Material and degradation effects in lithium-ion batteries are studied in three-electrode cells using electrochemical impedance spectroscopy. But half-cell impedance spectra are often superimposed by distortions caused by the individual cell arrangement. Finite Element Method simulations of the three-electrode cell were applied to identify and quantify these contributions. This study identified two basic mechanisms: (I) a radially inhomogeneous current distribution originating from geometric asymmetry of the electrodes; and (II) a frequency-dependent inhomogeneous current distribution in the electrolyte caused by an electrochemical asymmetry. Mechanism II is caused by different electrode materials, and enhanced when the electrolyte diameter exceeds those of both working and counter electrode. With the help of the FEM model, we evaluated three-electrode cells featuring different reference electrode geometries: (a) point-like, (b) wire and (c) mesh reference electrode. The results of these FEM simulations are shown as half-cell and full-cell impedance data, disclosing the magnitude of distortions and artifacts for each type of reference electrode geometry. The mesh reference electrode, proposed in literature but not widely adopted, showed the largest potential for error-free impedance spectra. The FEM simulations were supported by experiments, comparing a point-like with a mesh reference electrode in a three-electrode cell (see part II).

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Lithium-ion batteries have become a key technology in our everyday lives, and interest has grown tremendously during the past decade about both the suitability of new materials and the aging behavior of all cell components. The internal cell resistance is an important measure of power capability and state of health (SoH). More details on material characteristics and aging behavior become accessible when the internal cell resistance is measured as a function of the frequency. This method is called electrochemical impedance spectroscopy (EIS) and results in an impedance spectrum that can be difficult to interpret.

The motivation of an impedance spectroscopy study is to quantify ohmic and polarization contributions and to determine in which ways anode and cathode contribute to the cell impedance. The latter is challenging in full-cells, but feasible using symmetrical cells with two nominally identical electrodes. Unfortunately, symmetric cells (a) cannot be cycled for investigating aging behavior, and (b) have to be freshly assembled for each state of charge. Using a three-electrode setup is advantageous. Here a full-cell is continuously cycled while a constant potential is provided by a reference electrode (RE) without any current flow, as schematically shown in Figure 1.

During the EIS measurement a current \( I \) flows between working electrode (WE) and counter electrode (CE). The potential drop between the two electrodes of the full-cell can be measured, as well as the half-cell voltages between WE and RE and between RE and CE. This results in the half-cell impedances, calculated as the ratio of the Fourier transforms of the potential difference \( \tilde{V} \) and the current \( \tilde{I} \):

\[
Z_{WE}(\omega) = \frac{\tilde{V}_{WE-RE}}{\tilde{I}} \quad [1]
\]

\[
Z_{CE}(\omega) = \frac{\tilde{V}_{RE-CE}}{\tilde{I}} \quad [2]
\]

The sum of the half-cell impedances always results in the full-cell impedance, which can also be directly measured between WE and CE. However, the measurement results are only correct when the electrolyte potential at the reference electrode (RE) remains constant. This condition is guaranteed at open-circuit conditions, or when the system under investigation exhibits perfect symmetry. In the case of asymmetry, (either geometrical or electrochemical) the RE potential will change at non-open-circuit conditions. As a matter-of-fact, the experimental realization of three-electrode cells is challenging; measured half-cell impedances are actually error-prone and their interpretation is highly questionable.

In a previous publication we reviewed the frequently used Swagelok T-cells by experiments and finite element method (FEM) simulations. This proved that “perfect” symmetry of working and counter electrodes is of utmost importance, but cannot be reliably put into practice. We pointed out that location and shape of the reference electrode can minimize or fully avoid measurement artifacts.

Meanwhile, the reported effects have also been studied by other groups. In the following, we will therefore focus on publications about different aspects of reference electrodes, published between 2012 and 2016.

Levi et al. confirmed that (a) the Swagelok T-cell with point-like reference is less suitable for faultless impedance measurements, only slightly surpassed by (b) the ring-shaped reference electrode from Hohsen and (c) coin cells with a point-like reference electrode located at the edge of the electrodes. The authors conclude that artifacts arising from arrangements a, b & c are almost unavoidable and they therefore recommend impedance measurements in symmetric two-electrode cells.

