are difficult to validate and distortions due to geometric effects are hard to separate from those due to energetic distributions.

In this work, we adapted a cell with coaxial geometry [14] as model for FEM studies and identified typical distortions evoking from electrochemical asymmetries, such as differences in C_{dl} and R_{ct} between the working electrode (WE) and counter electrode (CE), as well as from cell misalignments.

2   Experimental

FEM simulations were conducted using Comsol V 4.2a. The cell geometry was taken according to [14], consisting of two opposing annular ring electrodes E1 and E2 with an outer diameter of 12 mm and an inner hole diameter of 2 mm. The reference electrode (RE) was implemented as a 0.5 mm disc-shaped lithium reference electrode, located in a coaxial position inside E1 (**Error! Reference source not found.**a). Electrochemical impedance (EI) spectra of E1 and E2 have been denominated as R-E1-E2 and E2-E1-R, respectively.

The electrode thickness was set to 400 µm, which corresponds to the typical thickness of commercial lithium foil. The electrodes are separated by an electrolyte with a thickness of d_e. The values of d_e were, depending on the parameter set, 400 µm or 25 µm, and approximately corresponding to the thickness of a glass fibre separator used in lab scale tests and commercial PE/PP foil separators (such as Celgard), respectively. The electrolyte conductivity σ_{el} was adjusted to 0.2 Sm^{-1}, which is comparable to a rather poorly conducting electrolyte in a 40 % porosity separator such as 1 M LiPF$_6$ in EC:DEC 1:1 wt.-% electrolyte below 10 °C [16]. For the simulation of electrode misalignment, a shift in electrodes Δx of 200 µm was introduced for some parameter sets.

The electrochemical behaviour was simulated by a simplified Randle circuit (see figure 1b) consisting of a resistor R_{ct} (charge transfer resistance of lithium intercalation) in parallel to a capacitor C_{dl} (capacitance of the electrochemical double-layer). Inductive elements are not considered in the equivalent circuit (EQC). Any inductive behaviour observed in the impedance spectra of our model therefore originates from frequency dependent current line distributions. In another set of parameters, this EQC of the WE was described with a capacitor C_f in series with the resistor (faradaic pseudocapacitance), which represents the limited charge capacity of the active material (see figure 1b). For sake of simplicity, diffusion was not taken into account. Potential and current distributions were computed using a free tetrahedral mesh with a fine mesh around the reference electrode and the inner electrode edges. Impedance spectra were calculated in the frequency spectrum from 100 kHz to 100 mHz, with 10 frequency points per decade in logarithmic spacing. The EI spectra of WE and CE were calculated using the reference electrode, while the full cell impedance spectrum was calculated using a two-electrode setup. As reference, impedance spectra were also calculated from the corresponding EQC using the ZSim module (Bio-Logic EC-lab V10.22) assuming that the current line distribution was ideally independent from frequency. In this case, R_{el} was arbitrarily set to fit the FEM simulation.

3   Results & Discussion

It has been shown by experiment [14] as well as by FEM [15] that distortions of EI spectra typically observed in Swagelok three-electrode test cells can be explained by the frequency-dependent distribution of current lines in the electrolyte. Using optimized cell geometries like the one proposed in [14] these distortions can be substantially decreased. It was, however, an open question if a coaxial arrangement of electrodes yields reliable EI spectra for all relevant types of electrodes when a natural range of misalignment in the cell assembly is taken into account. The answer to this question is also important in addressing concerns on the reproducibility and reliability of experimental data obtained from EIS. Therefore, several sets of geometric and electrochemical parameters were tested to investigate the influence of *i)* geometric asymmetries (i.e. misalignments and/or edge effects), *ii)* electrochemical asymmetries (e.g. varying R_{ct} or C_{dl}), and *iii)* a combination of both asymmetries on (simulated) EI spectra. While electrochemical reactions in a porous battery electrode are difficult to constrain in a mathematical model, the simulation of EIS may be conducted using a much simpler model, since distortions in the spectra can be ascribed to the change of the current line distribution in

the separator. We therefore chose to model the lithium de/insertion by a simplified Randle circuit as described in section 2.

