Detection of Binder Gradients Using Impedance Spectroscopy and Their Influence on the Tortuosity of Li-Ion Battery Graphite Electrodes

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Drying battery electrodes at high rates leads to binder migration and has shown to affect the mechanical as well as the electrochemical properties of Li-ion battery electrodes. Up to now, little evidence has been shown as to why the performance suffers. Here, we investigate the influence of an inhomogeneous binder distribution on the total ionic resistance within an electrode. First, we model the impact that vertical inhomogeneities have on the impedance spectrum and the total resistance of an RC (resistor, capacitor) transmission line model. We show how different resistance profiles lead to characteristic changes in the impedance spectrum, in phase angle and magnitude, with high resistances close to the separator leading to a significantly increased overall resistance. We then show energy dispersive X-ray spectroscopy cross section data for electrodes dried at different temperatures and give experimental evidence for the formation and extent of the binder gradients. These electrodes are then measured using blocking electrolyte electrochemical impedance spectroscopy in a symmetric cell setup. It is demonstrated that, depending on the extent of the binder gradient, the phase angle changes and that just from impedance data one can detect binder gradients qualitatively without the need for other time-consuming analysis methods.

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Understanding the influence of process parameters during Li-ion battery production on the electrode properties plays a pivotal role in the upscaling process from lab-scale electrodes to commercial-scale cells. The electrode film drying rate plays a vital role in electrode production, as it not only influences the cost of production but also the mechanical, electrical, and electrochemical properties of the electrode.1–5 Jaiser et al.5 investigated the adhesion and the rate capability of slow and fast dried graphite electrodes, showing that a faster drying process is detrimental for both adhesion and rate capability. Using energy dispersive X-ray spectroscopy (EDS), they show that when they apply higher drying rates, the polyvinylidene fluoride (PVDF) binder migrates toward the top of the electrode (i.e., toward the surface which constitutes the electrode/separator interface in an assembled cell). Their drying process was conducted at constant drying temperature (76.5 °C) but at different ventilation speeds, highlighting that the observed binder migration is not an effect of temperature but rather of the overall drying rate. A more detailed study on the extent of binder gradients across the electrode thickness vs. drying rate was presented by Müller et al.7 based on EDS cross-sections of graphite anodes dried at different rates.

To understand the binder migration process, experimental as well as modelling approaches are discussed in the literature.6–9 Hagiwara et al.9 and Jaiser et al.7 froze samples at different stages of the drying process and analyzed the composition of the electrode cross section. Hagiwara et al.6 used Raman spectroscopy to determine the styrene-butadiene rubber (SBR)-distribution in water based graphite anodes. Their results showed that the binder gradient formation (i.e., strong enrichment of the binder at the free electrode surface) occurred at late stages of the drying process, i.e., when most of the water (>80%) had already evaporated. On the other hand, while Jaiser et al.7 found a similar surface segregation of the binder upon drying of NMP based slurries of graphite and PVDF binder, they observed the formation of a binder gradient already at early stages of the drying process, initiating once only 14% of the solvent were evaporated.

As a result of the binder migrating away from the region of the electrode near the current collector (CC), the adhesion of the electrode was found to be reduced.13 The loss in the rate performance of graphite anodes due to binder segregation to the free electrode surface was speculated to be due to the more extensive coverage of the graphite particles near the free electrode surface by the segregated binder, thereby increasing the resistance to Li-ion intercalation; as an alternative hypothesis, the authors also suggested that the simultaneous segregation of the conductive carbon to the free surface would lead to a high electrical resistance near the current collector, even though this seems unlikely in the case of graphite electrodes.1 Ultimately, however, neither one of these hypotheses could be proven. A yet different hypothesis for the effect of binder gradients is that they influence the tortuosity of the electrode, i.e., that a binder-rich surface region might result in a high ionic resistance in the electrolyte phase near the electrode/separator interface. This is suggested by the recently observed strong effect of the type of binder on the tortuosity of graphite electrodes (quantified by AC impedance), even at low binder contents (≤5% by weight), whereby electrodes with a high tortuosity exhibited poor rate capability.10

To investigate the latter hypothesis, this work examines the influence of ionic resistivity gradients in the electrolyte phase normal to the electrode surface on the modeled electrochemical impedance spectroscopy (EIS) response, and compares it to the experimentally obtained EIS response of electrodes which exhibit binder gradients normal to the electrode surface. While inhomogeneities of the ionic resistance across the thickness of a porous electrode have been analyzed analytically in the past using a transmission line model, this phenomenon was not correlated at that time to binder migration induced by the drying of electrode ink coatings.11–13 We therefore focus in our study on the effect of various ionic resistance distribution patterns across the thickness of a porous electrode on the modeled EIS response, and compare them with the experimental EIS response of graphite electrodes dried at different temperatures. The resulting PVDF binder gradients will be determined experimentally by EDS analysis of resin embedded and polished electrode cross-sections. Lastly, we will show the impact of binder gradients on the rate performance of graphite anodes in half-cells with a lithium reference electrode.