On the other hand, three-electrode cells with modifications have also been proposed. Klink et al. describe a Swagelok-type cell with a coaxial 0.5 mm lithium reference electrode. This arrangement is less error-prone, compared to a point reference electrode, as long as the electrodes are precisely aligned, a 400 μm thick glass fiber separator is used, and the lateral electrode surfaces are not wetted by electrolyte.

Delacourt et al. propose a similar coaxial three-electrode arrangement, realized in a coin cell, where the reference electrode was positioned behind a central hole in the counter electrode. They found that it is essential that both working and counter electrode have a central hole to maintain symmetry. Otherwise the resulting radial current toward the center of the counter electrode lead to distorted impedance...
La Mantia et al.13 evaluated LiFePO4 and Li4Ti5O12 coated onto an aluminum mesh as reference electrode in a three-electrode cell. They demonstrated stable cycling results, but no impedance spectra were shown. Hoshii et al.11 assessed the position of a point-like reference electrode using FEM simulations. They observed distortions and inductive loops in the spectra, caused by the electrochemical asymmetry between the working and counter electrode. The best placement for the reference electrode was identified as outside the working and counter electrodes. However, they did not investigate the effect of a geometric asymmetry, which would (in most cases and to the best of our knowledge) disqualify a point-like reference electrode placed outside the working and counter electrodes.

Buenzli et al.12 studied a design with a coaxial reference electrode centered relative to one of the ring-shaped main electrodes. They demonstrated a good cycling stability and minimal effects on the working electrode impedance, as long as the impedance value of the counter electrode is lower than the impedance of the working electrode. With this restriction in place the error mechanism is still active but quite effectively reduced.

Periyapperuma et al.10 used Conflat vacuum fittings to build temperature resistant three-electrode cells. These feature a ring-shaped reference electrode which is supposed to be well suited for polymer electrolyte studies at elevated temperatures. They demonstrated stable cycling results, but no impedance spectra were shown.

For this reason we continued our FEM simulations and experimental studies (reported in Ref. 5), now using three-electrode setups featuring the same cell dimensions as the EL-Cell, then the processing of a reference electrode using an aluminum mesh coated with Li4Ti5O12 powder, and finally the validation of our FEM simulations in terms of experimentally measured half-cell and full-cell impedance spectra.

**Cell Housing and FEM Model**

The three-electrode housing ECC-Ref from EL-Cell15 serves as the basic setup for our investigations. It was chosen because of its larger electrode diameter of 18 mm (compared to standard Swagelok cells), its reproducibility and reliability, and the option to realize different reference electrode geometries.

The FEM model used in this work is similar to the model already used for the investigation of the Swagelok T-cell design.5 It consists of four domains (Figure 1a), the working, counter and reference electrode, connected by the electrolyte phase. The nature of the model is purely electric, reflecting the electric conductivities of the electrodes and the electrolyte, which are coupled through interface impedance expressions. Neither the electrode microstructures nor the electrolyte diffusion processes are covered by the model.

Figure 1 shows a schematic representation of the FEM model as well as the geometry (as implemented in COMSOL Multiphysics 4.3b). In the basic configuration, the working electrode (WE), the counter electrode (CE) and the electrolyte are disc shaped with a diameter of 18 mm. Their respective thicknesses used in the model are 0.1 mm, 0.4 mm and 1.5 mm, approximating the real dimensions of the ECC-Ref housing from EL-Cell. Accordingly, the reference electrode is modeled as a small cylinder, positioned at a height of 0.9 mm above the bottom of the cell sandwich, corresponding to a vertical position at one third of the separator thickness. The diameter of the reference electrode is 0.3 mm and it extends 0.1 mm into the electrolyte, resembling the lithium that is slightly pressed into the separator.

