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Thema:

**Metallic fleece enabling thick lithium-ion electrodes by
ultrafast metal surface ion diffusion**

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To my mom

ABSTRACT

Lithium battery cells suffer from limited lithium-ion mobility and high internal electrical resistance. Therefore, standard cells require electrodes with a thickness of less than 100 μm to keep charge carrier paths in the electrodes short and enable charging. As a consequence, today's rechargeable batteries are overcomplex in design and carry lots of material which does not contribute to energy density, e.g. metal foils and separators. Therefore, it is tempting to insert a compound that can provide shortcuts for fast electron transport and fast ion transport within electrodes of rechargeable batteries. For the first time, this work describes electrochemically-functional, ultra-thick anodes of up to 1.2 mm and 32 mAh/cm^2 areal capacity. Common thin metal foil current collectors are replaced with an elastic, truly 3-dimensional fleece made of ultrafine copper fibers. The fleece electrodes use half of the copper amount in comparison to traditional foil-based electrodes and therefore provide significantly higher volumetric and gravimetric energy density. Experiments demonstrate an increased lithium-ion diffusivity in ultra-thick anodes, possible due to perfect infiltration of the metal fleece into the active material which adds channels for ultrafast lithium-ion diffusion through the entire active material. A microfluidic chip in combination with Raman spectroscopy and molecular initio-dynamics quantitatively and mechanistically demonstrate the increased lithium-ion diffusivity on the charged copper surfaces. This demonstrates a new, previously unknown mechanism for enhancing the diffusivity of lithium-ions which enables ultra-thick electrodes by simultaneously increasing energy density. Moreover, this discovery enabled the construction of functional full cells. By applying 3D metal fleece on anode and cathode side, a battery with $\sim 10 \text{ mAh}/\text{cm}^2$ area capacity is successfully constructed. Due to the low electrical and diffusive resistance, the full coin cells are able to provide high energy density and relatively high-power density at the same time.

The enhancement of energy transport and mass transport achieved by embedding the metallic fiber network into the active material enables us to build functional ultra-thick electrodes with high areal capacity. Towards further developing and optimizing this novel electrode design, I performed a physical-based mathematical modeling study of the electrode with a battery digital twin, which provides deeper insights into underlying mechanisms and provides the means to evaluate and predict the battery's charging/discharging performance, cycling stability, cell heat dissipation, and degradation behavior under various operational conditions. Building on this data a structural and morphological optimization of the electrode can be carried out, including the optimization of the geometry of the metal fibers, fleece density, fiber orientation, active material filling, and more.

ZUSAMMENFASSUNG

Lithium-Ionen-Batteriezellen leiden unter begrenzter Lithium-Ionen-Mobilität und hoher interner elektrischer Widerstand. Daher benötigen Standardzellen Elektroden mit einer Dicke von weniger als 100 μm , um die Ladungsträgerwege in den Elektroden kurz zu halten und das Laden zu ermöglichen. Als Folge davon sind die heutigen wiederaufladbaren Batterien im Design überkomplex und enthalten viele Materialien, die nicht zur Energiedichte beitragen, wie z. B. Metallfolien und Separatoren. Daher liegt es nahe, eine Verbindung einzuführen, die schnelle Elektronen- und Ionenströme innerhalb der Elektroden von wiederaufladbaren Batterien ermöglicht. Zum ersten Mal beschreibt diese Arbeit elektrochemisch funktionale, ultra-dicke Anoden von bis zu 1,2 mm und einer arealen Kapazität von 32 mAh/cm². Übliche dünne Metallfolien-Stromabnehmer werden durch ein elastisches, tatsächlich dreidimensionales Vlies aus ultrafeinen Kupferfasern ersetzt. Die Vlies-Elektroden verwenden im Vergleich zu traditionellen Folien-basierten Elektroden nur die Hälfte der Kupfermenge und bieten daher eine deutlich höhere volumetrische und gravimetrische Energiedichte. Mit der galvanostatischen intermittierenden Titrationstechnik zeigt die Arbeit eine erhöhte Lithium-Ionen-Diffusivität in ultra-dicken Anoden, die aufgrund der perfekten Infiltration des Metallvlieses in das aktive Material möglich ist. Dies fügt Kanäle für ultrafast Lithium-Ionen-Diffusion durch das gesamte aktive Material hinzu. Ein mikrofluidisches Chip in Kombination mit Raman-Spektroskopie und molekulardynamischen Simulationen demonstriert quantitativ und mechanistisch die erhöhte Lithium-Ionen-Diffusivität auf den geladenen Kupferoberflächen des Vlieses durch die Bildung einer Helmholtzschen elektrischen Doppelschicht. Dies demonstriert einen neuen, bisher unbekannten Mechanismus zur Erhöhung der Diffusivität von Lithium-Ionen, der ultra-dicke Elektroden ermöglicht, indem gleichzeitig die Energiedichte erhöht wird. Darüber hinaus ermöglichte diese Entdeckung den Bau funktioneller Vollzellen. Durch die Anwendung von 3D-Metallvlies auf der Anoden- und Kathodenseite wurde erfolgreich eine Batterie mit ~10 mAh/cm² Areal-Kapazität konstruiert. Aufgrund des niedrigen elektrischen und diffusive Widerstands sind die vollständigen Münzzellen in der Lage, gleichzeitig eine hohe Energiedichte und eine relativ hohe Leistungsdichte bereitzustellen.

Die Verbesserung des Energie- und Massen-Transports, die durch die Einbettung des metallischen Fasernetzwerks in das aktive Material erreicht wird, ermöglicht den Bau funktionaler ultra-dicker Elektroden mit hoher arealer Kapazität. Zur Weiterentwicklung und Optimierung dieses neuartigen Elektrodesigns habe ich eine physikalisch basierte mathematische Modellierung der

Elektrode mit einem digitalen Batteriezwilling durchgeführt, der tiefere Einblicke in die zugrunde liegenden Mechanismen bietet und die Möglichkeit gibt, die Lade-/Entladeleistung, Zyklenstabilität, Zellwärmeabgabe und das Degradationsverhalten unter verschiedenen Betriebsbedingungen zu bewerten und vorherzusagen. Aufbauend auf diesen Daten kann eine strukturelle und morphologische Optimierung der Elektrode durchgeführt werden, einschließlich der Optimierung der Geometrie der Metallfasern, der Vliesdichte, der Faserausrichtung, der Befüllung mit aktivem Material und mehr.

LIST OF ABBREVIATIONS

LiBs	Lithium-ion Batteries
SiBs	Sodium-ion batteries
CBP	Conductive binder phase
EDL	Electrical double layer
GITT	Galvanostatic intermittent titration technique
CAGR	Compound annual growth rate
3D CC	3-dimensional current collector
CNT	Carbon nanotube
SOH	State of health
SOC	State of charge
LFP	lithium iron phosphate, LiFePO_4
NCM	Lithium-nickel/cobalt/manganese oxide
SEI	Solid electrolyte interphase
EC	Ethylene carbonate
DMC	Dimethyl carbonate
DEC	Diethyl carbonate
EMC	Ethyl methyl carbonate
PC	Propylene carbonate
FEC	Fluoroethylene carbonate
VC	Vinylene carbonate
EIS	Electrochemical impedance spectroscopy
CEI	Cathode electrolyte interphase
CVD	Chemical vapor deposition
FEM	Finite element method
FVM	Finite volume method
DFN	Doyle Fuller Newman model
AH	Asymptotic homogenization
FHM	Fully homogenized model
RVE	Representative volume element
AM	Active material
CB	Carbon black
CMC	Carboxymethyl cellulose
SBR	Styrene butadiene rubber
PVDF	Polyvinylidene fluoride
CC	Constant current
CV	Constant voltage
OCV	Open circuit voltage
μ -CT	Micro-computed tomography
PDMS	Polydimethylsiloxane
CIP	Contact ion pair
SSIP	Solvation separated ion pair
PTFE	Polytetrafluoroethylene
MD simulation	Molecular dynamic simulation
EDL	Electrical double layer
P2D	Pseudo 2 dimensional
RMSE	Root mean squared error
LMB	Lithium metal battery

LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
LiFSI	lithium bis(fluorosulfonyl)imide
SEM	scanning electron microscopy
Rpm	revolutions per minute
UV	ultraviolet
NMP	N-Methylpyrrolidone

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I BACKGROUND AND MOTIVATION

Renewable energy sources, such as wind, solar and hydropower have been developed intensively in recent years and have become established alternatives to major fossil energy sources that emit greenhouse gasses. Secondary battery systems like lithium-ion batteries, which convert chemical energy to electric energy, feature zero-emission properties, a compact design, and considerable energy density (**Figure 1**⁹). Since their first market introduction in 1991, LiBs have achieved great success with their broad applications in portable electronic devices, grid storage systems, and electric vehicles. In 1991 Sony Corporations commercialized the first LiBs under the lead of Yoshio Nishi. This battery employed soft carbon (rather than graphite) as the anode material and LiCoO_2 as the cathode material. Since then, publications about electrochemical power sources have increased exponentially.¹⁰ In the past 30 years the global batteries market as well as the demand have grown exponentially. In 2014 the battery market size was US \$62 billion doubling to US \$120 billion in 2019. Global battery consumption is anticipated to increase fivefold in the next ten years¹. LiBs are projected to reach a value of US \$53.8 billion by 2024, with a compound annual growth rate (CAGR) of 11% between 2019 and 2024. Meanwhile, intensive research has focused on improving LiB intercalation compounds, the conductive binder phase, the electrolyte, and the membrane, resulting in a 3-fold increase in the volumetric energy density with a 10-fold decrease in costs since 1991.¹¹ In 2019 the significant societal impact of this technology was recognized by the Nobel Prize in Chemistry.