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Experimental

Impedance modelling.— An impedance model was built in COMSOL Multiphysics, using the included battery and fuel cell module which is based on the Newman model. A 2D representation of two identical porous electrodes is used to mimic the experimental setup for symmetric cell EIS measurements (see below), even though a 1D representation would also be sufficient for the here pursued modelling approach. If not stated otherwise, the parameters described below are chosen arbitrarily, as the qualitative model results are independent of the chosen double layer capacity, electrode surface area, and geometry. The electrode dimensions were chosen to be 50 μm × 260 μm (width × thickness). The electrolyte bulk conductivity was set to 0.258 mS/cm, corresponding to the experimentally chosen electrolyte (see below), and the electrical conductivity of the solid phase was set to 10 S/cm, which is in the range of typically found values for graphite electrodes. With this low ratio of electronic to ionic resistance in the electrolyte phase of the porous electrode (the latter being lower than the bulk conductivity due to electrode porosity and tortuosity), the resistance of the electronic path in the transmission line model becomes negligible, so that the changes in the EIS response depend solely on changes in the ionic resistance. The electrode porosity, was set to 55% and was considered uniform throughout the electrode, as the volume fraction of the binder for application relevant electrodes is generally negligible. This entails that the specific surface area of the graphite active material is also uniform throughout the thickness of the electrode. The separator thickness was set to 50 μm, and its porosity and tortuosity was set to one, as their value will only affect the high frequency resistance and not the shape of the observed transmission line model EIS response. For our reference case without binder gradient, the tortuosity was set at 5, which is a commonly observed value for graphite active materials.

In the COMSOL modelling framework, faradaic reactions were disabled, leaving only the double layer capacity at the surface of the spherical particles (set to the default settings of c_{dl} = 0.2 F/m^2 and a graphite particle radius of 10 μm; approximated specific surface area (particle surface area per electrode volume) a_{dl} = 3 × (1 - ε) r_p = 1.35 × 10^4 m^2/m^3) as current sink/source. This represents the behavior of a graphite electrode in a so-called “blocking electrolyte”, which is composed of ions which do not intercalate into graphite. The ionic resistance within the porous electrodes (i.e., the tortuosity, since the porosity was set constant) was then varied linearly or stepwise as described later on. A harmonic perturbation of 20 mV was used in a resistance within the porous electrodes (i.e., the tortuosity, since the

Slurry preparation and drying.—Graphite (T311, Timcal, 19 μm D50, 3 m²/g) and polymer binder (polyvinylidene fluoride (PVDF), Arkema) at a ratio of 95:5 (wt:wt) were mixed with N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, anhydrous, 99.95%) at a solid:liquid ratio of 5:4 (wt:wt) in a planetary mixer (Thinky ARV-310) at 2000 rpm for five minutes. The prepared graphite slurries were coated onto a copper current collector foil (MTI, 12 μm) attached to a glass plate using a gap bar coater (RK PrintCoat Instruments, UK). The wet film thickness was either 150 μm for electrodes used for rate performance tests or 500 μm for EIS and EDS analysis; the resulting thicker electrodes for the latter was used to allow a better quantification of the binder gradients by EDS.

Electrode drying was performed using an infrared (IR) lamp (IH2000IR, ELV electronics, Germany, 1300 W) mounted in a fume hood. An aluminum plate was placed below the IR-lamp, and the temperature was controlled by the distance between the lamp and plate. The temperature was measured by a thermocouple placed on top of the aluminum plate after temperature equilibration, and the glass plate with the freshly coated electrode was then placed onto the aluminum plate until the coating was dry. The time until the coating was visually observed to be dry was ~2 min for the aluminum plate heated to 125 °C (28 cm distance to lamp), ~7 min when heated to 100 °C (41 cm distance to lamp), ~18 min when heated to 75 °C (63 cm distance to lamp), ~90 min when heated to 50 °C (91 cm distance to lamp), and several hours for the room temperature (RT) dried sample (lamp turned off). For electrodes used for EDS measurements and EIS analysis, the thickness of the dried electrodes was ~245 μm (±6%), corresponding to graphite loadings of ~25.5 mg/cm² (±6%); for the rate capability tests, the thickness of the dried electrodes was ~74 μm (±2%), corresponding to graphite loadings of ~7.4 mg/cm² (±2%) with a capacity of ~2.4 mAh/cm² (calculated for a theoretical graphite capacity of 350 mAh/g). The electrodes were not further compressed/calendered, and their porosity was ~55% (based on thickness and areal weight measurements). The dried electrodes were punched out to a diameter of 10.95 mm (equating to an area of ~0.94 cm²) using an electrode punch (Hosken Corp. OSAKA, Japan).

Tortuosity determination.—The impedance measurements for the determination of the electrodes’ tortuosity were performed at 25 °C in a symmetric cell setup (T-cells; two electrode configuration; measured at open circuit voltage) using 100 μL of a non-intercalating electrolyte as described previously, viz., a 3:7 (wt:wt) mixture of ethylene carbonate (EC, BASF, anhydrous, 99.99%) and ethyl methyl carbonate (EMC, BASF, anhydrous, 99.99%) containing ~10 mM tetrabutylammonium perchlorate (TBAClO₄, Sigma Aldrich, ≥99.0%). The conductivity was measured using a conductivity sensor (SI-Analytics, LF 1100 T+) to be 0.258 mS/cm at 25 °C.

SEM/EDS.—Cross-sectional EDS mapping was conducted with the above described thick electrodes. The current collector was manually peeled off the electrodes, taking care not to damage the electrode (easily possible for such thick electrodes), followed by placing each of them between two aluminum plates (1 × 1 × 0.1 cm) and fully immersing the stacked up electrode into a liquid resin (EpoThin 2, BUEHLER, USA). With the resin still liquid, the sample stack was placed into a desiccator, which was then evacuated to ensure complete filling of the pores by the resin. After the resin had hardened, the sample stack was polished with SiC paper (CarbMet S, P320, Buehler Ltd.) until the electrode cross section was fully exposed. Afterwards the electrode was polished using a finer SiC paper (CarbMet S, P1200, Buehler Ltd.) and lastly with a diamond solution (MetadSi Supreme, Polycrystalline Diamond Suspension, 9 μm, Buehler Ltd.) applied onto a micro cloth (TexMet C, Buehler Ltd.). Elemental analysis was performed using a JCM-6000 (JEOL, Japan) scanning electron microscope (SEM), imaging an area of ~600 × 300 μm². Fig. 1 shows an optical microscope image of polished electrode cross sections, embedded in resin and mounted between aluminum sheets. For a better quantification of the EDS data, the signal from each electrode sample was split into five segments of equal length (i.e., five horizontally aligned segments in Fig. 1, representing the top, the bottom, and three middle sections across the electrode thickness), determining the average fluorescence concentration in each segment. The background correction was done by taking the spectrum signal for the entire measured electrode area (separately for each electrode) and subtracting one fifth of the total background signal from the five individual segments, as the software did not allow to reliably correct the background for the five individual segments separately.