The electrical conductivity of each component was specified (Table I). The lower boundary of the counter electrode was set to ground while a current density was applied to the upper boundary of the working electrode. At the electrode-electrolyte interfaces the coupling was defined specifying a current density. In the case of the working electrode this is

\[ j_{\text{load}} = \frac{(\Phi_{\text{WE}} - \Phi_{\text{EL}})}{Z_{\text{WE}}} \]  

Each electrode can be specified with an arbitrary impedance expression, \( Z_e \), e.g. in the case of the working electrode

\[ Z_{\text{WE}} = \frac{\rho_{\text{WE}}}{1 + i \omega \cdot \rho_{\text{WE}}} + \frac{1}{i \omega \cdot C_{\text{WE}}} \]
with \( p_{WE} \) being the area specific resistance, \( \omega \) the frequency and \( \omega_{WE} \) the characteristic frequency of the resistance contribution. The characteristic frequency \( \omega = 2 \pi \cdot (R \cdot C)^{-1} \) was used here to describe the RC Element instead of the capacity so that the discussion of the different frequency responses of WE and CE becomes easier to follow. For an RC element it describes the frequency where the absolute value of the imaginary part of the impedance is maximal. The second part of the equation represents a capacitive constant phase behavior with \( C_{WE} \) being the corresponding capacity and \( n_{WE} \) the exponent, specifying the slope of the constant phase element. This equivalent circuit model was chosen to represent the main characteristics of the WE impedance, being a polarization process and a capacitive behavior. It is not intended to describe the physical processes and was selected over a Randles model for sake of easier implementation.

For the counter electrode and the reference electrode, a resistor in parallel with a capacitor is used as equivalent circuit model. In case of the CE, this describes electrodeposition at a lithium electrode, which also holds true for point-like lithium metal reference electrodes or lithium coated wire electrodes. As pointed out in the introduction, a Li4Ti5O12 coating will be considered for the mesh reference electrode. Even though the lithium is intercalating into the active material, the potential remains constant due to the two-phase reaction mechanism. This corresponds to an infinite differential capacity. From a simplified system point of view, the Li4Ti5O12 within the two-phase regime behaves like a lithium metal electrode with a different potential. Therefore we use the same equivalent circuit model with just one RC element also for the mesh reference electrode.

The parameters used in the simulations can be found in Table I. The parameter values were chosen to be similar to typical values obtained with commercial electrodes.

All simulations were performed on a quad-core desktop computer with 12 GB of memory. Each simulation consists of 35 stationary simulations in frequency space, covering the range from \( 10^0 \) to \( 10^{-1} \) Hz.

### Basic Mechanisms Leading to Impedance Spectra Distortions

In our earlier work\(^5\) we divided the observed artifacts into two categories, based on the cause of occurrence; either geometrical or electrochemical asymmetry. The mechanisms which lead to the artifacts are later discussed in more detail.

#### Radial current flux (geometric asymmetry).—The first mechanism that causes artifacts in impedance spectra is caused by a radial current flux at the location of the reference electrode and originates from what we called geometric asymmetry in our previous paper.\(^6\) Figure 2 presents two-dimensional simulations to visualize how it occurs. For these simulations, electrochemical symmetry was assumed, resulting in two half-cell impedances of exactly the same size and shape.

For the 2D simulations, an electrode length of 10 mm was assumed, with a 1 mm thick separator. The reference electrode contacts the separator in the middle of its thickness over a length of 0.2 mm. The area specific impedance was set to 10 \( \Omega \cdot cm^2 \) with a characteristic frequency of 1 \( kHz \) for working and counter electrode and to 10 \( \Omega \cdot cm^2 \) with a characteristic frequency of 10 \( kHz \) for the reference electrode. These values have been chosen for demonstrative purposes and do not describe a specific electrode, even though they were chosen to be similar to values observed in measurements. All other parameters and conditions were set as described in Cell housing and FEM model section and Table I. The frequency used for creating the equipotential line plots is 0.1 Hz, unless otherwise noted.

If the working electrode WE, counter electrode CE and electrolyte are equal in length and well-aligned to each other, the equipotential lines within the electrolyte and at the location of the reference electrode are parallel (see Figure 2a).

