Experimental Correlation of Anionic Mass-Transport and Lithium Dendrite Growth in Solid-State Polymer-Based Lithium Metal Batteries

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**SUMMARY**

Various metal deposition models were proposed for alkali metal batteries but experimental accessibility of designated driving forces and characteristics of specific morphologies is still limited. A combined method portfolio comprising *operando* 1D 19F MRI, *in situ* 7Li NMR and *dynamic* EIS experiments is presented. Experimental evidence of the relation of capacity degrading dendritic lithium metal growth and anionic mass-transport quantities beyond Sand’s time in polymer-based lithium metal batteries is demonstrated. Comparison of anionic mass-transport and morphological changes of Li metal in Li||Li and NMC622||Li cells revealed that elevated anion drift velocities within electrolytes are correlated with pronounced dendrite growth. Higher cell voltages are associated with increased anion drift velocities and hence dendrite growth, as reflected by a 2.5-fold increase in velocities in NMC622||Li compared to Li||Li cells. This highlights the potential of the introduced method portfolio for experimental evaluation of polymer electrolytes and artificial coatings suitable for alkali metal batteries.

**KEYWORDS:** Lithium Metal Batteries, Polymer Electrolytes, All-Solid-State, Mechanisms of Capacity Retention, Morpho-logical Changes of Li Metal, Mass-Transport Limitations, operando 19F MRI Profiling, dynamic EIS, in situ 7Li NMR

**INTRODUCTION**

Unfavorable morphological changes of alkali metal deposits during electrochemical operation of rechargeable alkali metal batteries, in particular lithium metal batteries (LMBs), may impose safety risks and severe capacity fading, thereby limiting the exploitation of alkali metal batteries in contemporary electric vehicle applications. Specifically, upon cell operation at faster-charge conditions (>2C), unintentional occurrence of high-surface area (needle- or, dendritic-shaped) metal deposits results in pronounced cell capacity fading due to the formation of so-called ‘dead-metal’ fractions (i.e., electronically isolated alkali metal fragments), and internal short circuits.1-4 Though several macroscopic determinants5 with respect to alkali metal morphology changes were identified (e.g. temperature, electrolyte composition, current densities, overpotentials, stack pressure), salient mechanistic details of alkali metal nucleation and propagation are subjects of continued discussion, thus critically confining tailored developments of active materials and other cell components, comprising artificial coatings, metal pre-treatments, and electrolyte constituents. Note that a sufficient reversibility of alkali metal inventory is paramount to enhance the longevity and applicability of metal-based cell designs, thus rendering better mechanistic understanding on actual operational conditions is crucial.6 Despite that a variety of rather complex models was proposed, aspects of alkali nucleation and propagation remain insufficiently understood. An in-depth discussion of available models, mostly focusing on Li metal deposition, can be found in recent reviews,1, 5, 7-10 but briefly summarized, the models rely on key characteristics that determine alkali metal deposition: 1) “lithiophilicity” of lithium metal electrodes; 2) composition and properties (e.g. structural uniformity) of solid electrolyte interphases (SEI) present at metal surfaces; 3) surface-tension and rheological features of alkali metal electrodes, the (solid) electrolyte and the SEI layers; 4) crystallographic properties of alkali metal (anisotropies and defects) as well as alkali metal motion at the surface; and 5) a mass-transport limitation of metal deposition. The various models contrasting initiation and propagation mechanisms indicate that the critical driving forces for obtaining distinct metal deposit morphologies are challenging to access experimentally, hence limiting further adjustment of present models. Relevant access to these quantities may be achieved by various *in situ* and *operando* methods,11-12 where imaging techniques with sufficient temporal and spatial resolution (i.e., optical, SEM, TEM, X-ray, neutron, NMR/MRI, EPR, AFM etc.) constitute valuable qualitative and partly quantitative techniques to evaluate the trends of alkali metal morphology evolution and alkali metal deposit growth. Here, NMR techniques are advantageous since, particularly, Li metal morphologies can be quantitively distinguished,13-15 *via* characteristic changes of bulk magnetic susceptibility (BMS) associated with the different Li metal morphologies, as reflected by the observable 7Li NMR chemical shifts of Li metal species. In combination with *operando* chemical shift imaging (CSI), actual Li metal morphology changes were successfully resolved.16-18 In Li||Li cells operated with liquid electrolytes, Grey et al. monitored the Li deposit morphologies ranging from mossy- to dendritic-shaped Li metal deposits occurring at the Sand’s time when applying current densities above 0.51 mA cm-2 (constant current charging).17 Sand’s time marks the time when charge carrier depletion at electrodes’ surfaces most likely occurs. The CSI experiments revealed the formation of concentration gradients of Li-ions within the bulk electrolytes, where the Li-ion concentration decreased in the vicinity of the lithium electrode at which lithium plating has taken place, while it increased towards the counter lithium electrode (lithium stripping). It was concluded that at conditions above a critical current density, mass-transport limited Li metal deposition will be a dominant contributor to the Li metal propagation as soon as Sand’s time has been reached. A similar conclusion was proposed by Bai and Bazant et al., comparing theoretically predicted Sand´s times and on-set times of dendrite growth derived from optical microscopy of Li||Li cells.19 Moreover, the on-set of Li dendrite growth appeared to be correlated to sudden voltage peaks, in good agreement with Chazalviel´s dendrite growth model.20-23 In this model, anionic mass-transport limitations at lithium metal electrode surfaces yield pronounced dendrite growth (5) where the growth velocity of a ramified lithium front (propagation velocity) reflects an anion drift velocity within electrolytes. Anion motion is induced by the applied electric fields, and accordingly, anion drift velocities determine the nature of inhomogeneous metal deposition and Li dendrite growth (see **Figure 1**). It should be noted, that Chazalviel’s model quantifies dendrite growth at charging conditions above a critical current density, while actually, commercial batteries operated with liquid electrolytes are cycled well below such critical current densities. Also, morphological changes from mossy- to dendritic- shaped Li metal deposits were already identified for Li||Li cells at conditions below any specific critical current density and prior to reaching Sand’s time, in contrast to the model’s predictions.17,23 It could be shown that even at low current densities, the Li dendrite growth followed the velocity at which the anions drifted within bulk electrolytes. Here, anion drift velocities were estimated by Ohm’s law while the dendrite growth was evaluated by optical microscopy. A correlation of these velocities seems to hold true even well below the critical current densities. Notably, a limited applicability of Chazalviel’s model for cell cycling at low current densities may be attributed to oversimplified assumptions of electrode surfaces, where characteristics such as local inhomogeneities and the impact of the present SEI layers were not accounted for. Despite this, Chazalviel’s model (5) was initially applied to polymer electrolytes,22-23 in which mass-transport limitations are more prevalent compared to typical liquid electrolytes. Due to comparably low ionic conductivities of solid polymer electrolytes, the actually applied current densities in practical lithium ion batteries may exceed specific critical current densities of solid polymer-based electrolytes.24 Thus, models based on mass-transport limitations are consulted while developing polymer-based solid-state electrolytes for (Li, Na) metal batteries,25-30 which are expected to be relevant in the field of next-generation of lithium batteries.31 To unravel detailed insights and gain better understanding of how mass-transport induced dendrite growth governs capacity fading and operational safety of promising polymer-based Li metal batteries, the corresponding anion drift velocities can be exploited for evaluation of polymer electrolytes, artificial coatings and Li metal pretreatments, respectively. However, reviewing the literature, these velocities have not been experimentally determined while (dis-)charging LMBs yet. The ion drift velocities in binary or ternary electrolytes were determined by E-Field NMR to derive mass-transport properties such as ion mobilities and transference numbers. For this, blocking electrodes (Pt/Pd) and voltages of up to 200 V have been required, hence decoupling mass-transport properties from respective electrode redox kinetics.32-36 In contrast, Goward’s group quantified the charge carrier transport in liquid electrolytes while polarizing graphite||Li cells, thereby including effects of concentration gradients arising from (sluggish) electrode kinetics (Li-ion intercalation to graphite, lithium stripping). The concentration-dependent mass-transport properties such as ion diffusion coefficients, transference numbers and ionic conductivities were successfully mapped in typical liquid electrolytes.18, 37-40 Compared to symmetric Li||Li cells, graphite||Li cells are advantageous in this respect since the (bulk) electrolyte mass-transport becomes stationary (steady-state concentration gradients) after a certain charging/polarization time (Li-ion intercalation into graphite), facilitating calculations of mass-transport based on rather diffusive and migrative transport equilibria.39 To determine electrolyte transport properties even in Li||Li cells under polarization with non-stationary mass-transport, Monroe et al. reported a thermodynamic approach for superconcentrated electrolytes. Experimental observations of ion distributions (MRI) and overpotentials (potentiometric) while polarizing symmetric Li||Li cells agreed closely with the model’s predictions.41 Nevertheless, the work focused on the concentration dependent transport properties reflected by charge carrier diffusion coefficients, ionic conductivities and transference numbers. Morphological changes of Li metal deposition due to mass-transport limitations, in particular due to anionic mass-transport, were out of scope. Cheng et. al. examined the ion depletion under galvanostatic conditions in polymer-based Li||Li cells and showed based on operando stimulated Raman scattering experiments that reduced ion concentrations, measured at least 5 μm apart from the electrode surface, led to more pronounced dendritic metal deposition, in good agreement with previous MRI results.17,42 In addition, the authors were able to derive metal dendrite growth velocities between 2.0 μm/min (=120 μm/h) and 5.2 μm/min (312 μm/h). While the correlation of ion depletion and morphological changes seems to be profound, further experimental insights into correlations of dendrite growth and mass-transport as proposed by Chazalviel’s model are still missing, leaving main model predictions such as the claimed space-charge region and the relation of dendrite growth velocities to anion drift velocities yet to be validated. Hence, in the present work, the corresponding anion drift velocities within polymer-based Li||Li and Li||NMC622 cells are determined experimentally based on *operando* 1D 19F MRI anion concentration profiles and numerical evaluation (**Figure 2**). Beyond Chazalviel’s model as well as scopes of previous studies, state-of-the art cathode materials (NMC622) are considered to unravel impacts of operating voltages (above 3 V) on mass-transport and metal deposition. By simultaneously acquiring dynamic electro-chemical impedance spectroscopy (EIS) spectra and analyzing the distribution-of-relaxation times (DRT), impedance changes within the Li metal electrode interphases are identified and correlated to the respective trends in anion drift velocities within the considered polymer electrolytes. Also, Li metal morphologies derived from *in situ* 7Li NMR experiments are evaluated with respect to both anion drift velocities and redox processes at the electrode interfaces. While primarily exploiting 7Li NMR, the proposed procedure in principle holds for other metal-based cell chemistries such as sodium metal (23Na), though the stronger quadrupolar interaction could impede spectral resolution. Polyethylene oxide-based polymer electrolytes are used as a ‘proof-of-concept’ model, but the introduced methodology can be similarly applied to other types of (polymer) electrolytes43. In summary, for the first time, anion drift velocities and Li dendrite growth are correlated experimentally in case of polymer-based lithium metal batteries, paving the way for a more tailored design of polymer electrolytes and of artificial coatings that could allow for faster-charge applications of LMBs.