Rate capability test.—For electrochemical analysis, rate tests were performed using a three-electrode cell setup (Swagelok T-cell) with a Li-metal reference electrode (described in more detail in Fig. 1a in Ref. 19). The cells were built inside an argon filled glove box (MBraun, 25 C ± 1 C, oxygen and water content < 0.1 ppm, Ar 5.0, Westfalen). The cells were assembled with a graphite working-electrode (areal capacity ~2.4 mAh/cm²), a Li-metal counter-electrode (0.45 mm
thick and 11 mm diameter, Rockwood Lithium), and two porous glass fiber separators with a diameter of 11 mm (VWR, 250 μm uncompressed thickness, 90% porosity).

All cell parts were dried at 120 °C in a vacuum oven (Büchi, Switzerland) for 8 h before being transferred into an Ar-filled glove box. 80 μL of LP57 electrolyte (1 M LiPF₆ in EC:EMC 3:7 (w/w), battery grade, BASF) were added to the main compartment and 50 μL were added to the reference electrode compartment. Using a potentiostat (Maccor, Cambridge (UK)) the cells were cycled in a temperature-controlled chamber (25 °C, Binder) between 0.01–1.5 V vs. Li⁺/Li, controlled and measured against the Li-metal reference electrode. The cycling protocol started with a 3 h open circuit voltage phase to allow for complete wetting of the electrodes. Lithiation of the graphite working-electrode was performed galvanostatically (CC lithiation) without any preceding formation cycles at various C-rates: first 4 cycles at C/10, followed by five cycles each at C/5, 1 C, 1.5 C, 2 C, 2.5 C, 3 C, 5 C, and 10 C; on the other hand, delithiation cycles were measured and the plotted values represent the average and the standard deviation of the measured capacities (note that this procedure is very similar but not identical to that described previously by our group).¹⁰

Results and Discussion

**Modeled EIS response of porous electrodes with different R_{ion} profiles.**—To examine numerically how the EIS response of a porous electrode is affected by gradients in the ionic resistance in the electrolyte phase (R_{ion}), which we hypothesize to be caused by binder segregation during the drying process, we will be considering the five different R_{ion} distributions across the thickness of a porous electrode shown in Fig. 3 (note that the total ionic resistance across the entire electrode thickness is equal in all cases). Their EIS response in a blocking electrolyte is then calculated based on a simplified transmission line model (TLM) using RC elements, R representing infinitesimal elements of R_{ion} and C the double-layer capacitance of the graphite electrode, shown exemplary in Fig. 2a without resistance gradient and Fig. 2b with gradient. As stated above, the electronic resistance contribution in this RC-TLM can be neglected (discussed in detail in Ref. 17).

In modelling the EIS response, the selected ionic resistance value (on the order of R_{ion} = 1 kΩ cm²) is representative of what we obtained for our thick electrodes in the blocking electrolyte. However, the imaginary and real resistances in the shown Nyquist plots were normalized by (R_{ion}/1.5), so that they are more generally applicable, i.e., so that the Nyquist plots would look identical for electrodes with different average R_{ion} values. The frequency range needed to probe across the entire electrode thickness will be different for different electrodes, since it depends on the double-layer capacity and the ionic resistance of the electrode, so that the modeled Bode plots are specific to a given modeled electrode. The qualitative features of the Bode plots, however, are independent of these values, as long as the above-mentioned condition of low electronic resistance compared to ionic resistance is fulfilled.

Figs. 4a and 4b show the Nyquist and the phase angle plots for the EIS response of electrodes with different R_{ion} profiles. The modeled RC-TLM impedance response for a homogeneous R_{ion} profile (see black curve labeled ng (“no gradient”) in Fig. 3.), subsequently referred to as reference case, is shown by the black lines in Fig. 4. This reference case first exhibits an initial 45° line in the high frequency region of the Nyquist plot (Fig. 4a), which is represented by a plateau at 45° extending from high toward low frequencies in the phase angle plot (Fig. 4b). There, it is followed by a small dip to a lower phase angle (~43.4°) before increasing to higher phase angle values, due to the predominantly capacitive behavior of the RC-TLM at lower frequencies. The difference between the high frequency x-axis intercept (here set to zero) and the linear extrapolation from low frequencies toward the x-axis (dashed black line in Fig. 4a for case ng) when normalizing the impedances by (R_{ion}/1.5) corresponds to the ionic resistance in the electrolyte phase of one porous electrode in the symmetric cell, namely to 2/3 × Re(Z) in the symmetric cell. While this represents the ideal case for a macro-homogeneous resistance distribution across the thickness of a porous electrode, which one would expect for a
homogeneous binder distribution, we will now explore the effect of an inhomogeneous resistance profile on the EIS response of a porous electrode.