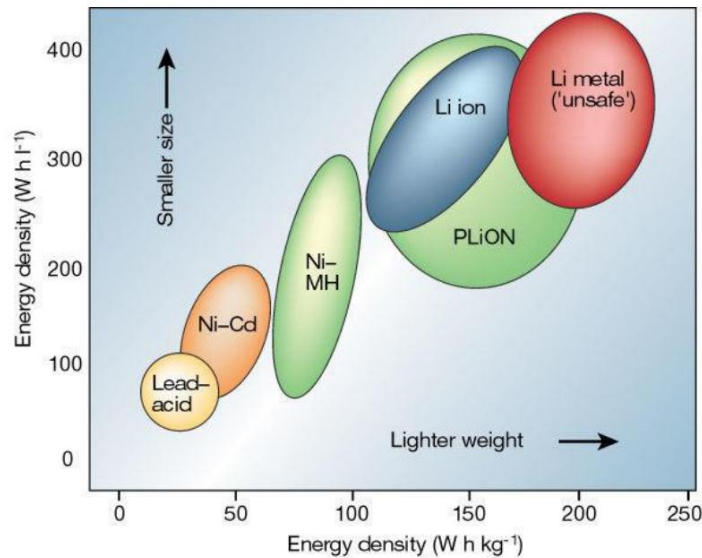


Figure 1. Ragone plot comparing different battery technologies in terms of volumetric and gravimetric energy densities⁹.

Considering the urgent demand to achieve carbon neutrality and a rapid electrification of the transportation sector, further optimization of LiB technology is essential to meeting the ever-increasing need for high energy and high-power technology. Towards this end, research has focused on improving material chemistry, battery configuration, and nanostructure design. These efforts can be assigned to two main categories⁶:

1. The exploitation of possible chemistries: the development of different materials for insertion, which are able to influence and optimize electrochemical processes;
2. Architectural design: improving the morphology and characteristics of the intercalated material, separator, electrolyte, and current collector with a focus on reducing mass diffusion path lengths and increasing the electron and ion transport abilities.

The latter research is generally able to provide a more general solution with transferability to many chemistries and materials. Although advances in the material and chemical design have been achieved, there often remains a discrepancy between the expected and actual behavior of the active compounds, resulting in undesired internal resistance and significant energy losses of the constructed batteries. This presumably originates from restrained kinetic behaviors, which is why a comprehensive understanding of mass and energy transport kinetics over multiple length scales and time scales is imperative to improving the architectural design of the whole system in the quest for high energy, high power batteries with long-term stability.

On the one hand, increasing electroactive material loading (and thereby decreasing the ratio of passive components) has been widely adopted as the most straightforward approach to reach the high energy density goal; on the other hand, the increase of electroactive material has created new challenges like poor mechanical stability, and most importantly, high polarization. Intensive studies^{6,12,13} have revealed that in thick electrodes polarization is predominantly caused by diffusive resistance rather than electrical resistance, because the convoluted ion pathways in the vertical direction lead to a sluggish mass transport of lithium. Therefore, recent research has focused on establishing a deep and reliable temporal and spatial understanding of the transport mechanism, while seeking solutions to improving transport kinetics. For example, Lu et al. developed a fast-charging LiB with a dual-gradient structural design,¹⁴ which optimizes the lithium-ion path within the pore structure, Tsuda et al¹⁵ used a laser drill technique to generate a lithium-ion shot path in the vertical direction, and Ming Jiang et al¹⁶ synthesized a Ni-rich layered-oxide cathode material to enhance Li-ion diffusion within the active materials. All of these studies are devoted to establishing a breakthrough towards achieving a combination of high energy density and high-power density (**Figure 2**). Research has also clearly shown that a profound and reliable understanding of transport kinetics is essential for the creation of thick electrodes. This thesis provides an integrated and detailed understanding of transport kinetics on multiple length and temporal scales as well as data obtained from experiments and simulations characterizing these novel batteries.

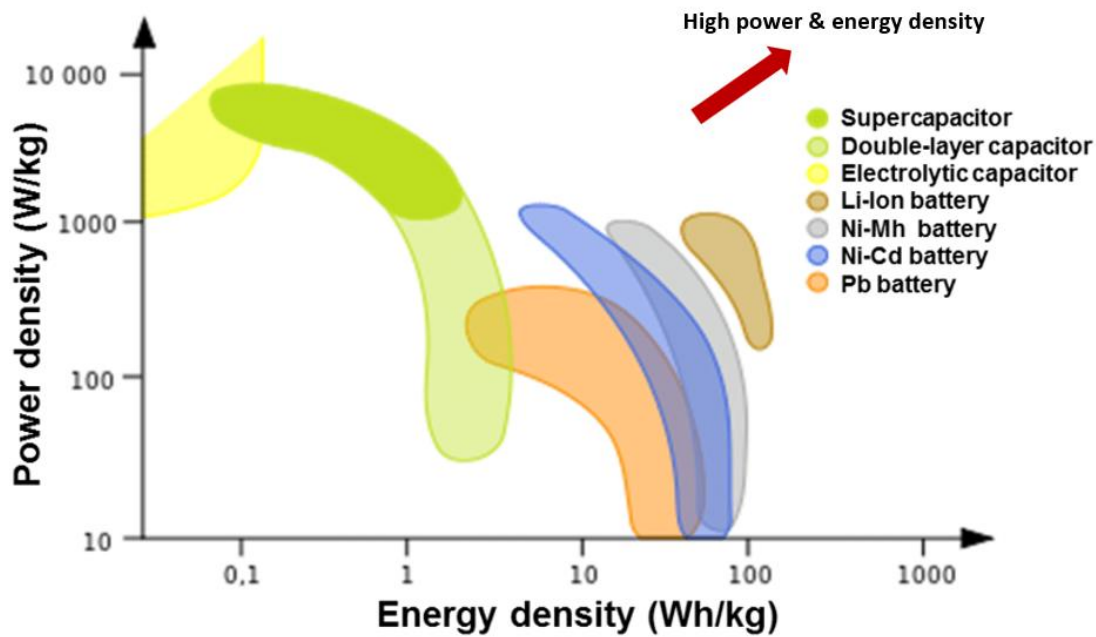


Figure 2. Energy and power density of various energy storage devices.

Of the different types of architectural designs, 3-dimensional current collectors (3D CC) have presented themselves as a very promising solution, as they are able to not only enhance transport kinetics but also provide a scaffold with high mechanical stability for thick electrodes^{17–20}. As an important component of the battery, current collectors in both the anode and cathode are used to support the active material, deliver electrons between active material and external circuits, and homogenize the heat dissipation in the electrode film. In a typical LiB current collector are made of metallic foils in order to achieve certain electrode characteristics: (1) freestanding and self-supporting, (2) mechanically robust, (3) electronically and thermally conductive, (4) electrochemically inert as well as (5) light weight and low cost. Based on these considerations, aluminum foil is typically selected as the cathode current collector. This is due to its low price and because the dense oxidation layer of aluminum that develops during operation has a high stability at high working potentials versus Li/Li^+ . This is in contrast to the anode side, where the working potential is in the range of 0.01V to 0.25V versus Li/Li^+ and electrochemical oxidation of the collector does not occur. For the anode copper foil is commonly selected to avoid any alloying reactions. Reducing the mass fraction of the current collectors, which are inactive components within the battery, can be an effective method for increasing the energy density. Nonetheless, the mechanical stability of the battery must not suffer at the expense of a light-weight design. For thick electrodes the utilization of a foil structure is unsuitable, because the material tends to crack and sluggish transport kinetics limit the performance of the electrodes. Recently, 3D current

collectors have been described as an effective way to achieve mechanically stable thick electrodes, as they have the ability to enhance electronic transport by establishing a percolation path and enhancing the ion diffusion rate by modifying the ion pathway tortuosity. In these batteries carbon and metal are widely used materials for 3D current collectors to ensure inertness.