**RESULTS and DISCUSSION**

**Determination of Anion Drift Velocities**

In the present work, anion drift velocities are derived from *operando* 1D 19F MRI concentration profiles, as briefly described below, then anion drift velocities in Li||Li and Li||NMC622 cells are compared and related to Li metal morphology evolution as observed by *in situ* 7Li NMR. Also, DRT analysis of dynamic EIS spectra yields relevant insights to electrode interphasial processes while mass-transport limited Li metal deposition occurs.

By following the versatile framework of Chazalviel, a numerical approach is presented to derive corresponding anion drift velocities from *operando* 1D 19F MRI anion profiles acquired for polarized Li||Li & Li||NMC622 cells. For the sake of clarity, utilized cell notation (‘cathode’||’anode’) refers to charging processes and not to the commonly used discharging processes, i.e., all cells are polarized so that lithium metal is deposited on the lithium metal electrodes, designating them as cathodes (reduction) and either Li or NMC622 counter electrodes are labeled as anodes (oxidation). A detailed description on how to derive the anion drift velocities numerically at non-stationary mass transport conditions as well as an error discussion can be found in the supplemental information (Note S1 and Note S3). Note that the following experimental input is required:

1. *Operando* 1D 19F MRI anion intensity profiles of the bulk electrolyte while plating Li metal
2. Applied cell voltage while plating Li metal
3. Concentration dependent ion diffusion coefficients obtained from PFG NMR (concentration series of the electrolytes)

In brief summary and using mathematical analytic statements, one-dimensional anionic mass-transport might be derived based on a reduced Nernst-Planck approach (without convection), describing the spatial and temporal dependent anionic particle flux density as a sum of diffusive and migrative contributions.