The EIS response for a linear $R_{\text{ion}}$ gradient across the thickness of the electrode, with a maximum value at the bottom (CC-side) of the electrode (profile $lb$ (“linear bottom”), see blue line in Fig. 3) is shown by the blue lines labeled $lb$ in Fig. 4. Here, we chose a 1.5-fold higher resistance at the current collector side of the electrode and a 0.5-fold lower resistance at the separator side of the electrode, both referenced to the average $R_{\text{ion}}$ value across the electrode thickness (the latter being the same as that for the homogeneous $R_{\text{ion}}$ distribution, case $ng$). Such a distribution decreases the apparent ionic resistance by $\sim25\%$ compared to the reference value (see Fig. 4a). In this case, however, the phase angle plot (blue line in Fig. 4b) shows a constantly increasing phase angle from the $45^\circ$ value at high frequencies to an intermediate maximum of $\sim48.6^\circ$ at $\sim0.3$ Hz. Reversing the linear resistance distribution so that the maximum $R_{\text{ion}}$ value is at the top of the electrode (i.e., at the separator-side; see red line in Fig. 3), the modeled impedance response (profile $lt$ (“linear top”), red curves) shows the opposite trend: a $\sim25\%$ higher apparent $R_{\text{ion}}$ value compared to the reference case (see red vs. black lines in Fig. 4a) and a comparably more pronounced phase angle minimum of $\sim40.3^\circ$ at a frequency of $\sim0.1$ Hz (see red line in Fig. 4b). Thus, linear $R_{\text{ion}}$ gradients across the thickness of a porous electrode affect the apparent $R_{\text{ion}}$ values, and their presence and direction is indicated by characteristic maxima/minima in modeled phase angle plots.

To further explore these impedance characteristics, we also modeled a second set of resistance distribution profiles, namely modeled stepped profiles with either the bottom quarter of the electrode (CC-side) or the top quarter of the electrode (separator-side) exhibiting a

![Figure 3](image-url)  
Figure 3. Chosen ionic resistance distributions in the electrolyte phase across the thickness of a porous electrode used for modeling its EIS response with a blocking electrolyte. Here, and furtheron, “bottom” refers to the interface between the current collector and the electrode, and “top” refers to the electrode/separator interface. The various shown profiles are described as follows. $ng$ (“no gradient”); represents a uniform resistance profile, i.e., without gradient, and is given for reference (black curve). $lb$ (“linear bottom”) represents a linear $R_{\text{ion}}$ profile with higher resistance ($1.5 \times R_{\text{ion}}$) at the bottom (CC-side, blue curve); $lt$ (“linear top”) represents a linear $R_{\text{ion}}$ profile with higher resistance ($1.5 \times R_{\text{ion}}$) at the top (separator-side, red curve). $sb$ (“step bottom”) represents a step function profile with a higher resistance in the bottom quarter of the electrode ($2.5 \times R_{\text{ion}}$, dashed green curve); $st$ (“step top”) represents a step function profile with a higher resistance in the top quarter of the electrode ($2.5 \times R_{\text{ion}}$, dotted magenta curve). Note that the total ionic resistance summed up over the entire electrode thickness is the same in all cases.

![Figure 4](image-url)  
Figure 4. Modeled EIS response (high frequency corrected) for a porous electrode with a blocking electrolyte (RC-TLM model) for a constant ionic resistance in the electrolyte phase ($R_{\text{ion}}$) across the electrode thickness (eg, black lines) as well as various resistance distributions as shown in Fig. 3. The latter are linear resistance gradients with a maximum resistance either at the top of the electrode ($lt$, red) or at the bottom of the electrode ($lb$, blue) as well as step functions with a maximum resistance either at the top ($st$, magenta, dotted line) or at the bottom of the electrode ($sb$, green, dashed line); here, “top” refers to the separator side of the electrode and “bottom” to the current collector side of the electrode. a) Nyquist plot of the scaled negative imaginary part of the impedance vs. the scaled real part of the impedance; b) corresponding phase angle plot (Bode plot). The chosen model parameters resemble those of the experiments conducted with the thick electrodes shown in Fig. 6: electrode thickness $260\ \mu$m; electrolyte conductivity $0.258\ \text{mS/cm}$; porosity $55\%$; tortuosity $5$; the double-layer capacity is based on the area of spherical particles ($r_p = 10\ \mu$m, approximated by the specific surface area (particle surface area per electrode volume) $a_{\text{DL}} = 3 \times (1 - 0.55)/r_p = 1.35 \times 10^5\ \text{m}^2/\text{m}^3)$ and a double layer capacitance of $0.2\ \text{F/m}^2$. 

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high ionic resistance (2.5-times of the average $R_{\text{ion}}$ value), whereby the average $R_{\text{ion}}$ value across the electrode thickness was again chosen to be the same as that of the homogeneous case. These distributions are shown in Fig. 3, labelled as $sb$ (“step bottom”, green dashed curve) or as $st$ (“step top”, magenta dotted curve), respectively. The modeled EIS response for these $R_{\text{ion}}$ profiles is shown in Fig. 4. For the profile with a higher resistance at the CC-side ($sb$, green dashed lines), the apparent $R_{\text{ion}}$ value is $\sim 46\%$ lower than that of the reference case with a homogenous $R_{\text{ion}}$ profile (see Fig. 4a). In the phase angle plot, the $sb$ profile starts with a $45^\circ$ value at high frequencies and passes through a very shallow minimum of $\sim 44.5^\circ$ at low frequencies. In analogy with the above discussed linear $R_{\text{ion}}$ profiles, a stepped profile with the maximum $R_{\text{ion}}$ value at the top (separator-side) shows a reversed trend (st profile, magenta dotted lines in Fig. 4): the apparent $R_{\text{ion}}$ value increases by $\sim 66\%$ compared to the reference case and shows a significantly more pronounced phase angle minimum of $\sim 39.1^\circ$ at low frequencies.