### Table I. Electrical parameters of the electrodes, the electrolyte and their corresponding interfaces, as used in the basic model. Deviations from these parameters are given for individual simulations.

| parameter | value |
|-----------|-------|
| \( \sigma_{WE} \) | \( 10^3 \text{Sm}^{-1} \) |
| \( \sigma_{CE} \) | \( 10^3 \text{Sm}^{-1} \) |
| \( \sigma_{RE} \) | \( 10^3 \text{Sm}^{-1} \) |
| \( \rho_L \) | \( 1 \text{Sm}^{-1} \) |
| \( \rho_{CE} \) | \( 8 \text{Ωcm}^2 \) |
| \( \rho_{RE} \) | \( 16 \text{Ωcm}^2 \) |
| \( \omega_{WE} \) | \( 10 \text{kHz} \) |
| \( \omega_{CE} \) | \( 1 \text{kHz} \) |
| \( \omega_{RE} \) | \( 10 \text{kHz} \) |
| \( C_{WE} \) | \( 10^8 \text{Fcm}^{-2} \) |
| \( n_{WE} \) | 0.8 |

Figure 2. Simulations of WE and CE with identical electrical parameters (same resistance and characteristic frequencies). If the system is geometrically symmetrical (a) the two half-cell impedances are equivalent. In the case of a geometrical asymmetry (one electrode 0.5 mm smaller than the other) (b, c) the current density in the electrolyte exhibits a radial component at the location of the reference electrode. This results in a transfer of a fraction of the impedance from one electrode to the other (scaling effect).
The simulation parameters are the same as in Radial current flux (geometric asymmetry) section, except that the characteristic frequencies are now chosen to be 100 Hz for the working electrode, 10 kHz for the counter electrode and 1 kHz for the reference electrode.

If the geometrical conditions are ideal (same sizes for working electrode, counter electrode and separator, all being perfectly aligned), no distortion of the half-cell impedances can be observed (Figure 3a). Luckily, this means that an electrochemical asymmetry arising from differing electrode materials is not an intrinsic problem. But as soon as the separator disc soaked with liquid electrolyte is larger than the investigated electrodes, it becomes problematic. In this case the equipotential lines encroach and bend into the overlapping part of the electrolyte, indicating an inhomogeneous current density (Figure 3b). Moreover, the actual current density within this part of the electrolyte is determined by the interface impedances of counter and working electrode, which are frequency dependent. This leads to the shape of the equipotential lines being frequency dependent, and with this to a frequency dependent reference electrode potential (for more details see the next paragraph and Figure 4). Thus, the frequency dependent part of the electrolyte potential drop increases the measured impedances of the working or counter electrode. Therefore, this type of distortion/artifact scales with the electrolyte resistance. Figures 3b and 3c show the same geometric arrangement but with an electrolyte resistance differing by a factor of three (conductivity 1.0 and 0.33 Sm^{-1}). The artifacts in Figure 3c preserve their shape while being a factor of three larger, which is proportional to the ohmic part of the full-cell impedance.

Figure 4 shows a visualization of the equipotential lines from the simulation shown in Figure 3b. At low frequencies (almost DC conditions) the equivalent polarization of counter and working electrode results in the equipotential lines showing a symmetric shape (Figure 4a). With increasing frequency, the central equipotential line bends toward the counter electrode, resulting in a maximally-asymmetric shape at around 1 kHz (Figure 4b). With further increasing frequency, the central equipotential line shifts back toward the reference electrode (Figure 4c). This behavior results in a frequency dependent reference electrode potential, as shown in Figure 4d. The plotted potential is calculated as the difference between the hypothetical lithium RE and lithium CE, which was defined to be at 0 V. At high frequencies it shows the expected behavior of a potential shift at around 10^{6} Hz, originating from the increase of the counter electrode impedance. The distortion of the equipotential lines at around 10^{5} Hz leads to an overshoot of the potential (highlighted with a red ellipse) before it approaches its low frequency limit.