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|  | (1) |

Here, mass transport is governed by anionic concentration gradients and experimentally applied electric field strengths ) rather than the electrochemical potential gradients used in the more general framework of Newman’s concentrated solution theory.44 Ion diffusion is solely described by Fick’s 1st law, including anion diffusion coefficients , while ion migration results from the applied electric field strengths and actual anion mobilities within the electrolytes:

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| --- | --- |
|  | (2) |
|  | (3) |

Nernst-Planck’s dilute solution theory does not take ion/ion diffusional drag interactions into account41, limiting the model’s applicability to ideally diluted binary electrolytes. However, the most widely investigated and already commercialized polymer electrolyte PEO/LiTFSI with reasonably high ion dissociation degrees satisfies the pre-requisites of Nernst-Planck’s dilute solution theory.36, 45-46 Since Chazalviel’s model is also based on dilute solution theory, we limit our interest to binary electrolytes in agreement with previous work22-23, 47-49 focusing on PEO/LiTFSI electrolytes, to permit a derivation of anion drift velocities with a modest number of experimental parameters. The overall anionic particle flux density within the bulk electrolyte can be derived from *operando* 1D 19F MRI anion concentration profiles by invoking mass conservation (continuum equation).

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|  | (4) |

Integration of eq. 4 leads to an expression for the anionic particle flux density :

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| --- | --- |
|  | (5) |

Upon determination of the concentration-dependent (self-) diffusion coefficients of the anions from 19F PFG NMR of a PEO/LiTFSI concentration series, (**Figure S3**) the impact of concentration changes on the anion diffusion coefficients and anion mobilities are considered. Based on the Nernst-Einstein relation (eq. 6), the anion mobilities and diffusion coefficients can be converted into each other.

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| --- | --- |
|  | (6) |

and represent faradaic, and gas constants as well as temperature, respecitvely. From the indefinite integration in eq. 5 (left hand side) arises an initial value problem, which might be solved by taking the applied cell voltage into account. The applied voltage is assumed to be composed of electric field contributions in the x direction, thereby neglecting potential gradients parallel to the electrodes’ surfaces, Ohmic contributions of electrolyte as well as charge-transfer resistances at the electrodes.

|  |  |
| --- | --- |
|  | (7) |

and correspond to a current density and resistivity (ionic and interfacial), respectively. Here, the electric field strengths governs the anion drift velocities (eq. 3). Under mass-transport limited Li metal plating conditions (galvanostatic cell polarization at limited current densities), the concentration overpotentials primarily determine the resulting cell voltages. Ion depletion eventually occuring at the lithium cathode is tackled by an increase in cell voltage and thus by an increase in electric field strength. Changes of the ionic conductivities across the diffusion layer of the electrodes and Ohmic contributions of charge-transfer processes are assumed to be comparably small50-51. Thus, Ohmic contributions to the cell voltages might be neglected, and eq. 7 can be reduced to:

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|  | (8) |

This simplification is derived from previous MRI experiments that have been modeled utilizing an irreversible thermodynamic approach. Wang et. al. showed for super-concentrated electrolytes in Li||Li cells that Nernstian contributions of the cell voltage due to concentration polarization increases over time during a galvanostatic polarization experiment, while Ohmic contributions resulting from the IR drop as well as partially from surface kinetics kept constant or decreasing over time.41 Thus, it is to be expected that Nernstian contributions dominate the cell voltage as soon as severe concentration polarization (=mass-transport limited redox reaction) occurs. To thoroughly validate this simplification, however, Nernstian and Ohmic contributions resulting from a diffusion layer and charge-transfer process under mass-transport limited conditions should be elucidated by simulation and experimental means in more detail, but is beyond the scope of the present work.

**Anion Drift Velocities in Li||Li and Li||NMC Cells**

To evaluate the impact of anion drift velocities on lithium metal plating, anion drift velocities in Li||Li and Li||NMC622 are determined. Due to uneven operating voltage windows (0 to 1.5V for Li||Li and 3 to 4.2V for Li||NMC622), various mass-transport processes and thus different lithium metal morphologies are expected. In both cases, Li metal is plated on top of the lithium metal electrodes while charging the cells. The lithium plating reaction was galvanostatically driven into a mass-transport limited condition and then held there, potentiostatically. In this way, concentration changes near the lithium electrode surface are carried in the bulk electrolyte, where anion concentration changes are observed by *operando* 19F MRI (time resolution = 8 min 33 s). In case of both cell chemistries (Li||Li and Li||NMC622), steady-state anion concentration profiles in *operando* experiments could not be observed, that is, the anion mass-transport is non-stationary. Under galvanostatic operation (at constant current density, CC = 0.1 mA cm-2), lithium plating becomes mass-transport limited, as indicated by the sudden cell voltage increase, after ca. 90 min and 135 min for Li||Li and Li||NMC622 cells, respectively **(Figure 3A,C**). An additional OCV step is required for the NMC622 cathodes to account for the potentially competing capacity limitation of the cathodes. However, a voltage drop of 0.5 V after the CV step as well as available cathode capacity of 50% compared to the theoretically estimated cell capacities (obtained based on applied/measured currents and faraday’s law) convincingly demonstrates the presence of mass-transport limitations. Furthermore, Sand’s time can be calculated from cation and anion diffusion coefficients and might be employed as a predictor when mass-transport limitations start to dominate the redox kinetics. According to Chang et al., Sand’s time can be estimated by eq. 9.:17