The change in the apparent resistance for inhomogeneous resistance profiles stems from the directionally dependent weighing of the ionic resistance profile of the electrolyte phase. For such a case, assuming the current sink (capacitive elements) is homogeneously distributed throughout the electrode, higher current flows through the resistances near the separator region than the current collector region (reflective boundary condition case). This is analogous to the transport phenomena involved in a Li-ion battery, where the ionic current, all of which passes through the electrode/separator interface, must be consumed (intercalated) along the thickness of the electrode. No ionic current passes through the current collector. Hence a resistance at the top (electrode/separator interface) is weighed higher than a resistance at the bottom. This is in contrast to a setup with transmissive boundary condition, where the measured apparent resistance is directionally independent, as the resistances through the electrode are weighed solely by their thickness fraction of the electrode. In such systems, all of the resistance profiles shown in Fig. 3 would yield the same apparent resistance (hence the same apparent tortuosity). The above mentioned description of the system using the RC-TLM is valid for a two-phase system, here the binder and graphite active material. In a system incorporating conductive carbon or other additives, as would be necessary for most cathode active materials, the above mentioned prerequisites (e.g. low electrical resistance) might not hold true anymore and could lead to data misinterpretation.17

**Preparation and EIS analysis of graphite electrodes with binder gradients.**—While the above numerical analysis reveals that $R_{\text{ion}}$ gradients across the thickness of a porous electrode can be detected by the electrode’s EIS response, no direct proof has yet been provided that $R_{\text{ion}}$ gradients may be caused by binder gradients. This would not necessarily be obvious for the here examined electrodes, since the PVDF binder only accounts for $\sim 6\%$ of the solids volume (graphite and PVDF), corresponding to only $\sim 2.7\%$ of the electrode volume (calculated from the 95/5 graphite/PVDF mass ratio, the graphite and PVDF densities of $\sim 2.2$ and $\sim 1.8$ g/cm$^3$, respectively, and the electrode porosity of $\sim 55\%$). Thus, for the following analysis, we first prepared electrodes with different binder gradients, then quantified the binder gradients by EDS cross sectional mapping, and finally examined their EIS response. The binder distribution was affected by drying electrodes at different temperatures, which was shown to result in different extents of binder migration.8 The graphite electrodes examined in the following were dried between 50–125°C using an IR-lamp as well as at room temperature (RT, $\sim 23°C$), as described in the experimental section. It is emphasized that the intrinsic driving force to generate different binder gradients is not the drying temperature, but rather, as mentioned above, the drying rate, for which reason we have provided the visually observed drying time in the experimental section and in Fig. 6.

To quantify the extent of binder migration and to directly correlate it to the impedance obtained from the dried graphite electrodes, we analyzed the electrode cross section of electrodes dried at temperatures from RT up to 125°C using EDS. An exemplary line scan of the measured aluminum, carbon, and fluorine signal is shown in Fig. 5a for the sample dried at 100°C. The aluminum signal stems from the two aluminum spacers at the top (separator-side of the electrode, right side in Fig. 5) and bottom (CC-side, left side in Fig. 5) of the electrode (also compare Fig. 1). The decrease in the aluminum signal and the intermediate carbon signal plateau marks the top and bottom of the electrode, seen on the right and left side of Fig. 5a (marked by the vertical dashed orange lines), respectively. The fluorine signals (blue line) between the vertical dashed orange lines stem from the PVDF binder, whereas the EDS signals at the fluorine energy before/after the dashed orange lines are caused by an interference with the EDS signals from aluminum.

The fluorine signals across the thickness of electrodes dried at different temperatures are shown in Fig. 5b. The signal was split into five parts of equal length (from bottom to top of the electrode), corrected for the background signal, and averaged (see experimental section); the average fluorine signal for each segment is marked at the midpoint of each segment by the symbols in Fig. 5b, connected with dashed lines serving as a guide-to-the-eye. The black symbols depict the fluorine signals for the RT dried electrode across the electrode thickness. While it is reasonably constant, indicating a rather homogeneous binder profile across the electrode thickness, there is a slightly stronger fluorine signal toward the bottom of the electrode, which

![Figure 5. EDS cross section line scans for electrodes dried at different temperatures with a final thickness of $\sim 245\,\mu$m ($\pm 6\%$), coated at a wet film thickness of 500 μm.](Image 306x409 to 546x716)
could possibly be caused by a small degree of binder sedimentation due to the extremely slow drying process at room temperature (several hours). The 50 °C dried sample however already shows first signs of binder migration to the top of the electrode (separator-side) and a concomitant slight depletion of binder at the bottom of the electrode (current collector-side), as reported in the literature for higher drying temperatures and the associated faster drying rates.\(^{1,2,6}\) The extent of binder migration to the top surface of the electrode clearly increases with drying temperature (i.e., with increasing drying rate), so that the electrode dried at 75 °C (light green line) already shows a binder gradient which resembles a linearly increasing binder distribution toward the separator-side. For higher drying temperatures, this gradient buildup continues, showing the strongest gradient formation for the sample dried at the highest temperature (125 °C, dark green line). The fact that the fluorine signal at the bottom of the electrode goes slightly below 0 is caused by background correction errors related to the extremely small fluorine signal at this position; the low binder content at the CC-side for the electrode dried at 125 °C is also reflected by the very poor adhesion of the electrode coating to the current collector, which allowed us to also prepare freestanding electrodes in this case.\(^{1,2,6}\)