Carbon-based 3D architectures have significant advantages in LiBs, due to several factors. The 3D carbon architecture helps to anchor high-capacity active cathode materials. This conductive scaffold's high surface area and porous structure, which supports the creation of a continuous conductive network²¹, results in a high mass loading. In addition, the carbon architecture can also be employed as a host for Li^+ . This supports very stable cycling and suppresses dendritic Li growth²². Other advantages include the low cost and light weight of 3D carbon-based materials. Crosslinked carbon nanotubes and graphene foam are now widely used to accommodate the active material²³. Here, the type of connections and pore structure both play an essential role. Crosslinking the carbon constituents through covalent bonding, rather than relying on connections through van der Waals forces, significantly enhances the electrical conductivity as well as mechanical robustness. Pore structure is another key factor. Ruoff et al. have shown that the pore size distribution significantly impacts the active material utilization when they loaded LiFePO_4 into graphene foam²⁴. This enabled them to fine-tune the pore structure by changing the Ni template, resulting in a functionalized electrode with a reversible areal capacity of 10 mAh/cm^2 and an active material utilization of 91%.

Most 3D metal current collectors that are employed are made from Ni, Cu, or Al foam, all three of which are commercially available. Chen et al. deposited highly reactive sulfur nanodots on a commercial Ni foam, creating a functionalized cathode for a Li-S battery with a high initial capacity of 1458 mAh/g and 528 mAh/g at 5C for 1400 cycles²⁵. On the downside, large reticulated metal structures result in a high areal density of the current collector, which decreases the energy density of the battery. In addition, the process of filling the metal foam appears to be another challenge. Due to the high metal content and high tortuosity value within the foam structure, the active material loading density is relatively low compared to loading when using a foil current collector. Moreover, compression of the 3D electrode can lead to fractures in the metal foam and thus cause higher polarization. This, in turn, limits the mass density and energy density of these electrodes. In the same vein, researchers have also utilized metal nanowires to assemble a network structure as a scaffold for the active material. Compared to foam structures, the fibrous network can provide an electrical conductivity of 10^7 S/m with a low areal weight. Yin et al²⁶ designed a light-weight 3D composite anode containing Cu nanowires and multi-walled carbon nanotubes.

These exhibit high specific capacities and Coulombic efficiency, meanwhile exhibiting a high flexibility supported by the Cu nanowire network. Worthwhile mentioning is the fact that, besides an increase of the electrical conductivity of the electrode, an enhanced lithium-ion diffusion was also observed when increasing the Cu nanowire content. Yin et al. explain that the rigid framework of the current collector prevents the expansion and shrinkage of the active material, thereby ensuring the lithium-ion pathway.

Obviously, such a metallic structure network overcomes the drawbacks of a metal foam, as it is able to provide better electronic and ionic conductivity with lower areal mass and at the same time allows a densification of the active material. This thesis focuses on creating an in-depth understanding of electrode processes in a newly designed metal fibrous 3D current collector for a lithium-ion battery made from ultra-fine metal fibers produced using a melt-spinning process and then thermally sintered to create an interconnected 3D fibrous network. This mesh is filled with active material particles and then compressed to produce working electrodes. The 3D structure of the current collectors provides significant advantages for transporting both electrons and ions. To better understand why the metal frame is able to enhance ion diffusion within the cell, an experimental set-up combining microfluidic chips and Raman micro-spectroscopy was designed for this thesis. Utilizing this set-up I discovered that the ions are able to diffuse with ultra-high speed along the metallic surface when the surface is charged. My results reveal that fast surface diffusion along the electrical double layer of the current collector enhances the ion diffusion rate within the LiB. This stands in contrast to previous explanations of enhanced ion diffusion when employing 3D current collectors, which focused on variations in ion path way tortuosity. Moreover, my data from galvanostatic intermittent titration technique experiments as well as electrochemical impedance measurements show that the sluggish ion flow within the electrodes is significantly mitigated in the presence of the metallic fleece. Building on these properties, a super thick electrode ($\sim 800\text{ }\mu\text{m}$) was functionalized with an ultra-high reversible areal capacity (20 mAh/cm^2). Detailed information and a discussion of these results can be found in Chapter IV.

Furthermore, for the purpose of optimizing this fleece electrode, a mathematical modeling technique, which takes ion surface diffusion along a current collector into consideration, is used to simulate the electrochemical reactions within batteries with a 3D current collector. Inspired by Arunachalam et al²⁷, a macroscale model is derived by Asymptotic Homogenization (AH) of the mass and energy transport equations. The AH model homogenizes the electron transport, ion diffusion and migration process within a small representative volume element. As a result, the model is able to provide insight into the morphology of a real electrode while homogenizing the

surface and bulk diffusion process. A series of experimental techniques are developed to carry out the parameterization and validation of this LiB mathematical model. The mathematical modeling and simulation-based optimization are discussed in Chapter III and Chapter IV in greater detail.

Regarding my personal motivation and vision for this research, I believe that my study on surface diffusion can be transferred to a wide range of applications, such as batteries, super capacitors, electrocatalysis systems and permeation membranes. I also hope that this study will stimulate a systematic study of ion diffusion along electrical double layers on metallic surfaces. Moreover, I would like to highlight my wish to contribute to sustainable and environmentally-friendly LiB technology with my work on this 3D metal fleece that offers a promising architectural design for high energy and high-power density batteries.

II INTRODUCTION

Lithium-ion batteries reversibly convert chemical energy into electrical energy. Fundamentally any battery or super capacitor can be characterized by one thermodynamic parameter and two kinetic parameters: stoichiometry (C), electrical conductivity (K), and chemical diffusivity (D). In LiBs the stoichiometry is determined by the intercalated material, the electrical conductivity is defined by the electrodes, and the chemical diffusivity is determined by the electrolyte. The next section describes the working principle of LiBs focusing on these 3 key parameters.²⁸

2.1 WORKING PRINCIPLE

A lithium-ion battery consists of two electrodes, namely anode and cathode. For typical LiBs the cathode is cast from aluminum foil and the anode is cast from copper foil. The two electrodes are separated by a porous insulation membrane (the separator) soaked with electrolyte (liquid or solid ionic conducting media). During charging and discharging of the battery the lithium-ions lose electrons, are de-intercalated from one electrode, diffuse through the separator, and are then intercalated into the other electrode, where in a final step they receive electrons (**Figure 3**). In typical LiBs the anode material is graphite and the cathode material consists of lithium metal oxides $LiMO_2$ (e.g., $LiCoO_2$). The reversible reactions occurring at the electrodes upon charging and discharging can be expressed in the following way²⁹:

Anode reaction:



Cathode reaction:



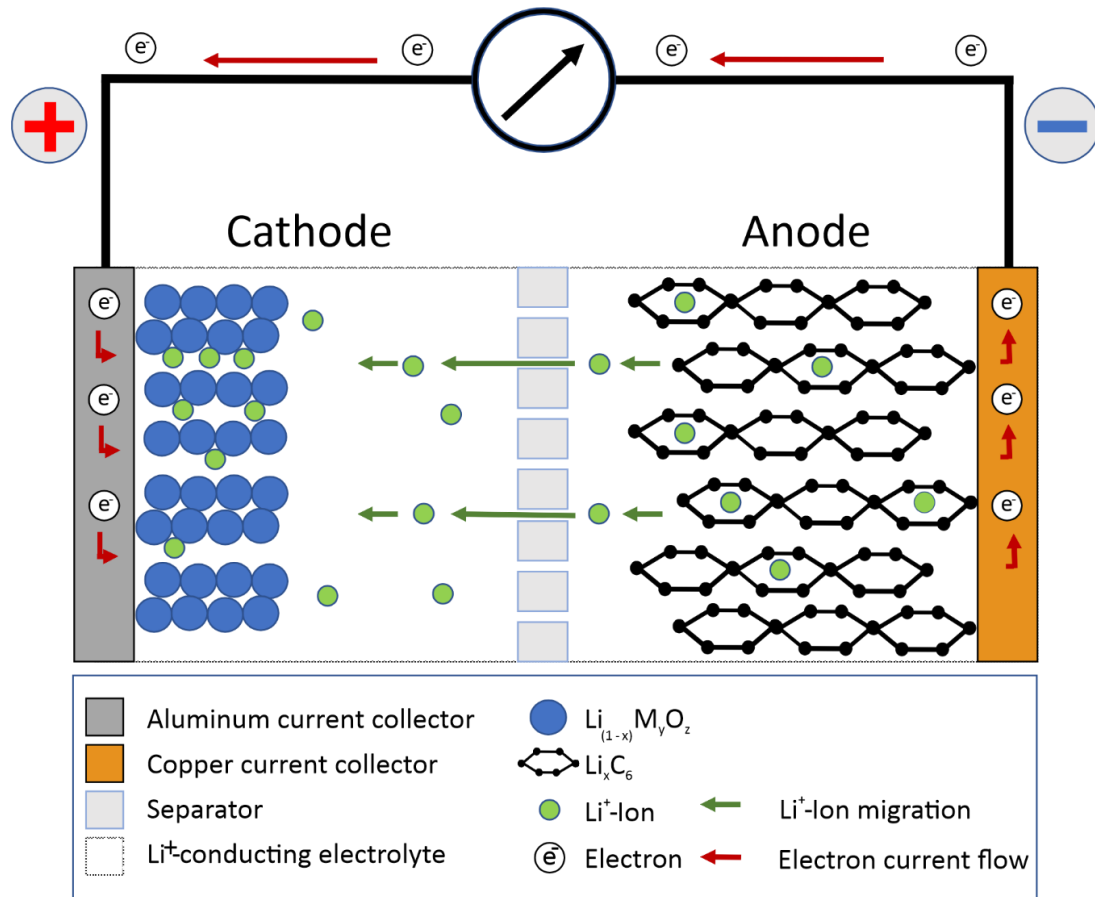


Figure 3. Working principle of typical LiBs.