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| --- | --- |
|  | (9) |

where and represent the ambipolar diffusion coefficient [m2 s-1], the particle concentration [L-1], elemental charge [As] and the anion transport number, respectively. Considering the obtained anion diffusion coefficient of 1.3 x 10-12 m2 s-1 at 40°C (see SI), a typical anion transport number of 0.9 for PEO-based electrolytes, a particle concentration of 9.94 x 1023 L-1 and applied current density of 0.1 mA cm-2 results in a Sand´s time of 103 min. Please note, that the ambipolar diffusion coefficient was assumed to be 2.53 x 10-13m2s-1 and was derived by first calculating the cation diffusion coefficient based on the anion diffusion coefficient and the anion transport number as well as second, by invoking Nernst-Einstein relation to calculate ion mobilities. The sudden voltage changes observed at 90 min and 135 min are in close proximity or after the estimated Sand´s times, indicating that the lithium metal deposition becomes mass-transport limited as soon as the voltage increases in both cases. Interestingly, sudden voltage changes in case of Li||NMC622 cells are delayed, which might be attributed to the elevated applied cell voltage compared to the Li||Li system, since the calculation of Sand’s time only takes diffusive but not migrative contributions to the mass-transport into account. This simplification might be sufficient for Li||Li cells with applied voltages close to 0 V, but may be not valid for more realistic cell setups like Li||NMC622 with applied voltages between 3.0 V and 4.2 V. Further differences between both cell configurations can be determined while comparing the derived anion drift velocities. While mass-transport limitations deploy, an increase in anion drift velocity is observed in both cases (**Figure 3B,D**). Maximum anion drift velocities of 385 μm/h and 1041 μm/h for Li||Li and Li||NMC622 are derived, respectively. The order of magnitude of the maximum anion drift velocity derived from Li||Li cells is in good agreement to previously derived lithium dendrite growth velocities (312 μm/h) based on stimulated Raman scattering experiments in polymer-based Li||Li cells42, corroborating the proposed correlation (of dendrite growth velocity and anion drift velocity) according to Chazalviel’s model. Moreover, the derived anion drift velocities in Li||NMC622 cells are consistently larger compared to Li||Li cells, suggesting more pronounced lithium dendrite growth in Li||NMC622 cells. A minus sign indicates the direction of the anion motion (against the electric field). Noteworthy, the spatial distribution of anion drift velocities diverges over time. Chazalviel’s model relates a distinct anion drift velocity to a dendrite growth velocity. Spatial divergences might be reduced by introducing a moving frame to the presented numerical approach, which scales with the divergences. In his model, Chazalviel introduced this moving frame to account for volume changes of the electrodes while stripping and plating lithium from one lithium electrode to the other. Here, the frame velocity represents the anion drift velocity which is correlated to the dendrite growth velocity. Since only a minor fraction of lithium metal is plated (about 10% of lithium metal capacity) any volume changes of the electrodes are assumed to be comparably small while a computation of moving frame velocities would require to invoke additionally minimizing methods. Thus, we limit our interpretations to the magnitude and spatial divergence over time of derived anion drift velocities while comparing the drift velocities of both cell chemistries. Note that in this case a more pronounced spatial divergence reflects an elevated moving frame velocity. In **Figure 3B,D** six prominent anion drift velocities of three different profiles (belonging to the initial state, after CC and after CV), marking the profiles’ edges, are highlighted, thereby illustrating temporal and spatial evolutions of anion drift velocities. For clarity, all cell lengths are normalized to their numerically evaluated cell region (region of interest: ROI), slightly varying due to electrode size differences of Li metal and NMC622. Hence, at and at lithium metal deposition and stripping/lithium-ion deintercalation (NMC622) occurs. Comparing spatial distributions of anion drift velocities over time, an increase towards the lithium metal cathode (at which lithium plating occurs) and continuous decline over space () is observed for both cell chemistries and at all times. The spatial differences from to are smaller in Li||Li cells (max. spatial difference of ca. 18% at the end of CV) than in Li||NMC622 cells (max. spatial difference of ca. 24% at the end of CV). Enhanced decelerations of anions in Li||NMC622 over space likely due to smaller volume changes of NMC622 electrodes (anions piling up) are suggested. An increase of 6.3% (Li||Li) and 10.5% (Li||NMC622) in anionic velocities at during a constant voltage step (after achieving the mass-transport limitation) can be noticed. During the same time, at a comparable increase of ca. 5% (5.1% and 4.8%) was detected in both cases. All these data strongly imply pronounced lithium dendrite growth in Li||NMC622 cells according to Chazalviel’s model. To evaluate actual Li metal deposition morphologies, *in situ* 7Li NMR spectra were recorded after cell polarizations.

**Morphology of Lithium Metal Deposits**

7Li NMR can be utilized to evaluate morphology changes of lithium metal deposits due to bulk magnetic susceptibility (BMS) differences of the various lithium morphologies. Due to the “Knight-shift" pristine lithium metalcan be assigned to 7Li signals at 245 ppm, mossy and dendritic morphologies induced by lithium metal deposition shift the 7Li NMR signals to higher ppm´s. Typically, signals arising at 260 ppm and 270 ppm are assigned to mossy- and dendritic-shaped lithium metal deposits, respectively.13, 17 Please note, that the ppm shift of different morphologies is due to the orientation-dependency of the BMS to the static magnetic field. The more parallel individual deposits grow with respect to the magnetic field (perpendicular to the electrode surface) the higher the respective 7Li shift. Thus, the assignment of distinct morphologies to certain ppm´s represents rather the general trend than the exact microstructures.13 The exact same cells invoked for the derivation of anion drift velocities are utilized, without disassembly, to derive the impact of anion mass-transport on the respective Li metal morphologies. Note that only the rf-coils were changed (19F 🡪 7Li). To account for bulk magnetic susceptibility changes of the pristine lithium metal and thus shifted 7Li NMR signals attributed to cell insertion/ejection while changing rf-coils, all spectra are referenced internally to the major 7Li signal of pristine lithium metal electrodes at 245 ppm. Slight misadjustments (1 ppm) of cylindrical cell axis and the external magentic field along z-axis are thus compensated (ideally the unit normal vector of electrodes’ reactive sides should match the z-axis).52 *In situ* 7Li NMR spectra of Li||Li and Li||NMC622 cells are shown in **Figure 4**. After cell polarization, broader signals arise next to pristine lithium metal signals and cover a range of shifts, indicating the presence of high-surface area lithium metal deposits (mossy, dendritic etc.). Note that signal intensities of both cells are normalized to the pristine lithium metal signal at 245 ppm~~.~~ Experimentally obtained signals are deconvoluted into three different signals, thereby obtainingfitted 7Li NMR lineshapes that match the experimental data within R2=99.8%. Lineshape deconvolution is carried out without chemical shift constraints to distinguish lithium metal morphology differences in both considered cell chemistries. Shifts of the deconvoluted signals are rounded to nearest whole values. Further, we limit our interpretation to the BMS shifts (center of gravity) of deconvoluted signals, since the counter lithium electrode in Li||Li cells as well as skin-depth effects prevent quantification and comparison of signal intensities (at least in case of pristine lithium metal signals).53 Nonetheless, a comparison of BMS shifts (purple deconvoluted signal) reveals that the lithium metal deposits are more of dendritic shape in Li||NMC622 compared to Li||Li cells since a shift towards higher ppm (268 ppm) can be observed in case of Li||NMC622, while more mossy morphologies at 263 ppm are identified in Li||Li cells. Though, the optimization method invoked (Levenberg-Marquardt) ran without shift constraints (upon deconvolution), two signals at 245 ppm and 250 ppm, respectively are present in both cells~~.~~ While the signals at 245 ppm obviously belong to bulk lithium metal, the signals at 250 ppm might reflect dense lithium metal deposits arising from the nucleation process during the constant current polarization (until Sand’s time has been reached), or can be assigned to asymmetric contributions of the bulk lithium metal signals due to long-range BMS effects of mossy & dendritic shaped lithium metal deposits at even higher ppm´s affecting the symmetry of the bulk lithium signals as previously reported by Bhattacharyya et al. 54 Here, the authors required an additional signal upon deconvolution to account for the mentioned asymmetry of the bulk lithium metal signal. The additional signal is shifted few ppm higher than the pristine Li metal signal, in good agreement with our results. Thus, morphological differences in both cells and a correlation between anionic mass transport and dendrite growth can be reasonably assumed. To further explore the proposed relationship of anion drift velocities and lithium dendrite growth rates a combined approach of *operando* 7Li chemical shift imaging (spatially resolved observation of dendrite growth) and operando 19F MRI anion profiling may provide detailed insights, but is beyond the scope of the present work. Nevertheless, all the required experimental preparations are currently in progress and will be reported in due time.