First, EI spectra were simulated for a set of two perfectly aligned and electrochemically identical electrodes, serving as reference point for the later introduction of asymmetries (Set 1, **Error! Reference source not found.**). Second, the same simulation was repeated for two electrochemically symmetric, but misaligned electrodes (Set 2, **Error! Reference source not found.**) and two perfectly aligned but electrochemically asymmetric electrodes (Set 3, **Error! Reference source not found.**). Third, parameter sets for both asymmetries were combined to visualize expected distortions in "real" cell configuration (Set 4, **Error! Reference source not found.**). These sets were also complemented by introducing an edge effect (i.e. electrolyte covering the side surface of electrodes, Set 5, **Error! Reference source not found.**). Last, the EQC was complemented by a capacitor in series with the R_{ct} (pseudocapacitance), resembling the limited charge capacity of electrodes (Set 6, **Error! Reference source not found.**). In all cases, meaningful, but rather exceeding values for electrochemical parameters were chosen. An overview of all parameter sets is given in table 1.

3.1 Electrode alignment & electrolyte thickness

One major problem of commonly used Swagelok cells is that electrodes are not well aligned with respect to each other. This issue has recently been approached by introducing a positioning ring in the test cell, creating an electrode geometry as depicted in **Error! Reference source not found.**a. When a perfect alignment of electrodes is assumed, the electrolyte potential will evenly distribute throughout the electrolyte, leaving an area around the reference electrode which is sufficiently free from changes in the electrolyte potential (**Error! Reference source not found.**a). Simulated impedance spectra of both E1 and E2 will likewise appear as expected, i.e. appear as perfect semi-circles with a diameter of R_{ct} (**Error! Reference source not found.**b). Under such conditions, the influence of the RE position (on the side of WE or CE) is negligible.

In real cells, however, there are always slight shifts, and even in systems with positioning aids, they may occur to a magnitude of 0.1 mm. It can be seen from **Error! Reference source not found.**a that this shift generates a wider distribution of electrolyte potentials in the proximity of the reference electrode. In the case of thick electrolytes such as a glass fibre separator, the shape of simulated EI spectra remains mostly unaffected (below the experimental error of <1 %), resulting only in a shift of the electrolyte resistance (decreasing for E1 and increasing for the E2, **Error! Reference source not**

found.b). By decreasing the thickness of the electrolytefinally to values similar to commercial separators (25 µm, **Error! Reference source not found.**c), the effect of misalignment on the current density distribution becomes stronger resulting in a scaling effect. R_{ct} of E1 appears to be 0.5 Ω (i.e. about 10 %) smaller than its theoretical value, while R_{ct} of E2 appears to be 0.5 Ω larger (**Error! Reference source not found.**d). This effect has previously been described for Swagelok cells and can be attributed to a change of electrolyte resistances between E1/E2 and RE, which is decreasing for E1 and increasing for E2, since the RE is located on the side of the E1. The scaling is about 10 % of the real value, which shows a certain reliability of the cell even with misalignment.

3.2 Difference in electrochemical characteristics

The second major issue in test cells for lithium ion batteries is the obvious difference in the electrochemical behaviour of electrodes. The most common arrangement is probably the half-cell setup, in which a porous WE composed of negative or positive active materials with addition of conductive additives and binder is combined with a metallic lithium CE serving as infinite source of lithium ions. Nevertheless, this combination is probably one of the most difficult in terms of EIS, since the metallic lithium is known to have a large impedance compared to porous electrodes [11]. In addition to this, its surface morphology and surface area is constantly changing depending on formation of dendrites, dissolution and aging. To investigate the influence of the electrochemical parameters, three parameter sets were conceived (see Tab. 1), keeping the thickness of the electrolyte (400 µm) constant. In set 3a, C_{dl} was kept constant and R_{ct} was changed. In set 3b, R_{ct} was kept constant and C_{dl} was decreased. Finally, in set 3c f_r was fixed and R_{ct} and C_{dl} were changed accordingly. **Error! Reference source not found.**a shows an example of potential distribution in the electrode for set 3b. From figure 4b it can be deduced that the parameters influencing the distortion of the semicircle in E1 are due to differences in C_{dl}, which generate the inductive loop and differences in f_r from which the scaling effect derive. The most common case that appears by using metallic lithium as CE is the third one, in which the relaxation frequency does not change too much (resistance increases and capacitance decreases), and therefore inductive loops at high frequency are typically observed in real half-cell setups [14].