Upon applying a positive current on the anode, the lithium-ions start to migrate to the anode and intercalate as described in **Reaction 1**. This reaction occurs once a certain threshold voltage, referred to as the intercalation voltage, has been reached. On the counter electrode, the cathode, the reaction occurs in the opposite direction, in accordance with **Reaction 2**. In conclusion, for the intercalation and deintercalation of Li-ions to occur both the electrical conductivity and the availability of lithium-ions need to be sufficiently high throughout the active material matrix. This is necessary to ensure homogeneous intercalation and low electrical resistance.

As mentioned above, the porous electrodes as well as the separator are immersed within the electrolyte. Lithium-ions are able to diffuse within the electrolyte as soon as an electrical potential difference between the two electrodes is established. In typical LiBs the electrolyte is usually a mixture of cyclic and linear organic carbonates (ethylene carbonate and dimethyl carbonate), in which the lithium salt (LiPF_6) is dissolved. Cyclic carbonates have a high dielectric constant and are able to associate with lithium-ions, thus offering a higher dissolution ability. Linear carbonates decrease the viscosity of the electrolyte and enhance the ion mobility.

The separator typically consists of either a polymeric membrane (polyethylene, polypropylene) or a non-woven fabric mat (polyolefin, polyamide, glass fiber, etc.). The function of the separator is to insulate the two electrodes while guaranteeing sufficient ionic flow between the anode and cathode.

2.2 BATTERY DEFINITION

The total charge per weight or per volume transferred by the charging/discharging current I is:

$$Q = \int_0^t I dt = \int_0^Q dQ \quad (3)$$

The capacity $Q(I)$ depends on the current I . The discharge/charging current for one cycle is usually expressed as the C-rate, the measure at which a battery is discharged relative to its maximum capacity. For instance, 1C indicates that the battery will be fully charged/discharged in 1 hour, 0.5C indicates that the battery will be fully charged/discharged within 2 hours. It is worthwhile mentioning that at different charge/discharge rates the maximum extracted capacity also differs. The ability to achieve high capacity (relative to the theoretical capacity) at different rates is defined as the ‘rate capability’.

The reversibility of the charging/discharging process is described by the coulombic efficiency, calculated using the following equation:

$$Efficiency = \frac{Q_{dis}}{Q_{ch}} \times 100 \quad (4)$$

The capacity retention represents the ratio between discharge capacities in n th and 1st cycles, which is also known as the state of health (SOH), calculated as following:

$$Capacity\ retention = \frac{Q_{dis, nth\ cycle}}{Q_{dis, 1st\ cycle}} \times 100 \quad (5)$$

In the electric vehicle industry the cycle life of the battery is determined by the number of cycles in which the capacity retention is higher than 80% of the initial capacity.

2.3 ELECTRODE MATERIALS FOR LIBS

In a typical LiB the complete energy storage and extraction process originates from a reversible ion accommodation in the electrodes and the transportation in between. In principle, when the LiB is operating as a galvanic cell, the electrodes go through the oxidation and reduction process

separately; the anode undergoes an oxidation process while the cathode undergoes a reduction process. When charging the process is reversed. Graphitic carbon is generally used as the anode material, whereas lithium iron phosphate and LiMO_2 ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}$) function as the cathode material. Thanks to the layered crystalline structure of graphitic carbon and lithium metal oxides, the lithium-ions are able to easily diffuse into the active material where they are homogeneously intercalated and then go through the charge exchange process (see **Figure 3**).

The application of graphitic carbon as the anode, first described by Yoshio Akira¹⁰, was based on its high accommodation stability, low redox potential against lithium, high solid-state lithium diffusivity, high electric conductivity, moderated volume expansion, shrinkage upon lithium intercalation/deintercalation, and low cost. However, despite the high gravimetric capacity of graphite ($\sim 370 \text{ mAh/g}$), the volumetric capacity ($\sim 830 \text{ mAh/cm}^3$) is not high enough to satisfy today's increasing demand for energy density in a wide range of applications, such as electric vehicles. Recently, lithium metal and silicon anodes have moved into the focus of researchers because of their high energy density.

In general, graphitic carbon and non-graphitic carbon are categorized by the orientation of the crystalline grains (**Figure 4**). Graphitic carbon, also referred to as graphite, is a polycrystalline material which consists of graphene sheets bonded by van der Waals forces and stacked along each other. The graphite lattice belongs to the $P6_3/mmc$ space group and comprises two characteristic planes: the basal plane parallel to the graphene sheet and the edge plane perpendicular to the basal planes³⁰. Within the basal plane the hexagonal graphene layers provide the intercalation sites for the lithium-ions, resulting in the storage of up to 1 Li atom per 6 C atoms³¹. Thus, the intercalation of Li-ions can only occur through the edge plane. Lithium transport through the basal plane only happens where there are defects.

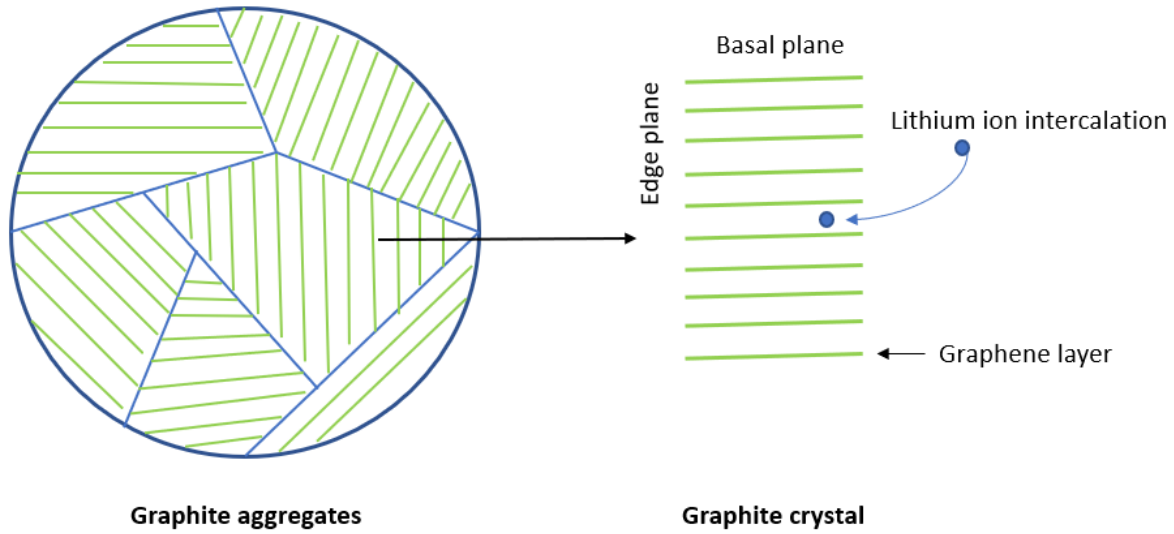
Anode (Graphite)

Figure 4. Lithium-ion intercalation mechanism in graphite.

Recent studies on anode active material have mainly focused on silicon and lithium metal for the anode. I will not go into further details here, as this is beyond the scope of our study.

Typical cathode materials are lithium iron phosphate (LFP) and LiMO_2 ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}$). LFP is an olivine-type cathode material (**Figure 5**³²) featuring a PO_4 group and a stable $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. LFP cathodes possess good thermal and chemical stability, offer a flat voltage plateau, a high theoretical capacity, very good safety properties, and can be produced at low cost³³. Nonetheless, due to the olivine crystal structure, the lithium-ions are only able to diffuse along a one-dimensional path (1D lithium diffusion)³⁴, which is also the reason why LFP suffers from sluggish lithium-ion transport. In addition, the low electrical conductivity also limits the power density of LFP³⁵. To address this issue a carbon coating is commonly applied to ensure electrical conductivity³⁶. Moreover, in recent years, Mn, Co and Ti have been tried as alternatives for the Fe in the lithium iron phosphate in an attempt to optimize solid-state lithium diffusion, working potential, structural stability, and electronic conductivity^{37,38}.