**Lithium Interphase Evolution – *Dynamic* EIS**

The profile’s edges obtained by frequency encoded 1D MRI are affected by *B*0 inhomogeneities and any eddy currents (due to rf-pulses & z-gradients) induced by the electrodes.55 Thus, we limit our presented numerical approach to anionic concentration profiles within the bulk electrolytes (ROI). Processes occuring directly at the lithium metal interfaces or within the diffusion layer are still obscured, therefore the existence of Chazalviel’s proposed space-charge region20 is not experimentally verified. To gain more insight into the electrode kinetics and mass transport processes in the vicinity of the electrode surfaces, dynamic EIS spectra are recorded simultaneously with *operando* 19F MRI profiling. **D**istribution of **R**elaxation **T**imes (DRT) analysis of operando EIS data are exploited to identify electrochemical processes based on characteristic relaxation time constants .56-58 Mass-transport-related changes within electrolytes observed by MRI are complemented by electrode inter-phase processes (e.g. charge-transfer, double layer or diffusion layer effects), so that time constants in the range of are explicitly considered. Note that the time-consuming low frequency EIS experiments (< 1 Hz, ) are neglected to reduce acquisition times of individual EIS spectra, as this is required for *operando* experiments, in which time invariant state-of-charge conditions upon EIS acquisition are necessary. **Figure 5B,E** displays normalized DRT functions during polarization (CC/CV) and normalized resistances (**Figure 5C,F**) resulting from the integrated DRT functions. Normalized resistances reflect intersections of RC-semi-circles with the *Z’*-axis in Nyquist plots. Similar to the derived anion drift velocities, the normalized DRT functions *h* increase at the end of each CC step in Li||Li and Li||NMC622 cells, and increase further during the CV step, while all peaks at shift towards lower time constants. A shift in time constants might be attributed to morphological changes of Li metal deposition and is currently being investigated. A continuous growth of interphase resistances monitored during the CV steps and a sudden decrease of interphase resistances after the CV step (**Figure 5C,F**) are noted in both cell chemistries, indicating dynamic interphase processes (e.g. varying size of diffusion layers). Also, resulting resistances of interphase processes are increasing upon CV, eventually approaching constant slopes, but no steady-state condition is reached, indicating continuous changes of all the underlying interphasial processes. Both, increase and continuous changes over time are consistent with transient evolution of anion drift velocities during CC/CV polarization, illustrating that non-stationary electrode kinetics cause non-stationary anionic mass-transport, which is observable by MRI. The non-stationary changes of the corresponding anion drift velocities during CV polarization likely reflect contributions from both moving boundaries (i.e. volume changes of the electrode) and ongoing changes of interphasial processes. Furthermore, resistances are usually associated with Ohmic contributions, which have been neglected when considering concentration overpotentials as part of resulting voltages (eq. 8). Interphase resistances typically include interphasial processes from both electrodes, so that accounting for both electrodes in Li||Li cells contributing equally to the actual interphase resistances, the interphase resistance of a singular electrode in Li||Li cells is half of the total. Even under these terms, the measured interphasial resistances in Li||Li cells are still higher than in case of Li||NMC622 cells ( 15 kOhm cm-2 vs. 10 kOhm cm-2 at the end of CV steps). Thus, the observed trend in anion drift velocities and hence Li dendrite growth ( is not affected by higher ohmic resistances. Note that capacitive impedances are also increasing during CC/CV steps.

**Methodological Restrictions and Broader Applicability**

The calculated anion drift velocities are derived from a dilute solution approach. To extend the applicability to a variety of polymer electrolyte systems, concentrated solution theory might be invoked. To this end, Chazalviel’s model needs to be derived from concentrated solution theory to demonstrate that the correlation of anion drift velocities and lithium dendrite growth is still valid. Eq. 10 might be used to describe anionic mass-transport in concentrated binary electrolyte systems composed of anions, cations and solvent (without convection):

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| --- | --- |
|  | (10) |

where are describing the total number of cations and anions produced by dissociation of one molecule electrolyte, , and represent the electrochemical potential of the electrolyte, the anionic transference number with respect to the solvent velocity and the current density, respectively. Please note, that Maxwell-Stefan diffusion needs to be considered rather than Fickian diffusion. For further details, please see chapter 12 (“Concentrated Solutions”) of Newman’s and Balsara’s 4th edition “Electrochemical Systems”.50