The FEM simulations have proven that geometrical and electrochemical asymmetries cause distortions in the half-cell impedances of three-electrode setups. In both cases the equipotential lines in the electrolyte were no longer in parallel orientation toward the position of the reference electrode, which is located at the outer rim of the electrodes. The two basic mechanisms are (1) a transverse current at the position of the reference electrode, which causes distortions ascribed to geometrical asymmetry, and (2) a frequency dependent inhomogeneity in the current density at the position of the reference electrode, which causes distortions ascribed to electrochemical asymmetry.

Keeping the two basic mechanisms in mind, reference electrodes differing in shape and location will be assessed in the next section.

Assessment of Different Reference Electrode Designs

Three different reference electrode geometries will be compared in the following sections: a point-like reference, as used in the standard EL-Cell ECC-Ref housing (Figure 5a), a wire reference electrode (Figure 5b) and a mesh reference electrode (Figure 5c). The three geometries were chosen because all of them can be realized in the EL-Cell ECC-Ref housing. Furthermore, no additional preparation is necessary, like cutting a concentric hole in one or both of working and counter electrode, promising easier and less error-prone cell assembly.
Figure 4. Visualization of the equipotential lines (a-c) for different frequencies with the central equipotential line highlighted in red. If the reference electrode potential (electrolyte potential at the position of the reference electrode) is plotted versus the frequency (d) it shows the expected behavior around $10^4 \text{Hz}$ originating from the increase of the counter electrode impedance. In addition, an overshoot (red ellipse) of the potential can be seen around $10^3 \text{Hz}$ caused by the frequency dependent potential distortion.

Figure 5. Visualization of three different reference electrode geometries: point-like reference (a), wire reference (b) and a mesh reference (c).

For the FEM simulations, the reference electrode is assumed to be electrochemically active with an area-specific impedance, similar to working and counter electrode. Due to the smaller surface, the absolute reference electrode impedance is, of course, much higher (approx. $15 \, k\Omega$ for the point-like reference). The topic of choosing a suitable reference electrode material is not covered here but is covered in the second part of the paper (part II).

Since a three-electrode system is commonly used to study real electrochemical cells, where we can almost never find identical electrodes, we neglect the electrochemically symmetric case from this point onwards and start with different electrochemical parameters for working and counter electrode. The parameters are listed in Table I whereas the working electrode exhibits a capacitive behavior in addition to the polarization process.

Point-like reference electrode.— In an ideal case there would be no geometric asymmetry between the counter and working electrodes. This means that the separator would be exactly the same size as the two electrodes, and all would be perfectly aligned. Remembering our discussion on the causes of artifacts in Basic mechanisms leading to impedance spectra distortions section, neither a radial current component nor current inhomogeneity at the rim of the electrodes is expected. Therefore, there should be no distortion of the half-cell impedances, which is proven by the simulation shown in Figure 6a.

In reality, it is almost impossible to have the working and counter electrodes perfectly aligned and of identical dimensions, especially when a metallic lithium counter electrode is used. Metallic lithium often sticks in the cell housing, so the counter electrode is usually punched-out with a slightly smaller diameter to enable easier assembly and to reduce the risk of short circuits. By doing so, we knowingly introduce a geometric asymmetry, as well as an additional degree of freedom. Depending on the cell design, the lithium counter electrode is sometimes punched with a larger diameter than the working electrode. Since the basic argumentation in terms of geometrical asymmetry remains the same, we focus here on discussing smaller diameters, as it is typical for the considered cell housings.

As shown in Figure 6b, even a well-aligned counter electrode with a diameter of 17.5 mm leads to artifacts caused by a combination of electrochemical and geometrical asymmetry. This worsens if the counter electrode is shifted away from the reference electrode by 0.25 mm (Figure 6c), which corresponds to the worst case of geometric asymmetry in this configuration.

Even if both electrodes are punched with the same diameter (17.5 mm) and are perfectly, coaxially aligned, the inhomogeneous current in the separator results in half-cell impedance distortions (Figure 6d), originating from the electrochemical asymmetry. Due to the changes in active electrode areas, the impedances change slightly, which can be observed best at the low frequency end of the full-cell impedances. Since the values are plotted as area specific values, the corresponding active surface of the working electrode was used for the calculation in all four cases.