3.3 Combination of geometric and electrochemical asymmetries

The most realistic scenario is a combination of both moderate geometrical misalignments caused by

cell assembly and electrochemical asymmetries due to two different electrodes such as the electrode of interest and a lithium foil CE. In the worst case, the electrode of interest has a small R_{ct} compared to the CE. This combination was simulated with set 4. In this case, the simulated EI spectrum highly depends on the electrolyte thickness. For rather thick electrolytes (set 4a), the impedance appears about 0.5 Ω smaller compared to the reference spectrum (**Error! Reference source not found.**b), and therefore yields still acceptable results. For thin electrolytes (set 4b), however, a large difference can be observed: the charge transfer process seems to be composed of two semicircles, giving a highly distorted form of the process (often attributed in real experiments to energetic distributions), and an absolute value of the charge transfer that is more than 10 Ω (double as large as expected).

3.4 Influence of edge effects

When a rather thick metallic lithium foil is used as CE, another effect is observed in the real experiment. In this case, the inner edge of the lithium CE is likely to be in contact with the electrolyte and distortions are observed at high frequencies (above 10 kHz [14]). When the inner edge of the CE was instead covered with an insulating material (realized through a small step in the cell base), these distortions were almost vanishing [14].

The electrolyte being in contact with the electrode edges was accordingly simulated with set 5 (see **Error! Reference source not found.**). Depending on the position of the reference electrode with respect to the working electrode, the effect can appear in three different ways. For E1 (RE on same side), the edge effects appears as an inductive bend of the semicircle in the high frequency region and the semicircle appears smaller than expected. For E2 (RE on opposite side), the electrolyte resistance appeared increased and the semicircle seems to include an additional capacitive loop and appeared larger.

3.5 Influence of equivalent circuit: pseudocapacitance

Active materials for lithium-ion batteries have a limited amount of storage capacity; this phenomenon is represented in the EQC by a faradaic capacitance (i.e. a pseudocapacitance), C_f, in series with the faradaic R_{ct}. Taking into account that most of the tests in research are performed against a metallic lithium foil CE (half-cell configuration), it becomes evident how important it is to understand the distortions arising from coupling of two electrochemically different electrodes, i.e. one with pseudocapacitive behaviour and one with purely faradaic behaviour. As discussed previously, the use

of a thin separator amplifies all distortions rising from misalignment and edge effects, and hence should be avoided in the study of the fundamentals of the reaction mechanism (see paragraph 3.1). For this reason, only thick separators have been taken into consideration in this paragraph.

In absence of any edge effect, an inductive loop is observed at the highest frequencies (figure 7a). This is due to the strong difference in the C_{dl} between the two electrodes as discussed in 3.2. Interestingly, when there is no misalignment between the two electrodes, the EI spectrum shows a slight bending of the capacitive behaviour C_f towards right, resembling a constant phase element and an ideal behaviour of the capacitances at the lowest frequencies. This distortion is due to the strong difference in relaxation frequencies between E1 and E2.

In presence of the edge effect (see figure 7b), the inductive effect remains and additionally the scaling effect is observed with a reduction of the apparent R_{ct} of about 20 %. It has to be pointed out that in the medium frequency range the EI spectrum does not rise straight up but bends towards left. This effect is from time to time observed in experimental data, but was not discussed previously due to the fact that it is restricted to a small frequency range, after which the classic capacitive behaviour is observed. Although the frequency range in which this effect appears is small, it is very important because it seems to be indicative of the edge effect in the most commonly used three-electrode configuration.