So far, morphological changes of Li metal have been described by various models covering distinct cycling conditions of LMBs, but often suffered from lack of experimental accessibility. Herein, a combined approach of *operando* 1D 19F MRI anion concentration profiling, *in situ* 7Li NMR and dynamic EIS is introduced to experimentally examine anionic mass-transport and inhomogeneous dendritic Li metal deposition, since the well-known model derived by Chazalviel correlates anionic drift velocities with growth velocities of a ramified lithium deposition front under mass-transport limited conditions. The model is often invoked for the development of next-generation solid-state polymer-based electrolytes for LMBs, in which mass-transport limitations occur due to limited ionic conductivities of solid polymer electrolytes. Based on our presented numerical approach, anion drift velocities within the bulk electrolyte are derived from *operando* 1D 19F MRI anion profiles in Li||Li and Li||NMC622 cells while charging the batteries and accounting for non-stationary mass-transport. Under mass-transport limited conditions (that is, at fast-charge conditions or higher current densities), a sudden increase in anion drift velocities up to several hundreds of μm/h is observed in both cell setups. The magnitude of derived anion drift velocities is in good agreement with previously observed dendrite growth velocities under mass-transport limited conditions supporting the proposed correlation between anionic mass-transport and dendrite growth velocity by Chazalviel’s model. Also, the respective anion drift velocities in Li||NMC622 cells exceed the anion drift velocities in Li||Li cells, which is most likely attributable to the higher operating cell voltage applied in case of NMC-type cathodes (3.0 V-4.2 V instead of 0 V-1.5 V). Due to the introduction of a NMC-type cathode electric-field contributions might become more dominant with respect to the ionic mass-transport, which might additionally be reflected by the observed delayed Sand’s time in case of in Li||NMC622 cells. Beyond that, spatial distributions of anion drift velocities are observed in both cases, while the spatial differences are more pronounced in Li||NMC622 cells. Subsequent *in situ* 7Li NMR spectra revealed Li metal deposits of more dendritic shape in case of Li||NMC622 compared to Li||Li cells. The elevated anion drift velocities and more pronounced dendrite growth rates are in agreement with Chazalviel’s model. In addition, DRT analysis of dynamic EIS spectra showed a reversible, but non-stationary increase in interphasial impedances (charge-transfer, double and diffusion layer effects) under mass-transport limited conditions, highlighting that metal deposition kinetics affect long-range (anion) mass-transport processes within bulk electrolytes (as observed by MRI). In both cases, a shift in relaxation times (DRT) of interphasial processes towards higher values indicates morphological changes of the metal deposition once mass-transport limitation conditions are established. In summary, the invoked experimental setup and numerical approach afford experimental accessibility to Chazalviel’s dendrite growth model and rates of metal deposition, revealing mechanistic insight to morphological changes of (Li, Na, etc.) metal deposits, depending on the actual conditions of cell operation. The anion drift velocity might be used as a performance indicator for polymer-based solid-state LMBs to evaluate reversibility of lithium inventory and thus capacity retention of LMBs. Adjusting anion drift velocities in the bulk electrolyte by optimizing anion and cation mass transport within the diffusion layer of Li metal electrodes, e.g., by incorporating single-ion conductors as artificial SEIs or by facilitating more homogenous electrode kinetics via optimized SEI formation (additives) or more advanced pretreatments of the lithium metal electrode, will permit a more tailored design of polymer electrolytes and coatings. This method portfolio gives access to these decisive anion drift velocities for the first time, and paves the way to faster charge applications of polymer-based (Li, Na etc.) metal batteries. It is noted that incorporation of *operando* (7Li) chemical shift imaging to the protocol in principle further extends the portfolio of accessible observables, mitigating current challenges of metal-based cell chemistries.

**EXPERIMENTAL PROCEDURES**

***NMR Setup for operando & in situ Experiments***

Simultaneous utilization of *operando* anion concentration MRI profiling and *operando* electrochemical impedance spectroscopy of solid-state Li||Li and Li||NMC622 cells with crosslinked PEO electrolyte is performed. All the NMR spectra were recorded on a BRUKER Avance III 4.7 T Spectrometer using a modified BRUKER Diff50 probe and a 10 mm 19F insert for 1D 19F MRI profiling, a 10 mm 7Li insert for 7Li NMR spectra and a 5 mm 7Li/19F insert for PFG experiments. The temperature was controlled with BRUKER BCU20 temperature units and kept at 40 °C for all the experiments. Since a TC1 thermo-couple of the commercial BRUKER probe was changed to a DC/AC-current lamella connector, the corresponding sample temperatures were calibrated based on data from an external thermo couple (+/- 0.02 °C). Similar to previous works,39, 59 a home-built cylindrical PEEK model cell housing was manufactured with a PEEK 3D printer (Apium P220).

***Operando* 1D 19F anion concentration MRI profiling.**

Operando 1D 19F anion concentration MRI profiles were acquired with a frequency-encoded and modified BRUKER ‘diffprof’ pulse program capable of constant pulse and receiver phases. To enclose the full cell stack, the field-of-view (FOV) was adjusted to 4 mm. A bandwidth of 100 kHz was selected to decrease the sampling time of *k*-vectors and avoid profile deformation at higher bandwidths, resulting in maximum gradient strengths of 62.4 G cm-1. 128 gradient steps (derived from the complex time domain, bandwidth and group delay) were applied, yielding an echo acquisition time of 1.48 ms and a nominal spatial resolution of 31.25 μm. With an echo delay of 160 µs, a recycle delay of 4 s and 128 scan repetitions, a single MRI profile was recorded within 8 min and 33 s. Note that the rf-field strength was set to 18181 Hz, corresponding to a π/2-pulse length of 13.25 μs. All the spectra were evaluated in BRUKER Topspin 3.5pl7 (magnitude mode and Fourier transformation) and further processed with an in-house custom-made MATLAB script.

***In situ* 7Li NMR spectra**

Static 1D 7Li spectra were recorded with a custom-made electrolyte suppression Hahn echo pulse program. To facilitate data evaluation (deconvolution) magnetization at around 0 ppm was averaged by pre-saturation (200 repetitions of a ‘sinc’-shaped pulse) prior to applying a common Hahn echo pulse program with short echo delays of 20 ms. The transmitter frequency was changed from 0 ppm (presaturation) to 255 ppm (Hahn-echo) during one repetition while the rf-power changes from a selective pulse (= 714 Hz) to a more broadband pulse (= 18181 Hz). 1024 repetitions and a recylce delay of 0.4 ms resulted in an experimental time of 8 min and 15 s. All spectra were internally referrenced to lithium metal (set to 245 ppm13). The 7Li spectra were acquired 1 h after obtaining the last 1D 19F MRI profile. Fast Fourier transformation and phase correction were done in BRUKER TopSpin 3.5pl7, whereas spectral deconvolution was done with dmfit software59. Note that no baseline correction was required.