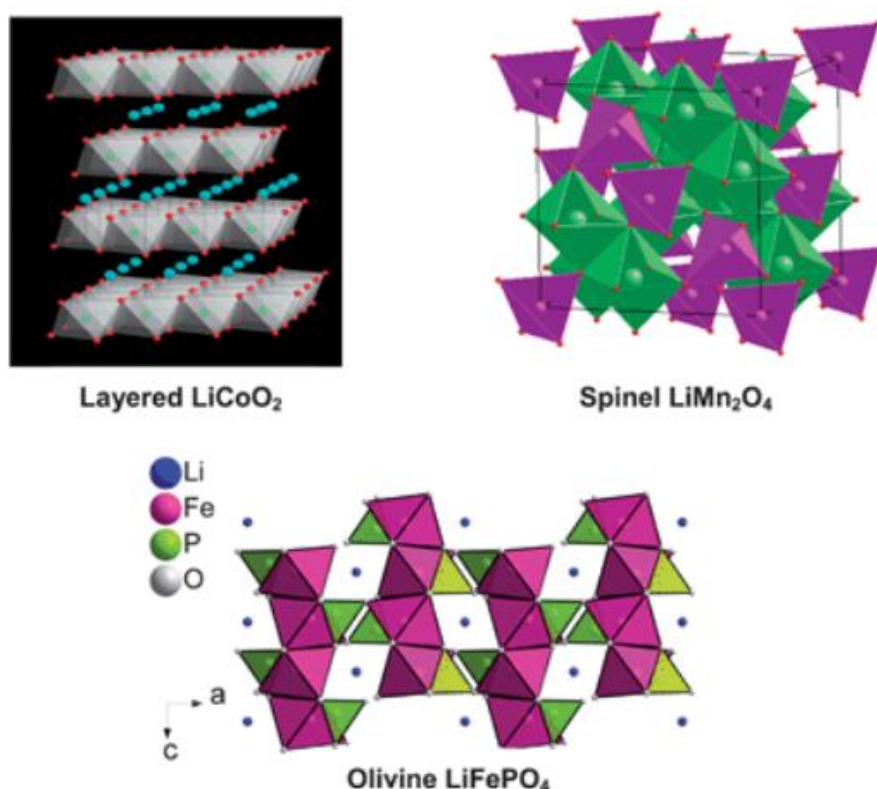


Figure 5. Different types of cathode material and intercalation mechanism³⁹.

Layered oxide cathodes (LiMO_2) have 2D pathways for lithium-ion diffusion (**Figure 5**) and generally have a higher solid-phase diffusivity and a higher theoretical capacity³⁹. LiCoO_2 , the first commercialized layered oxide cathode material, has a theoretical capacity of 274 mAh/g, low self-discharging properties, and good cycling performance⁴⁰. The main drawback of the material is its low thermal stability and high cost. Substitutions like LiNiO_2 and LiMnO_2 have been investigated to decrease the toxic cobalt content and lower the costs. However, the synthesis of LiNiO_2 is quite complex and LiMnO_2 tends to undergo a layered to spinel transformation during cycling. Large effort has been put into the development of a cathode from $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM)⁴¹, an excellent cathode material due to its high capacity, high thermal stability, and high operating voltage⁴².

Finally, the spinel-like structure of LiMn_2O_4 allows a 3D lithium diffusion path (**Figure 5**). Overall, these batteries feature a high solid-state diffusion coefficient as well as cheaper and abundant availability than LCO and NCM. However, similar to batteries with LiMnO_2 as the cathode material, Mn dissolution, oxygen loss, and phase changing impact the long-term performance of this cathode material^{43,44}. **Figure 6** shows the comparison of three cathode materials regarding cost, life span, performance, safety and specific power⁴⁵.

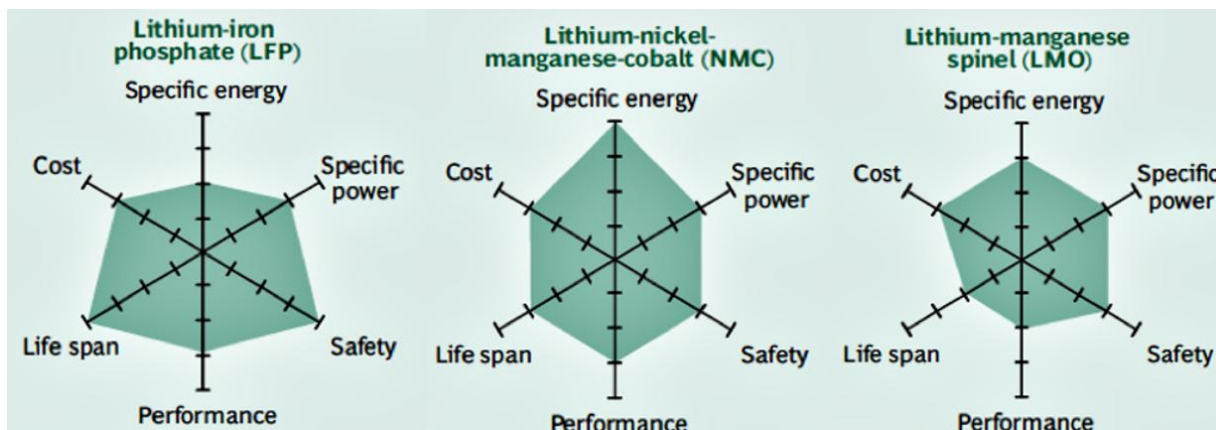


Figure 6. Comparison of LFP, NMC and LMO⁴⁵.

2.4 ELECTROLYTE FOR LIBS

As one of the most important and most expensive components in LiBs, the electrolyte enables the ionic flux between the anode and the cathode. Li^+ ion mobility during charging/discharging is regulated by the electrolyte characteristics, specifically, dissociation ability, dielectric constant and viscosity. The ideal LiB electrolyte should feature a good ionic conductivity, a wide electrochemical stability window to provide high power density, inertness towards anode and cathode material, and at the same time good wettability of electrodes. Typically, the electrolyte is composed of a mixture of aprotic solvent and conducting lithium salt. In addition, to adjust the electrolyte properties in favor of the formation of a solid liquid interphase (SEI) layer at the anode as well as suppress lithium dendrite formation, increase ion mobility, and enhance fire-retardant properties, small amounts of additives (salt, organic compounds) are included.⁴⁶

The general state-of-the-art electrolyte solvent is a mixture of cyclic and linear organic and aprotic carbonates, which each have desirable and undesirable features. Cyclic carbonates as a component offer the high dielectric constant needed for lithium salt dissociation as well as having a high melting temperature and an undesirably high viscosity. Linear carbonates feature the low viscosity required to ensure higher ionic conductivity, but have a much lower thermal stability. Key to producing a good electrolyte, therefore, lies in the balance of the two components.

Propylene carbonate (PC) was one of the first carbonates employed in LiBs due to its high dielectric constant and relatively low melting temperature⁴⁷, two properties that make it suitable for low temperature applications. However, two factors have limited its use: 1) it fails to form a stable passive layer (SEI) on graphitic anodes, and 2) PC also co-intercalates between graphene sheets and causes severe exfoliation of the graphite particles. Ethylene carbonates, because they provide excellent salt dissolution and form a stable SEI at the anode, have also been suggested as

cyclic carbonates. Although the melting temperature of ethylene carbonate (EC) is higher than room temperature, it can be dissolved into other low melting point linear carbonates to overcome this issue. Linear carbonates like dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) are commonly used together with EC in LiBs, where they lower both the viscosity and melting temperature, thus enabling a fast diffusion of Li-EC ion-solvation shells. **Figure 7** shows the most common cyclic and linear carbonates used as electrolyte solvents.

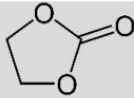
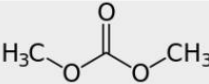
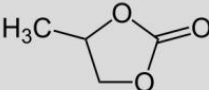
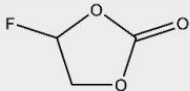
Solvent	Structure	Dielectric constant ϵ , 25 °C	Viscosity η , mPa s	T_m , °C	T_b , °C	Contribution to SEI
EC		89.78	1.90 (40 °C)	36.4	248	yes
DMC		3.107	0.59 (20 °C)	4.6	91	no
PC		64.92	2.53 (25 °C)	-48.8	242	no
FEC		~110	~3.5 (25 °C)	19-20	212	yes

Figure 7. Common carbonates used as electrolyte solvents.