4   Conclusions

Recently, we developed a three-electrode test cell with coaxial reference electrode which proved to yield reliable results in EIS experiments, especially in the medium to high frequency region. Using the finite element method, it was possible to identify the range of parameters for which the electrochemical and geometric asymmetries in the cell are not substantially affecting the experimental measurements. The simulated impedance spectra show only small deviations from the corresponding spectrum obtained from the equivalent circuit, when a 400 µm thick electrolyte resembling a glass fibre separator is used (less than 10% error, no distortion in the mechanism evaluation). More severe distortions were observed when a thin electrolyte of 25 µm (such as a Celgard separator) was used for simulation. Inductive loops could be observed when a CE with low double layer capacitance, C_{dl}, was used caused by different relaxation times between the CE and WE. However, only rather small distortions were obtained in this case. Scaling effects were observed from coupling electrodes with very different relaxation frequencies. When the electrodes are not well embedded in the insulation and

the edge surface is wetted by the electrolyte, the so-called edge effect is observed. This is causing severe distortions in terms of scaling effects and inductive loops at high frequency. Finally, when the finite capacity of the active material was taken into account in the EQC by a pseudocapacitance C_f in series with the charge-transfer, the resulting capacitive behaviour in the medium frequency range unexpectedly bended towards left when an edge effect was present. From the FEM simulations it was possible to conclude that the previous experimental observation can be generalized to a wide range of parameters. To steer clear from impedance distortions, misalignments and edge effect should be avoided by taking good care of the electrode cutting and insulation and thin film electrolytes such as foil separators should be avoided if possible.

5   Acknowledgements

6   Glossary

C   capacitor

CE   counter electrode

DEC   diethyl carbonate

E1, E2 electrode 1, 2

EC   ethylene carbonate

EI, EIS electrochemical impedance

EQC   equivalent circuit

FEM   Finite Element Method

LFP   lithium iron phosphate

Li   lithium

LIB   lithium ion battery

PE   polyethylene

PP   polypropylene

R   resistor

RE   reference electrode

WE   working electrode

d_e thickness of electrode

σ_{el} electrolyte conductivity

Δx electrode shift

C_{dl} double layer capacitance

C_f faradaic charge capacity

R_{ct} charge transfer resistance

C_f charge capacity

f_r relaxation frequency

7   References

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Figure captions

Table 1   Parameter sets used for FEM

Fig. 1   a) Geometry of coaxial impedance cell with two opposing annual ring electrodes E1 and E2; grid lines represent FEM tetrahedral mesh; b) equivalent circuits used for FEM simulation

Fig. 2   a) Potential distribution at high frequencies along the cross-section of two perfectly aligned symmetric electrodes; b) FEM simulation of impedance spectra for E1 and E2 and calculated spectrum from equivalent circuit (arbitrary electrolyte resistance)

Fig. 3   Potential distribution at high frequencies and simulated impedance spectra of electrodes E1 and E2, with E1 shifted by 200 µm. a,b) thick separator (400 µm); c,d) thin separator (25 µm)

Fig. 4   a) Example of potential distribution and b) simulated impedance spectrum of aligned but electrically asymmetric electrodes; electric asymmetry was introduced by altering R_{ct}, f_r and/or C_{dl}

Fig. 5   a) Potential distribution and b) simulated impedance spectra of combined geometric and electrical asymmetries (same C_{dl}, different R_{ct} and f_r) in thick and thin electrolytes, respectively

Fig. 6   Influence of edge effects, i.e. when the electrolyte is covering the inner edge of electrodes. a) Example of electrolyte potential distribution and b) simulated impedance spectra for perfectly symmetric electrodes

Fig. 7   Electrode impedance with pseudocapacitance. a) without edge effect; b) including edge effect

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Figure 1

a)

E1

E2

WE - x-shift
asymmetric setup

z-axis

RE

x-axis

Electrolyte

b)

C_{dl}

R_{ct}

C_{dl}

C_f

R_{ct}

Figure 2

Figure 3

a)

RE

E1   E2

b)

Figure 4

a)

b)

Figure 5

a)

b)

E1 5 Ω, 9.65 µF cm⁻², 3 kHz
E2 100 Ω, 9.65 µF cm⁻², 150 Hz
R-E1-E2, d_e=400 µm
R-E1-E2, d_e=25 µm
EQC

Figure 6

a)

RE

E1   E2

aligned

b)

Figure 7