***Dynamic* electrochemical impedance spectroscopy (EIS) and cell polarization**

All electrochemical experiments were carried out with a Zahner Zennium Pro galvanostat with an integrated EIS module and proprietary Thales software. *Operando* EIS test procedures consisted of four consecutives ‘direct current' (DC) steps while acquiring EIS spectra: 1. an open circuit voltage (OCV) step for 2.5 h (thermal equilibration), 2. a constant current (CC) step, 3. a constant voltage (CV) step for 5 h and 4. an OCV step for 2.5 h. A current density (CC step) of 0.1 mA cm-2 and a constant voltage (CV step) of 1.5 V for Li||Li or 4.3V for Li||NMC622 cells were applied. The CC steps ended when the voltage of the set constant voltage was reached (1.5 V or 4.3 V), whereas CV steps were only limited by time (5 h). The applied current densities (0.1 mA cm-2) and constant voltages were set sufficiently high to induce electrolyte mass-transport limitation of electrode reactions, in particular for lithium metal plating. This condition was noted based on a sudden voltage increase during CC steps. In case of Li||Li cells, this sudden voltage increase can be directly related to mass-transport limitations, whereas for Li||NMC622 cells, a comparison of open circuit voltages before and after CC/CV steps was additionally required to exclude capacity limitation from cathodes. Applying constant voltages of equal magnitude (compared to the last measured voltages at the end of each CC step) maintained a mass-transport limit for lithium metal plating over time. At the end of each 19F MRI anion profile acquisition, impedance spectra were recorded so that the experiments ended simultaneously. During the CC and OCV steps, the corresponding AC amplitude of the galvanostatic impedance experiments were set to one third of the applied DC current density, thus achieving reasonable impedance spectra without interfering with the state-of-charge. An AC amplitude of 50 mV was utilized for potentiostatic impedance experiments during the CV step. All impedance spectra were recorded in a frequency range from 1 Hz to 100 kHz resulting in an experimental time for each EIS spectrum of 1 min and 9 s (6 steps per decade and 4 repetitions). Experimental data were exported and analyzed by home-made python scripts to derived normalized distribution functions of relaxation times (DRT-analysis) as described elsewhere.61-62 Using a regularization parameter of 0.5 as well as 92 number of time constants, Kramers-Kronig residuals56 of less than 3 % were achieved. Relaxation times in a range from 1 s to 0.1 ms were assigned to electrode interphase processes, so that changes of the normalized distribution functions reflect changes within electrode interphases due to electrode reactions.56

**PFG NMR**

To determine 19F self-diffusion coefficients, a concentration series of LiTFSI in crosslinked PEO was prepared and measured using a double-tuned 5 mm 7Li/19F insert and a stimulated echo pulse sequence. 3 M KF in H2O was utilized for external calibration. The rf-power was set to 21276 Hz, the maximum gradient strength to 2946 G/cm, the diffusion time Δ to 60 ms, the gradient pulse length δ to 1 ms and the recycle delay to 6 s. Each of the 16 gradient steps were averaged from 16 scans. Self-diffusion coefficients of the fluorine species (anions) were derived from a stimulated echo sequence (BRUKER ‘diffSte’) after fitting the overall attenuated signal amplitudes (integration) to the Stejskal-Tanner equation that describes the case of ideal isotropic diffusion.

**Materials and cell assembly**

The introduced combination of *operando* techniques was applied to two cell systems. System 1 was a symmetric Li||Li solid-state battery, whereas system 2 represented a Li||NMC622 solid-state battery. Note that the actual operating voltage denoted the major difference among both cells. All cells were assembled within a MBraun glovebox (with values of <0.1 ppm O2, <0.1 ppm H2O, <0.1 ppm CO2).

**Electrode preparation**

Composite NMC622 (c-NMC622) cathodes were prepared by a slurry-based approach incorporating an interpenetrating polymer-based electrolyte system63 to afford good contacts of active material and polymers. The electrodes consisted of 60 wt % NMC622 (BASF), 10wt % carbon black (Super P, Targray) and 30 wt% electrolyte comprising LiTFSI (3M, predried), PEO (Mw = 400 kDa, Sigma-Aldirch) to PEGdMA (Mw= 750 Da, Sigma-Aldrich, pre-dried) mass ratio of 1:0.45 as well as a PEGdMA to AIBN (Sigma-Aldrich) mass ratio of 1:10 resulting in a molar EO:Li ratio of 10:1. They were produced by first dissolving PEO and PEGdMA in acetonitrile (400 wt% of total electrode mass) followed by the addition of NMC622, carbon black, LITFSI and AIBN. The mixture was homogenized using a VMA-Getzmann CV3-plus dispermate (2000 rpm for 2 h at 15°C). Then, the slurry was cast on aluminum foils using doctor blading prior to transferring the electrode sheets to a vacuum oven (Binder vacuum oven). Acetonitrile was evaporated at reduced pressure (10-3 mbar at 25 °C for 12 h) followed by polymerizing PEGdMA at 80 °C under N2 flux for 2 h, and subsequently drying for 12 h at 80°C at reduced pressure (10-3 mbar). Average cathode active mass (CAM) loading was set to 8.0 mg cm-2, sufficiently high to avoid capacity limitations during *operando* measurements. Before the cell assembly, all the electrodes were dried under high vacuum (10-7 mbar) and transferred to a glovebox. As received 300 µm Honjo Li metal (stored in a glovebox, <0.1ppm O2, <0.1ppm H2O, <0.1ppm CO2) was used as Li metal electrode for both systems.