Even though the ideal setup (Figure 6a) works well in simulations, it is virtually impossible to reliably control electrode alignment to a...
finer degree than 0.25 mm (as everyone who has ever been assembling a cell in a glove box knows). Additionally, the soft and sticky nature of metallic lithium makes it impossible to prepare a lithium electrode with a neat edge, which shows no electrochemical activity at the electrode’s outer rim. These round edges can even worsen the inhomogeneous and radial current density, amplifying the impedance distortions.

**Wire reference electrode.**—If we extend the point-like reference electrode until it ends at the center of the electrolyte, we have a reference electrode wire. It has the same diameter of 0.3 mm as the point-like reference electrode and a length of 9 mm. With the reference electrode’s increase in active area, fewer edge-effects are expected. Thus we start with a wire, where the whole surface is electrochemically active. Additionally, this case is the easiest to realize.

In the case of a symmetric setup (Figure 7a), no impedance distortions are observed in the simulation. Again, if the counter electrode is smaller than the working electrode, the distortions observed for the point-like reference electrode are reduced to a minimum for the wire reference electrode (Figure 7b). Even if the counter electrode is additionally shifted, the impedance distortions are negligible (Figure 7c).

To test the case of an insulated wire reference (where only the tip of the wire is electrochemically active), the lateral surface is set to insulating boundary conditions. This corresponds to a point-like reference electrode positioned at the axis of the cell sandwich. Again, the half-cell impedance distortions are only negligible. The difference in the appearance of the small artifacts in Figures 7c and 7d can be explained by a contribution from geometric asymmetry when the whole wire is active, which is missing if only the tip is active.

Overall, the simulations with a wire reference electrode yield promising results. Before we discuss how such a system can be realized, the simulations for a mesh reference are presented.

**Mesh reference electrode.**—When simulating the mesh reference electrode, the point-like or wire reference electrode was replaced by a mesh at the same vertical position. The working and counter electrode parameters were again kept constant, as well as the electrolyte thickness.

Two different mesh geometries were considered for the simulations. The first one is a thick and dense mesh shown in Figure 8a, with a wire thickness of 0.2 mm and gap-width of 0.5 mm. In this case the open area of the mesh is 51%. The specific charge transfer resistance at the mesh surface was set as 10 Ω cm² with a characteristic frequency of 10 kHz.

The impedance simulation of this mesh geometry when symmetrically aligned shows an additional high frequency semi-circle originating from the reference electrode impedance (Figure 9a). This represents a fundamental difference to the other reference electrode geometries, where the reference electrode impedance does not matter. The reference electrode impedance contribution, which is also present in the full-cell impedance, exists because of two parallel current paths. The ions can either travel in the electrolyte through the openings of the mesh, or there could be oxidation and reduction reactions at the two sides of the mesh. Although there are electrochemical reactions at the reference electrode, since we are only looking at periodic current
Figure 7. Simulations of different wire reference electrode assemblies. All simulations have identical electrical parameters, differing only in their geometrical setup: (a) WE, CE and separator are exactly the same size 18 mm in diameter, (b) CE with a diameter of 17.5 mm, (c) CE with a diameter of 17.5 mm and an additional shift of 0.25 mm away from the reference electrode and (d) the same as before, but only the tip of the wire reference is electrochemically active.

signals here, there is no problem with a polarization between the two sides of the mesh.

Simplified, the impedance contribution of the mesh and the electrolyte in the pores can be written as

$$Z_{\text{mesh}} = \left[ \left( \frac{R_{CT}}{1 + i\tau_\omega} \right)^{-1} + R_{EL}^{-1} \right]^{-1} = \frac{R_{CT}R_{EL}}{R_{CT} + R_{EL}} \frac{1}{1 + i\omega \tau_{REL}}$$

if the electronic conductivity of the mesh is assumed to be much higher than the electrolyte conductivity. $R_{CT}$ is the charge transfer resistance of the mesh (sum of upper and lower side), while $\tau$ is its characteristic time constant. $R_{EL}$ is the impedance contribution of the electrolyte inside the openings of the mesh. In the second form of the equation one can see that it still represents a RC element. The magnitude of this impedance contribution can be reduced by reducing the electrolyte resistance in the mesh openings, $R_{EL}$. The time constant can be shifted to smaller values (higher frequencies) if $R_{EL}$ is reduced or if $R_{CT}$ is increased.