Lithium conducting salts must fulfill essential requirements – a high dissociation constant, maximum solubility, thermal and electrochemical stability, and non-toxic properties. Lithium hexafluorophosphate (LiPF_6), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (LiFTFSI) have been employed as electrolytes, because these complex anions permit the efficient delocalization of negative charge and improve dissolution. However, although LiTFSI , LiFSI , and LiFTFSI feature a high thermal and electrochemical stability, they cannot form a protective layer on the aluminum, ultimately leading to the dissolution of the cathode current collector. Thus, they are always used in combination with LiPF_6 as a co-salt⁴⁶.

Besides the solvent and conducting salt, other additives are also commonly employed in industrial LiBs. These promote the formation of a stable SEI and CEI, enhance thermal stability, protect the current collector, and prevent overcharging of the battery⁴⁸.

Vinylene carbonate (VC) is a state-of-art reduction type additive, because it is able to improve the thermal stability and cycling performance of LiBs. It is reported to be reduced at the graphite surface at +0.9V vs. Li/Li⁺ (prior to EC), form flexible poly (VC), and provide a stable SEI during the expansion and shrinkage of the graphite⁴⁹. Fluoroethylene carbonate (FEC) as an additive seems to be beneficial for both the anode and cathode. The decomposition of FEC will form lithium fluoride (LiF) and poly (VC) on the anode surface, the former enhancing the ion conduction and the latter the mechanical stability of the SEI. Another common additive is tris(pentafluorophenyl) (TPFPB). It is reported to be an effective SEI modifier that re-dissolves the inorganic SEI and prevents continuous growth of the SEI, thereby decreasing cell impedance. Recently, researchers also discovered that the dissolution minimum of LiF in the electrolyte will greatly improve the thermal stability of LiPF₆⁴⁹. LiPF₆ can decompose by the following reaction: $\text{LiPF}_6 \leftrightarrow \text{PF}_5 + \text{LiF}$. PF₅ can deteriorate the SEI on the graphite surface via a series of reactions (**Figure 8**). As a consequence, the accumulation of LiF in the SEI increases, which can lead to gas generation and a build-up of pressure within the cell. Hiroi et al.⁵⁰ have shown that dissolving 0.05 wt. % of LiF can significantly reduce PF₅ formation by changing the decomposition reaction equilibrium:

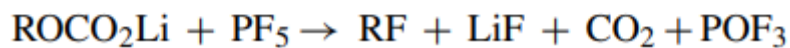
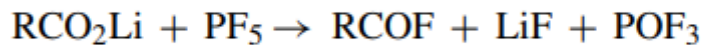
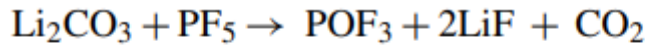


Figure 8. SEI decomposition due to PF₅.

Solid state electrolytes for use as the ionic conductor and electron-insulating material have received increased attention recently, due to their high energy density and significantly increased safety, but will not be discussed in greater detail here.

2.5 TRANSPORT KINETICS IN THICK LIB ELECTRODES ON MULTI LENGTH SCALES

LiB energy storage and release originates from lithium accommodation in the electrodes and lithium-ion transportation between electrodes, a process with several steps: (a) electron conduction from the current collector through the conductive binder phase to the active material, (b) solid-phase ion diffusion within the active material particles, (c) charge transfer at the interface between the active material and the electrolyte, and (d) ion diffusion within the bulk electrolyte inside the

porous structure (see **Figure 9**¹², which shows the processes inside a NMC cathode). The size dimensions as well as the characteristic time constants of the electrochemical processes are shown in **Figure 10**⁶. Electron conduction is happening at all length scales, which indicates that the conductive additive is necessary to establish a percolation pathway through the entire electrode width (thickness). Solid-phase diffusion and charge transfer happen within the active material as well as at the interface of the active material with the electrolyte, both characterized by a short length scale and a relatively small time constant; ion transport within the liquid phase contained in the porous structure is connected with the longest length scale as well as largest time constant, indicating that it is the main bottleneck of the overall kinetic processes of battery charging and discharging.

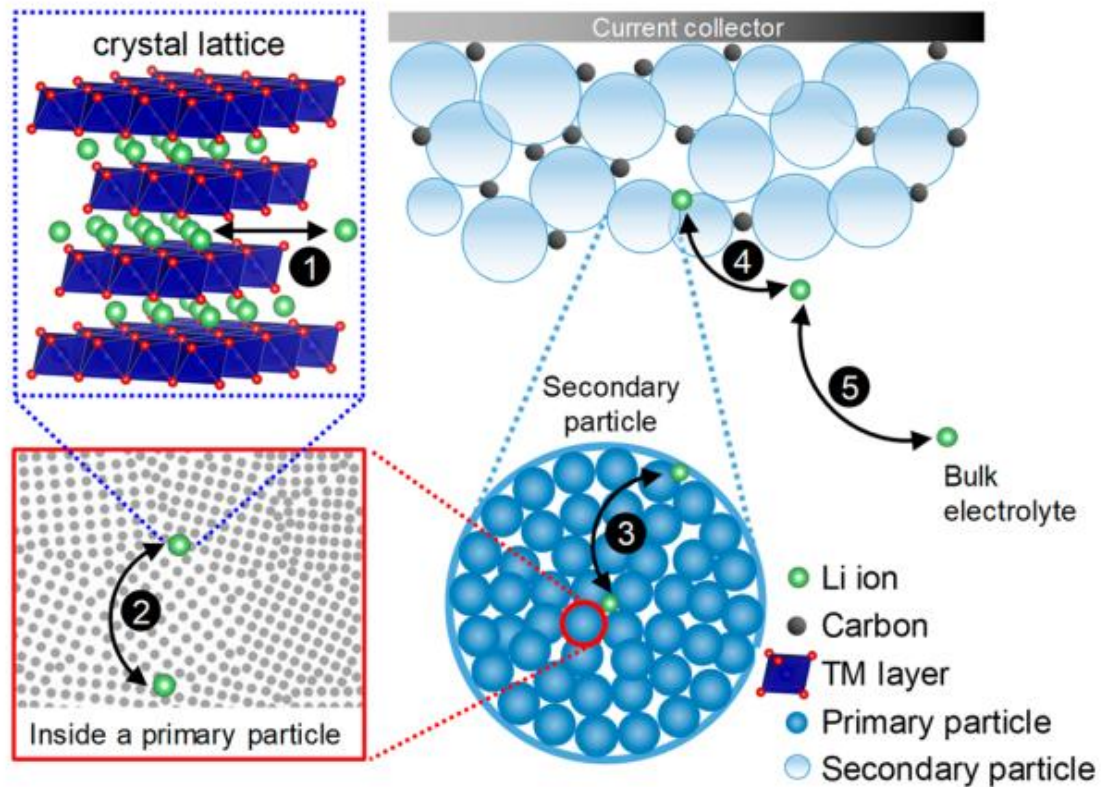


Figure 9. Schematic diagram showing the diffusion pathway of Li^+ at micro- and macroscopic length scales: (1) within the crystal structures, (2) within the primary particles, (3) within the secondary particles, (4) within the porous electrode, and (5) in the bulk electrolyte¹².