**Electrolyte preparation and cell assembly**

For solid-state LMBs, a crosslinked PEO-based polymer electrolyte was manufactured as described previously64. Electrolyte preparation was conducted in a dry room atmosphere (dew point < -65°C). 0.605 g PEO (5 Mio Da, Sigma-Aldrich) was mortared with 0.395 g LiTFSI (EO:Li = 10:1, purchased from 3M) and 0.05 g benzophenone initiator (TCI Germany). The mixture was formed to a ball, vacuumed sealed and heated to 100 °C for 24 h to ensure homogeneity. Regarding the concentration series, only the amount of LiTFSI was changed. The homogenized balls were hot pressed to 100 μm thin membranes at 100°C and 10 bar for 5 min and subsequently at 100 °C and 100 bar for 5 min. 5 min UV curing (Hönle UVA 100 cube) completed the membrane preparation. For the MRI cells, 65 mg of the homogen~~e~~ized balls was filled in a dummy cell consisting of a cell sleeve and two dummy plugs (without current collectors) to enclose a volume of 1.5 mm in height and 6 mm in diameter (volume of cell sleeve, see **Figure 6**), preventing lithium dendrites from short circuiting the cell and facilitating acquisition of distortionless MRI intensity profiles of bulk electrolytes. The cells were vacuum sealed (pouch foil) and heated to 100 °C for another 1.5 h to create cylindrical (6 mm diameter) polymer electrolyte pellets of 1.5 mm height (= active volume). Afterwards, the dummy cells were cooled to room temperature (= 21°C) and the dummy plugs were carefully removed from the cells to crosslink the polymer electrolyte based on 5 min UV curing (Hönle UVA 100 cube). The cell housings with the polymer electrolyte pellets were then dried at reduced pressure (10-7 mbar) and transferred to a glovebox for cell assembly. 6 mm (diameter) electrodes were added to the cells (Li||Li or Li||NMC622) and closed by pre-assambled plugs. Added electrodes were slightly pressed into the soft polymer electrolyte to ensure interfacial contact.65 The internal pressure was released by heating the cell up to the operating temperature of 40 °C as parts of the polymer-based electrolytes were squeezed past the electrodes (visible as small intensities next to the main anionic MRI profiles, see **Figure 6**). To counteract volume changes of the polymer electrolyte during heating, two beryllium copper disc springs with stroke distance of 0.15 mm each surrounded by two 1 mm thick contact plates ensuring electrical contact were included. In this way, a cylindrical measurement volume of minimum 6 mm in diameter times 1.5 mm in height was available. Due to the disc springs, a measurement volume of maximum 6 mm in diameter and 1.8 mm in height was guaranteed. Electrode’s thicknesses of 300 μm (Li metal) and 80 μm (NMC622) as well as malleability of the polymer electrolyte at 40°C have to be considered to estimate the measurement volume of the MRI experiments (see ROIs).

**Resource Availability**

*Lead Contact*

Further information and requests for materials, datasets, scripts and more should be directed to and will be fulfilled by the Lead Contact, Gunther Brunklaus (g.brunklaus@fz-juelich.de).

*Materials Availability*

Composite cathodes as well as MRI cell components generated in this study are available from the Lead Contact on request.

*Data and Code Availability*

The datasets and MATLab script generated during this study can be downloaded here: <https://doi.org/10.5281/zenodo.14103250>

The DRT script is available here: <https://doi.org/10.5281/zenodo.14067949>

Technical drawings of the MRI cell are available on request.

**SUPPLEMENTAL INFORMATION**

Document Supplemental Information. Supplemental Experimental Procedures and Data Evaluation, Supplemental Notes S1-S3.

Supplemental Note S1. Numerical Derivation of Anion Drift velocities from *Operando* 1D 19F MRI Anion Profiles.

Supplemental Note S2. 19F PFG NMR of a PEO/LITFSI concentration series

Supplemental Note S3. Error estimation S3 of numerically derived anion drift velocities

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**AUTHOR CONTRIBUTIONS**

Conceptualization: J.H.T and G.B.; Formal Analysis, Investigation and Methodology: J.H.T.; DRT examination: P.L. and J.H.T., Visualization and writing – original draft: J.H.T; writing – review & editing: J.H.T., M.M.M, P.L., G.B., and M.W.; supervision: G.B. and M.W.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

**FIGURES, TITELS AND LEGENDS**

**Figure 1. Introduction. Chazalviel’s model of dendritic lithium metal deposition.**

While charging LMBs, anions are drifting away from the lithium electrode where Li metal deposition occurs. A correlation of anionic mass-transport and Li dendrite growth is suggested by Chazalviel’s model. The growth velocity of dendritic lithium is equivalent to the anion drift velocity in bulk electrolyte. The nature of the electrode & electrolyte properties (incl. SEI) determine how fast anions are drifting within the bulk electrolyte.

**Figure 2. Introduction. Schematic representation of the experimental *operando* setup.**

Upon charging, anion drift velocitiesare obtained from numerical evaluation of corresponding anionic 1D 19F MRI concentration profiles *C*a(*x,t*)*.* At some point, anion depletion towards the negative pole (Li metal deposition: Li+ + e- 🡪 Li) is observed. Simultaneously, the electrodes’ interphase impedances are determined by dynamic EIS experiments and subsequent DRT-analysis. All obtained anion drift velocities and interphase impedances are correlated to the present morphologies of Li metal deposits monitored by *in situ* 7Li NMR.

**Figure 3**. **Anion drift velocities in Li||Li and Li||NMC cells upon charging.**

CC/CV-polarizations and derived anion drift velocities of Li||Li (A,B) and Li||NMC622 cells (C,D). Negative anion drift velocities indicate anion movement against the applied electric field. In both considered cases a sudden increase in drift velocities at the end of each CC-step was observed.

**Figure 4**. **Morphology of lithium metal deposits Li||Li and Li||NMC after charging.**

*In situ* 7Li NMR spectra of Li||Li and Li||NMC622 cells, immediately measured after polarization and the last OCV step. Three morphologies of Li metal deposits are accounted for. The deconvolution succeeded without chemical shift constraints to identify morphology differences. In both cases, deconvoluted line-shapes fit within R2=99.8%. More dendritic lithium metal deposition is observed in Li||NMC622 compared to Li||Li cells.

**Figure 5**. **Lithium interphase evolution – *Dynamic* EIS.**

CC/CV-polarization and DRT plots of Li||Li (A,B) and Li||NMC622 cells (D,E), respectively. C) and F) represent the integrated areas of B) and E) vs. time. The color code in B) and E) corresponds to selected operando EIS experiments equally separated in time (step size of CV equals five times CC step size). Relaxation times in the range of are attributed to processes at electrode interphases.

**Figure 6**. **Electrolyte preparation and cell assembly.**

Schematic representation of a MRI cell (top). Its outer diameter is 10 mm, the inner diameter (measurement volume) amounts to 6 mm. Within the measurement volume, the cell stack (e.g. Li|electrolyte|Li) is located. For the sake of clarity, electrolyte and electrodes are colored blue and grey. The insert at the left exhibits an exemplary 19F 1D anionic MRI intensity profile.

**Figure 7. Graphical Abstract.**

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