Having characterized the PVDF binder distribution across the thickness of electrodes dried at different temperatures, we will now examine their EIS response in symmetrical cells with non-intercalating electrolyte, and then compare them to the modeled EIS response for electrodes with different \(R_{\text{ion}}\) profiles. It should be noted that the direct comparison of ionic resistances of individual measurements is only of qualitative nature, as the measurement is dependent on (among others) the electrode thickness (standard deviation \(\pm 6\%\)). Averaged values for the tortuosities of four separate measurements per sample set are depicted in Fig. 6d. Figs. 6a and 6b show exemplary data of the experimentally determined Nyquist and phase angle plots, respectively, for the high frequency resistance (HFR), as was done for the modeled EIS responses shown in Fig. 4. The lowest apparent \(R_{\text{ion}}\) value for the as-prepared electrodes is obtained for the RT dried sample (black line in Fig. 6a), i.e., for the electrode with the most homogeneous binder distribution across the electrode thickness (black symbols in Fig. 5a). The apparent \(R_{\text{ion}}\) value increases \(\sim 1.4\)-fold for electrodes dried at 50 °C (red line) and 75 °C (light green line) and by \(\sim 1.7\)-fold for electrodes dried at 100 °C (blue line) and 125 °C (dark green line). Quite clearly, the apparent \(R_{\text{ion}}\) value increases with an increasing extent of binder migration to the electrode top surface (separator-side; see Fig. 5b). Comparing this trend with the modeled Nyquist plots (Fig. 4a) for electrodes with increasing \(R_{\text{ion}}\) values from the electrode bottom (CC-side) to the electrode top (separator-side) suggests that the experimentally observed binder gradients indeed cause an analogous \(R_{\text{ion}}\) gradient, despite the rather small volume fraction of binder (\(\sim 6\%\) of the solids volume or \(\sim 2.7\%\) of the electrode volume). Thus, even small amounts of binder can substantially influence the apparent ionic resistance through a porous electrode.

**Figure 6.** Experimental EIS response of graphite electrodes dried between 25 and 125 °C and with a final thickness of \(\sim 245 \mu m\) (\(\pm 6\%\)), coated at a wet film thickness of 500 \(\mu m\); the electrode labeled “125 °C reversed” was dried at 125 °C, removed from the current collector, and re-assembled such that the original CC-side of the electrode becomes the separator-side in the re-assembled cell. EIS measurements (20 mV amplitude, between 10 mHz and 200 kHz) were conducted in a symmetric cell setup (T-cells, \(\varnothing = 10.95 \text{ mm}\)) using a non-intercalating electrolyte (10 mM TBAClO\(_4\) in EC:EMC 3:7, with \(\kappa = 0.258 \text{ mS/cm}\)). a) High frequency resistance (HFR) corrected Nyquist plots with frequencies marked for the 75 °C sample. b) HFR-corrected phase angle plots. c) Phase angle plot of the 75 °C dried electrode corrected for the experimentally determined HFR of 226 \(\Omega\), but adding small deviations of \(\pm 2 \Omega\) (i.e., \(\varnothing \pm 1\%\)) and \(\pm 4 \Omega\) (i.e., \(\varnothing \pm 2\%\)) to the HFR correction, which are considered to be within the error of HFR quantification. d) Apparent tortuosities for the electrodes vs. the observed drying time (left axis, cubes) as well as minimum phase angles (right axis, circles; the value for the “125 °C reversed” sample was taken at the last visible plateau at low frequencies (\(\sim 1 \text{ Hz}\)) in the phase plot). Error bars indicate the standard deviation of four separate measurements; drying times were observed by eye, whereby the room temperature drying time was taken as 8 h (overnight). The two gray dashed lines were added as guide-to-the-eye for the changes in tortuosity and phase angle minima for the differently dried electrodes (excluding the data for the reversed electrode).
either by differences in binder distribution affected by the drying process as shown, or by the chemical nature of the binder as we had observed previously. Additional insight can be gained when examining the experimental HFR-corrected phase angle plots shown in Fig. 6b. Following the above indications that the observed binder gradients reflect analogous gradients in the electrode’s $R_{\text{ion}}$ values, the EIS models shown in Fig. 4 would predict (i) 45° phase angles at high frequency, and, (ii) increasingly pronounced phase angle minima with increasing binder gradients, i.e., with increasing drying temperatures. The latter can be clearly observed in the experimental data shown in Fig. 6b: the phase angle minimum is rather small for the RT dried electrode (black line) with its nearly homogeneous binder distribution (see Fig. 5b), while it becomes increasingly more pronounced as the drying temperature and thus the binder gradient increases. At the same time, however, the high frequency phase angles do not seem to approach the expected 45° phase angle. Apart from phase changes due to inhomogeneity within the electrode, this may also have to do with the fact that even minute errors in the HFR correction lead to large errors in the high frequency phase angle, as is demonstrated exemplarily in Fig. 6c for the EIS data obtained for the electrode dried at 75°C. Here, the experimental data were corrected for the experimentally determined HFR of 226 Ω, but adding small deviations of $±2$ Ω (i.e., $±1\%$) and $±4$ Ω (i.e., $±2\%$) to the HFR correction, which we consider rather small errors in the quantification of the HFR. Quite clearly, this results in dramatic variations of the phase angle plot in the high frequency region beyond the phase angle minima (i.e., at frequencies higher than $\sim1-2$ Hz), so that from an experimental point of view no reliable information can be obtained from the high frequency region. The sensitivity is evident when examining the Nyquist plot (Fig. 6a), where the first marked frequency of 37 Hz is close to the origin of the Nyquist plot, but spans almost 50% of the phase angle plot. On the other hand, at lower frequencies the curves start to overlap, illustrating that the extent of the phase angle minima is not affected by small errors in the HFR and can thus be used to deduce the presence/absence of binder gradients.