To realize both, we can reduce the mesh thickness and therefore the wire thickness to 0.1 mm and increasing the gap-width to 1 mm (Figure 8b). This geometry, which we call a thin and sparse mesh in the following, reduces the electrolyte resistance (82% open area) and decreases the mesh surface, leading to a higher charge transfer resistance. In the simulation we can additionally set the area specific charge transfer resistance to 100 $\Omega$ cm$^{-2}$, which further increases the effect.

With these measures, the mesh impedance was reduced and its characteristic frequency shifted to above 1 MHz. Therefore, only the impedance contributions of working and counter electrode are visible.

Figure 8. Geometries used for the mesh reference electrode simulations shown in Figure 9, with the reference electrode highlighted in red. The first thick and dense mesh (a) was only used for the first simulation to demonstrate the effect of an overly dense and thick mesh. The second thin and sparse mesh (b) was used for all other mesh reference electrode simulations.
in the simulated impedance spectra (Figure 9b). The electrical and geometrical parameters of the reference electrode were kept constant for the following simulations.

In the case where the counter electrode has a diameter of 17.5 mm (Figure 9c), there is, again, no visible distortion of the half-cell impedances. If the counter electrode is additionally shifted by 0.25 mm, the size of the half-cell impedances is still the same, showing only negligible distortions (similar to the case of the wire reference electrode).

Overall, the mesh reference electrode simulation results look good, as long as two conditions are fulfilled: (I) the mesh used as a reference electrode must be thin, with a large opening ratio. (II) The reference electrode impedance must not be too low, in order to prevent a considerable amount of current taking the path with the oxidation and reduction reaction.

**Discussion**

Understanding the mechanisms that lead to artifacts in impedance spectra, as obtained by the simulations in Basic mechanisms leading to impedance spectra distortions section, makes it clear that it is practically impossible to realize a point-like reference electrode. Additionally, the extremely small active surface of such a reference makes it prone to contact problems or to drying-up in the case of insufficient electrolyte. To prevent these problems wire-like and mesh electrodes were investigated.

The wire-like reference electrode showed very promising behavior in the simulations. Its disadvantage is the resulting inhomogeneity of the setup. The finite thickness of the wire either leads to a deformation of the electrodes or to a locally stronger compression of the separators. Furthermore, a thin wire is very flexible, resulting in possible alignment difficulties between the two separators.

In the case of the mesh reference electrode, an additional polarization process appears in the cell impedance spectrum, originating from the additional current pathway through the mesh. Fortunately both magnitude and characteristic frequency can be influenced by appropriately selecting the mesh parameters. By doing so this additional process should not disturb the measurements (in most cases). With respect to experimental realization, the mesh reference has the advantage of constant thickness and much easier handling compared to the wire reference electrode. The above-mentioned additional current pathway leads to lithiation and delithiation on the opposing sides of the reference mesh, which is not a problem for impedance spectroscopy (AC conditions) or OCV measurements.

Based on this deeper understanding of the relationship between reference electrode geometry and impedance artifacts, two other three-electrode setups are briefly discussed: the coaxial setup recently proposed in Ref. 7 and a ring-shaped reference electrode (as in the Hohsen® cell, investigated in Ref. 6).

In the co-axial setup the current paths within the central channel between the electrodes also depend on the interface impedances. Therefore, artifacts originating from an electrochemical asymmetry can also be expected in this setup. Furthermore, if the two holes in the electrodes are not perfectly aligned there is a current flow across this central hole, leading to a shift of the reference electrode potential

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Figure 9. Simulations of different mesh reference electrode assemblies. All simulations have identical electrical parameters for working and counter electrode, differing only in their geometrical setup: (a) WE, CE and separator are exactly the same size but with the thick and dense mesh and a low impedance, (b) same setup as before but with the thin and sparse mesh with a higher impedance, (c) thin and sparse mesh and a CE with a diameter of 17.5 mm, (d) thin and sparse mesh and a CE with a diameter of 17.5 mm, shifted 0.25 mm relative to the WE (away from the reference electrode).
and thus to impedance distortions, as Klink et al. have shown in their investigations.