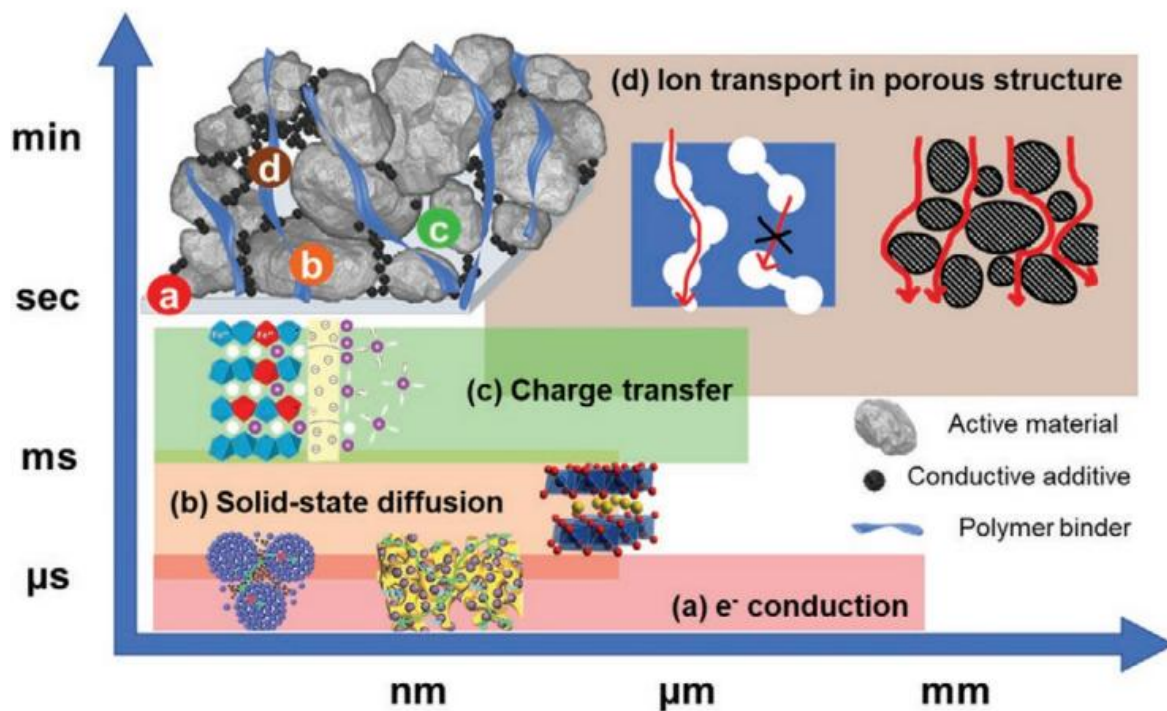


Figure 10. Schematic illustration of the characteristic size and time dimensions of the dominating electrochemical processes inside composite electrodes as they relate to design considerations⁶.

Given the fact that battery performance is highly dependent on the above-mentioned collective kinetics, figuring out the bottlenecks that hinder maximum usage of the energy contained in the battery by decoupling the complex kinetic processes is important. Within the battery system, the difference between the dynamic charging/discharging potential E to the thermodynamic equilibrium E_{equil} can be expressed as:

$$E = E_{\text{equil}} + \eta_{\text{ct}} + \eta_d + iR \quad (6)$$

η_{ct} represents the polarization due to the charge transfer resistance and η_d represents the polarization due to the ion concentration gradient. iR refers to the ohmic drop in the system. The galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) are two crucial methods for analyzing internal resistances and for decoupling and elucidating complex transport behaviors in detail. The GITT measurement is able to determine the equilibrium state of the battery system and analyze the transport mechanisms on a large time-scale (specifically, ion diffusion inside the pore structure)⁶; the EIS experiments represent a useful tool to analyze the internal resistance at different characteristic frequencies in various electrochemical systems^{51,52}. However, these measurements can only provide a limited and rough estimation, as they do not really take electrode geometry and the impact of electrode heterogeneity into consideration. Studies using these techniques have shown that lithium-ion diffusion inside the porous space and the active material causes general polarization, especially with increased mass loading of the active material. The ohmic drop usually does not contribute significantly, as the voltage gap between the dynamic and the equilibrium state is mainly due to diffusive polarization and charge transfer polarization. During fast charging/discharging the ions cannot be fully intercalated/de-intercalated in the preset voltage window due to the high polarization, which causes prominent capacity losses. In recent years, researchers have focused on developing novel technologies and methodologies, ranging from molecular-scale modifications to meso-scale morphology optimizations of both the active material design and the cell's architectural design⁵³.

This dissertation mainly focuses on LiBs with both high energy and high density. To achieve this the most straightforward way would be to increase the areal mass load of the battery's active material and build ultra-thick electrodes. However, this is associated with longer and more tortuous energy and mass transport pathways. Thus, the electrically conductive network and lithium-ion diffusion channels play essential roles in thick electrodes and are the main rate-limiting factor of their charging/discharging kinetics.

To improve the electrode's conductivity (decreasing iR in **Equation 6**), the conductive binder phase (CBP) is required to establish a percolation pathway and enable inter-particle electron transport; However, in high-capacity electrodes such a phase is insufficient for providing a conductive network throughout the entire electrode that enables the complete utilization of all active materials. As a consequence, researchers have been trying to find an alternative conductive filler that can ensure the percolation path of the charged entities throughout the network while adding as little additional content to the battery as possible. Towards this end, 1D and 2D conductive fillers have clear advantages⁵⁴ over carbon black, a 0D filler. Carbon nanotubes have recently been studied intensively. Park et al.⁵⁵ reported a segregated network composite electrode, formed utilizing a segregated carbon nanotube network. This electrode exhibits high electrochemical performance due to the increased conductivity as well as a robust mechanical stability even at high thickness. Graphene sheets are another candidate due to their extremely high electrical conductivity and light weight. The introduction of either graphene sheets or reduced graphene oxides (rGOs) has shown to considerably enhance electrode conductivity⁵⁶. These novel conductive fillers significantly enhance the inter-particle electrical connection. As a result, the potential gradient within thick electrodes is reduced, which ensures that all active materials are at their optimum intercalation voltage range.

Regarding its contribution to the electrochemical property of LiBs, ionic diffusion (η_d in **Equation 6**) – which includes lithium-ion diffusion in the electrolyte and in the solid active material – is of even greater importance than electronic conduction. Several studies^{12,12,53,57} have shown that large diffusive resistance is the main bottleneck to building thick electrodes. At room temperature the lithium-ion diffusion coefficient in the electrolyte is typically low. Also, due to the high tortuosity and long lithium-ion pathway in both the anode and cathode the effective diffusion coefficient within pores is even lower. This limitation is even more significant during fast charging and discharging of the battery. By increasing active material loading (either through increasing the cell thickness or by decreasing the electrode's porosity), greater electrode energy density can be achieved. However, this also means that the aperture size of the diffusion channels is decreased while at the same time the channel length is increased. This results in a decrease in the rate capability and high-power performance of these batteries. Moreover, the solid-phase diffusion coefficient within the typical active material, i.e., graphite or $N_xM_yC_zO_2$, is approximately 10^3 times slower than the liquid-phase diffusivity in the electrolyte. Both diffusive resistances limit the LiB's thickness and rate capability performance. In today's standard LiBs, the battery cell design is strongly affected by limited Li^+ diffusivity. In thick electrodes not all active material can be reached by Li^+ in time, which can cause the formation of an unfavorably strong solid electrolyte

interphase (SEI) layer as well as lithium plating and eventually even the loss of accessible capacity. These factors have restricted electrode thickness in various LiB designs, including those that are based on repetitive alternating layers consisting of current collector foils, anode and cathode active material layers, and separators. As a result, today's standard electrodes do not exceed a thickness of 100 μm (single-sided coating). For double-sided coated foils areal capacities of less than $< 7 \text{ mAh/cm}^2$ are the norm^{58,59}.

Creating holes or pores inside the electrode can effectively provide channels for lithium-ion diffusion within thick electrodes. Peng and co-workers⁶⁰ synthesized holey mixed transition metal oxide with nanopores that allow lithium-ion transport throughout the active material; Zhang et al.⁶¹ developed a 2-time doctor blading method to create gradient porosity anodes in order to enhance the rate capability. In these electrodes the high porosity of the electrode's upper side provides enough space for lithium-ion penetration and the low porosity side provides good electrical conductivity. With regards to electrolyte engineering, Lu et al.⁶² reported a novel electrolyte composition that utilizes small solvents with low solvation energy to achieve higher Li^+ diffusion by forming an ion-conducting ligand channel. Another approach has been to decrease lithium-ion path tortuosity by controlling the orientation of the active material. Sander et al. reported the construction of a pore array created by aligning the magnetic rods with an external magnetic field. The aligned channels can increase the C-rate in a 220 μm electrode to $C/2$ ^{13,63}.

The polarization caused by charge transfer resistance (η_{ct} in **Equation 6**) is relevant to the interaction between the active material and the electrolyte. Thus, a range of factors impact the charge transfer resistance, including the wetting of the electrode, electrolyte properties, active material morphology, temperature and cell degradation. During the initial cycling a passivation layer will form on both the anode (SEI) and cathode (CEI) produced by electrolyte decomposition. These layers allow Li^+ transport while at the same time electrically isolating the active material surface. This prevents further lithium-ion consumption during cycling and enhances the cyclability, rate capability, and safety of the LiBs. On the downside, however, this process also introduces a higher charge transfer resistance at the solid/liquid interface. Thus, the thickness as well as the characteristics of the passivation layer are key factors to consider when engineering batteries towards reduced charge transfer resistance.

In summary, energy and mass transport in LiBs are synergistical processes that take place across various spatial and temporal dimensions. While scaling-up electrode thickness provides opportunities to achieve high energy, this comes with tradeoffs in the electrochemical

performance, specifically the electrical conductivity and ionic diffusivity, which present the main bottlenecks.