The above observed correlations can be further confirmed by examining an electrode configuration, for which the binder gradient goes into the opposite direction, i.e., for which the binder concentration is highest at the bottom of the electrode (i.e., at the CC-side) and the lowest at the top of the electrode (i.e., at the separator-side). Such a reversed binder gradient can be mimicked by using a freestanding electrode dried at 125°C, as it easily detached from the current collector foil (see above), so that these freestanding electrodes could be re-assembled into symmetric T-cells now with the separator-sides of the original electrodes facing the current collectors. Symmetric cells assembled in this reversed configuration now have a binder profile which is a mirror image of that shown for the 125°C dried electrode (i.e., mirroring the dark green line in Fig. 5b around the $x = 0.5$ value). Its experimental impedance response is given by the magenta line in Fig. 6, with the Nyquist plot (Fig. 6a) showing a reduced apparent $R_{\text{ion}}$ value compared to the reference case with homogeneous binder distribution (black line), and with the phase angle plot (Fig. 6b) now revealing a characteristic local minimum at a phase angle of $\sim47°$, i.e., well above that of the reference case. The lower apparent $R_{\text{ion}}$ value and the shift of the phase angle minimum to above the reference case value is perfectly consistent with the EIS model for electrodes with a linear $R_{\text{ion}}$ gradient, where the same behavior is observed upon reversing the linear $R_{\text{ion}}$ profile with a maximum resistance at the top of the electrode (red line labelled $h$ in Fig. 6) so that the profile is reversed (blue line labelled $lb$ in Fig. 6).

As described above, the apparent $R_{\text{ion}}$ value for the different electrodes was obtained from the HFR-corrected Nyquist plots in Fig. 6a by interpolating the low frequency data to the Re(Z)-axis. From this, electrode resistance tortuosities ($\tau$) were determined using the electrolyte bulk conductivity ($\kappa = 0.258$ mS/cm) and the electrode pore fraction ($\phi = 0.55$), and the measured electrode thickness (ranging from 245 to 260 μm), as described in Ref. 18. Fig. 6d shows the thus determined apparent tortuosities together with the characteristic phase angle minimum (obtained from Fig. 6b) of the various electrodes vs. the approximate drying time. The trend to higher apparent tortuosities with decreasing drying time, i.e., with increasing drying rates, is evident: as the drying time is reduced at higher drying temperature, leading to more pronounced binder migration toward the top (separator-side) of the electrode, the apparent tortuosity increases. On the other hand, the electrodes dried at the highest temperature of 125°C but re-assembled in reverse configuration (i.e., the separator-side during drying now facing the current collector for the measurement) show a very low apparent tortuosity of $\sim2.7$, even lower than that of the RT dried sample, consistent with what one would expect based on Fig. 4a for an electrode with very little binder content at the separator. As discussed above, the best qualitative indicator for the extent and the direction of binder gradients are the phase angle minima observed in the phase angle plots (Fig. 6b), which are therefore plotted also in Fig. 6d (right axis). The angle shown for the “125°C reversed” (magenta) sample was obtained by taking the phase angle values of the last plateau at low frequencies ($\sim1$ Hz), before the phase angle increased continuously due to the capacitive behavior at low frequencies. Clearly, the decreasing values for the characteristic phase angle minima with shorter drying times (i.e., for higher drying temperatures) is consistent with what one would expect based on the experimentally observed binder profiles (Fig. 5b); furthermore, while the 100°C and the 125°C dried electrodes show similar tortuosities, the phase angle minimum of the latter is still lower, suggesting a stronger binder gradient, as indeed can be seen from the EDX based binder profiles (see dark green vs. blue lines in Fig. 5b).

Charge rate capability of differently dried graphite electrodes.— Previous studies on the rate capability of graphite/NMC full-cells have shown that cells with graphite anodes dried at a high drying rate are inferior to those with graphite anodes dried at low drying rate, which the authors related to binder gradients formed at high drying rate. Similarly, the effect of various binder types on the charge rate capability of graphite anodes was observed recently by Landesfeind et al., monitoring the onset of lithium plating upon the lithiation of graphite electrodes in half-cells by means of a reference electrode. In the following, we will therefore examine whether there is a correlation between the charge rate capability of graphite anodes dried at different temperatures (i.e., at different drying rates) and the extent of binder gradients indicated by their EIS response. For this charge rate capability tests, we examine graphite electrodes with industrially relevant areal capacities of $\sim2.4$ mAh/cm² (corresponding to graphite loadings of $\sim7.4$ mg/cm² (±2%) and thicknesses of $\sim74$ μm (±2%)) and dried at 75°C or 125°C. The results from the EIS characterization of these electrodes in symmetric cells with non-intercalating electrolyte of these electrodes can be seen in Fig. 7a. Both electrodes have similar apparent tortuosities (4.4–4.6), but the electrodes dried at 125°C show a significantly more pronounced minimum in the phase angle plot, suggesting that the binder is significantly more inhomogeneously distributed, namely with significant binder enrichment at the top of the electrode (separator-side), as one would expect based on the above discussed data with thicker electrodes. The charge (i.e., lithiation) rate capability is depicted in Fig. 7b, showing the inferior performance of electrodes dried at 125°C, analogous to what was shown by Jaiser et al. for slow-vs. fast-dried graphite anodes. These authors had suggested that the most likely reasons for the poor rate capability of fast-dried anodes would be either the suppression of the charge transfer resistance by thick binder films covering the graphite particles near the separator-side of the electrode or poor conductivity near the CC-side of the electrode due to the migration of carbon black. The latter clearly can be ruled out in the present case. On the other hand, since our impedance model based on $R_{\text{ion}}$ gradients across the thickness of the electrode (Fig. 4) very well describes the experimental EIS response for electrodes with binder gradients (see Fig. 5b and Figs. 6a, 6b), our results suggest that the underlying reason for the inferior rate capability of electrodes with strong binder migration to the top of the electrode may be caused by a high ionic resistance in the electrolyte phase near the anode/separator interface. Under this hypothesis, the
pending on the catalyst ink’s solvent type large ionomer patches were an influx of lithium ions into the interior of the graphite electrode. The distribution of the migrated binder within the plane of the electrode (parallel to the current collector), as it could either deposit as the anode/separator interface.