A ring-shaped reference electrode can only be realized with a separator larger than the two electrodes. Thus there will always be artifacts caused by electrochemical asymmetries, where their magnitudes depend on electrolyte resistance. For geometric asymmetry two cases have to be distinguished for this setup:

Firstly, if working and counter electrodes are not of the same size, there is a radial current at the location of the reference electrode. This is basically the same case as discussed before for the point-like reference electrode, resulting in impedance distortions.

Secondly, if the two electrodes are shifted relative to each other, one part of the ring is closer to the working electrode while the other part is closer to the counter electrode. This leads to an asymmetry that is contrary to the halves of the reference electrode, resulting in a current through the reference electrode. Unfortunately, the effects do not cancel each other out, so in the end there are still artifacts in the half-cell spectra.

It is worth noting that the ring-shaped reference electrode recently introduced by EL-Cell in their PAT series partially prevents these problems. They use a Freudenberg Viledon FS 3005–25 separator with a thickness of 25 μm. For use in impedance measurements they suggest additional glass fiber separators on both sides of the Freudenberg separator. By doing so, the inhomogeneous current distribution leading to electrochemical asymmetry effects should be confined to a very small region of the Freudenberg separator and should be barely influenced by the interface resistances. Simultaneously, the distance between the two electrodes is increased, so the relative influence of geometric asymmetry should also decrease.

Conclusions

Three-electrode cells can separate the total cell impedance into two half-cell impedances by using the third electrode as a potential reference. The reference electrode can be a point-like, wire or mesh electrode. The design and placement of such reference electrodes were studied using FEM simulations, which disclosed two fundamental effects causing distortions and artifacts in half-cell impedance spectra:

- The effect of a radial electrolyte current density at the location of the reference electrode, caused by geometric asymmetry. The geometric asymmetry arises from differently sized electrodes or a shift of the electrodes relative to each other.
- The effect of an inhomogeneous current density within the electrolyte. Occurrence of this effect is restricted to the case where the diameter of the separator (soaked with electrolyte) exceeds at least one of those of the two electrodes. Since the interface resistances at anode and cathode change with frequency, the current distribution within the portion of the electrolyte that exceeds the electrode diameter(s) varies as well, leading to a frequency-dependent shift of the reference electrode potential.

FEM simulations show these different types of distortion effects in half-cell impedance spectra, which manifest themselves as (a) change in the size of the impedance contributions, (b) distortions of the semicircles, (c) appearance of additional processes or (d) appearance of inductive loops.

With the help of these FEM simulations, the three reference electrode types were ranked according to their suitability for delivering reliable half-cell impedance spectra. While it is almost impossible to avoid the setup imperfections for a point-like reference electrode (which lead to all types of artifacts) these effects are less significant with the rarely used wire-like reference electrode. Finally, the negative influences can be almost completely eliminated with the newly-introduced mesh geometry, where the mesh should be as thin and sparse as possible.

For the experimental study, the three-electrode housing from EL-Cell was selected to realize the point-like reference electrode setup. The mesh reference electrode setup is realized in an in-house developed cell housing. This work is presented in the part II of this paper.

Furthermore, a discussion of Li4Ti5O12 as reference electrode material and the fabrication of the mesh reference electrode are provided, since a mesh structure cannot be made of pure lithium.

List of Symbols

AC alternating current
CE counter electrode
C, capacity
DC direct current
EIS electrochemical impedance spectroscopy
FEM finite element method
j current density
LiFePO4 Lithium iron phosphate
Li4Ti5O12 Lithium Titanate Oxide
OCV open circuit voltage
RC parallel circuit of resistor and capacitor
RT charge transfer resistance
REL resistance of the electrolyte
RE reference electrode
SoH state of health
WE working electrode
Zmesh impedance contribution of the mesh

Greek

ρ, area specific resistance
ω, characteristic frequency

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