Summarizing the above analysis, we would like to point out that the EIS response calculated for different drying rates (in situ or in a symmetric cell with a blocking electrolyte) is sufficient to collect the necessary data. Comparing the phase angle plots, one can quickly draw qualitative conclusions about the presence of any binder gradients and on the expected performance of the electrodes (see Fig. 7) and whether the obtained tortuosity value is suitable for use in a macro-homogeneous electrode model. Hence the phase angle minimum in the phase angle plot is an extremely important criterion to determine the presence of significant binder gradients and should not be neglected in the analysis of impedance data.

**Figure 7.** Impedance characteristics and charge rate capability of graphite electrodes with areal capacities of ~2.4 mAh/cm² (corresponding to ~7.4 mg_graphite/cm² (±2%) and electrode thicknesses of ~74 μm (±2%)) dried at either 75 °C (blue lines/symbols) or 125 °C (red dashed lines/symbols). a) HFR-corrected phase angle plots and tortuosity values obtained from symmetric cell measurements with non-intercalating electrolyte (~10 mM TBAClO₄ in EC:EMC 3:7). b) Charge (i.e., lithiation) capacity vs. C-rate for cycling the graphite electrodes between 1.5 V and 0.01 V vs. a Li-metal reference electrode. The error bars show the standard deviation of independent measurements with three nominally identical electrodes.

explanation for the inferior charge rate capability of the graphite anode dried at 125 °C would be an inferior access of lithium ions into the bulk of the anode due to a partially pore-blocking binder layer at/near the anode/separator interface.

Summarizing the above analysis, we would like to point out that it is not yet possible to quantitatively correlate binder gradients with $R_{\text{ion}}$ gradients, even though it is quite clear from the above comparison that the EIS response calculated for different $R_{\text{ion}}$ profiles behaves analogous to the EIS response measured for electrodes with experimentally determined binder gradients. Entirely unclear at this point is the distribution of the migrated binder within the plane of the electrode (parallel to the current collector), as it could either deposit as a homogeneous binder layer over the graphite particles or deposit in a web-like form which could span across the (sub-)μm-sized pores between the graphite particles, thereby preventing a homogeneous influx of lithium ions into the interior of the graphite electrode. The latter phenomenon was observed for fuel cell electrodes, where depending on the catalyst ink’s solvent type large ionomer patches were observed, covering large cross-sectional areas of the electrode parallel to the electrode surface. Quite clearly, an electrode performance model would have to consider the in-plane distribution on the binder near the anode/separator interface. Similar effects may also be the origin of the so-called “rollover” failure reported by Burns et al., who suggested that during extended battery cycling, the pores at the top of the electrode (separator-side) are becoming clogged and thereby cause the “rollover” failure, i.e., the point when batteries quickly lose their capacity over a short amount of cycles. Such a mechanism resembles the modeled behavior above (Fig. 3, profile x). As it is possible to measure impedance in blocking condition in-situ using a three electrode setup, this failure mechanism could be detected by analyzing the phase angle plot of the impedance spectrum.

The effect of binder migration may be one of the reasons for the discrepancies between EIS and X-Ray tomography measurements when it comes to tortuosity determination. Recently Landesfeind et al. showed that an at least partially unresolved binder distribution in 3D reconstructed electrodes causes an underestimation of tortuosity values compared to impedance measurements, an effect which exacerbates the dilemma faced by groups using 3D reconstruction techniques to model transport in porous battery electrodes. However, additional care also has to be taken when determining tortuosities from impedance data, as this approach usually uses homogeneous transmission line models and would thus misinterpret the extracted $R_{\text{ion}}$ and tortuosity values, which only have a well-defined meaning in a macro-homogeneous battery model in the absence of strong binder gradients. Conversely, in the presence of strong binder gradients (i.e., for fast-dried electrodes or electrodes dried at high temperature), the tortuosities extracted from impedance analysis are apparent tortuosities which obviously cannot be directly applied to a macro-homogeneous battery model.

The here provided EIS analysis approach is most useful when comparing electrodes of the same composition and loading, but with different drying/agining history. A quick impedance measurement in blocking condition (in situ or in a symmetric cell with a blocking electrolyte) is sufficient to collect the necessary data. Comparing the phase angle plots, one can quickly draw qualitative conclusions about the presence of any binder gradients and on the expected performance of the electrodes (see Fig. 7) and whether the obtained tortuosity value is suitable for use in a macro-homogeneous electrode model. Hence the phase angle minimum in the phase angle plot is an extremely important criterion to determine the presence of significant binder gradients and should not be neglected in the analysis of impedance data.

**Conclusions**

Up to now, visualizing binder migration required extensive and time consuming experimental effort, such as EDS. The analysis method in this publication gives the reader an additional tool to quickly screen electrodes for their homogeneity. Impedance model results show how high resistances toward the separator side of the electrode increase the overall resistance of the electrode significantly. This was verified by experimentally inducing binder migration by drying electrodes at low and high drying rates. EDS and impedance measurements combined confirmed that changes in the impedance spectrum give qualitative information on the extent of the binder gradient. Simple phase angle minimum analysis together with ionic resistances gathered from the same measurement give information about the presence of binder gradients and therefore the expected electrochemical performance. The ionic resistances gathered have to be considered with caution when applying them to an electrochemical model. Any calculated tortuosity is a mere apparent tortuosity and is, in the case of strong binder gradients, not representative for the entire electrode. Electrodes of similar apparent tortuosity but different degrees of binder gradients show significant differences in performance. While the exact mechanism of the poor performance of fast dried electrodes is still not clear, this analysis gives additional insight into the resistances within an electrode and help explain this phenomenon.
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