2.6 3-DIMENSIONAL CURRENT COLLECTORS

Apart from the active components, i.e., the active material and the electrolyte, the inactive components also impact the performance of LiBs. Current collectors in the anode and cathode are made from copper foil and aluminum foil, respectively, which is then coated with an active material layer. Current collectors bridge the conductive pathway from active species to external circuits in addition to also enhancing the mechanical strength of the electrode. Recently, current collector design has been a focus of battery engineers focusing on light weight designs. The average values from five manufactures^{18,64} regarding the weight percentage of the cathode, anode, Al foil, Cu foil, separator and other components are 29%, 13%, 5%, 13% and 35%, respectively. The active materials (anode and cathode) make up the highest proportion, 42% of the total weight. The two current collectors take second place with 18%. Engineers have thus worked on decreasing the thickness of the current collectors from 20 μm (copper) and 30 μm (aluminum) thickness to much less, 8 μm for copper and 12 μm for aluminum⁶⁴. In the meantime, alternative materials have also been studied, namely nickel, titanium, stainless steel, and carbonaceous materials^{18,23}. The goal here is to reduce contact resistance and increase the corrosion resistance of the current collectors, which will support increasing the capacity, rate capability, efficiency, and cycle stability of the resulting LiBs. The main requirements for current collectors in LiBs are: (1) electrochemical stability, (2) high electrical conductivity, (3) mechanical strength, (4) light weight, and (5) sustainability and cost.

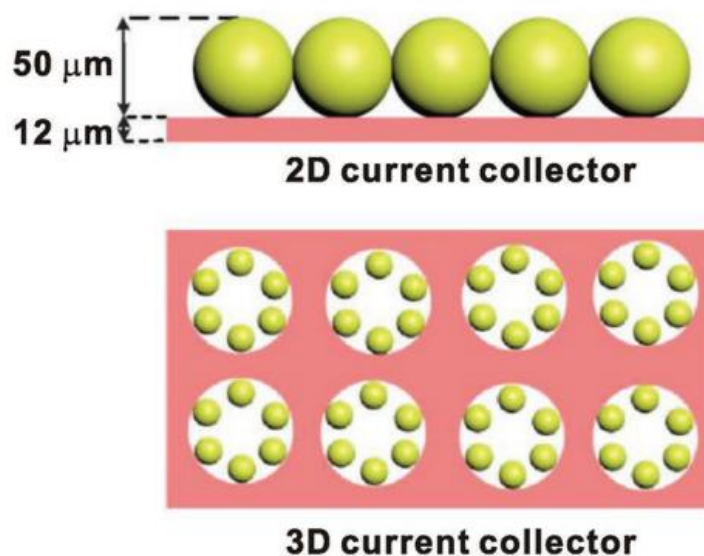


Figure 11. Schematic illustration of 2D current collector and 3D current collector.

Attention has also been shed on the structure of current collectors. Recently the concept of multidimensional current collectors has been explored and proven to be an effective way to enhance the electrochemical performance of batteries. Towards this end, 3-dimensional current collectors (3D CC) have been investigated intensely, usually consisting of a porous or a fibrous substrate filled with active material (**Figure 11**) that is then filled with electrolyte and assembled as a battery. These designs have been proven to minimize the tortuosity of ion and electron transport pathways, especially in highly loaded electrodes²⁰, because 3D CC provides a greater interface area and, therefore, decreases the diffusion length. Meanwhile, the high electrical conductivity of the 3D CC can efficiently mitigate the electrical potential gradient within the electrode, thus more active material is at its optimum intercalation potential and charge transfer can take place. A common concern with high-loading electrodes is the fact that they are susceptible to mechanical cracking, which is a consequence of volume expansion and shrinkage during cycling. 3D CC can effectively alleviate this and simultaneously also improve the robustness of the electrode compared to electrodes coated on 2D metal foils. In sum, the advantages enhance the energy density of the battery and guarantee cycling stability at the same time. Carbon and metal materials are most widely used for 3D current collectors owing to their high electrical conductivity, electrochemical stability, high mechanical strength, and wide range of sources.

For metal current collectors, electrochemical stability is the most crucial factor when selecting the metal. The working potential range on the cathode lies between 2-5 V versus Li/Li^+ , which is why Al and Ti – which both form dense passivation layers – are good choices to prevent corrosion. On

the anode side the challenge is to avoid alloying reactions between the Li and the metal at low working potentials, making Cu a preferred choice. Ni and stainless steel are stable within a potential range between 0-4 V. This makes it suitable for certain LiB applications at both the anode and cathode. The 3D metallic structure can be obtained via two different strategies: molding the metal with a 3D template (metal) or microstructure and/or nanostructure assembly.

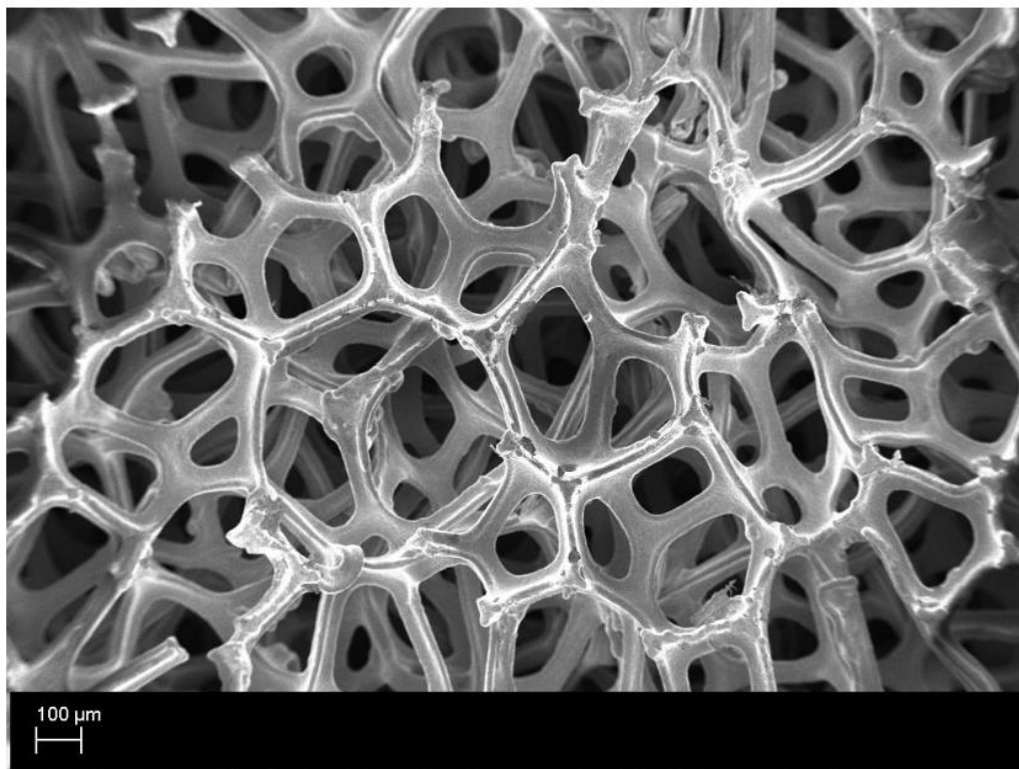


Figure 12. Copper foam with 95% porosity.

Metal foams as current collectors provide a very high surface area that allows for increased active material loading. Cu, Ni and Al foams are fabricated utilizing a polyurethane foam consisting of interconnected pores of hundreds of microns in diameter as a template⁶⁵ (**Figure 12**). By employing a foam structure, an active material weight proportion in the battery that is comparable to film electrodes with ultra-thin current collector foils can be achieved. Chen et al. have reported the design of current collectors with electrodeposited sulfur nanodots on a commercially available Ni foam that serve as the cathode in a Li-S battery²¹. The Ni foam current collector provides a high electrical conductivity as well as a high initial capacity of 1458 mAh/g at 0.1 C and a reversible capacity of 528 mAh/g at 5C after 1400 cycles. Yang et al⁶⁶ fabricated a nanoporous Cu current collector by dealloying a Cu-Zu alloy. The removal of Zn led to the creation of nano-sized pores within the Cu substrate. Their 3D CC was afterwards paired with an LFP cathode and used as a substrate for lithium metal batteries. Based on this design, the resulting full cell demonstrated a

reversible capacity of 136 mAh/g with high Coulombic efficiency cycling at 0.5C. Similarly, Li et al⁶⁷ reported a lithium metal battery anode produced employing a commercially available 3D porous Cu mesh (Shown in **Figure 13**). The porous structure of the mesh provides a ‘cage’ as well the advantage of a high surface area for lithium deposition and the high conductivity that can be achieved mitigates the potential distribution, thus enabling a more homogeneous deposition and suppressing dendrite formation. Metal nanowires and assemblies of nanowires were also used to create batteries with 3D CC. Yin et al²⁶ reported a novel light-weight 3D anode composed of Cu nanowires and multi-walled carbon nanotubes. This design improved both ionic and electronic conductivity. In addition, the freestanding and flexible anode exhibits a high specific capacity and Coulombic efficiency.

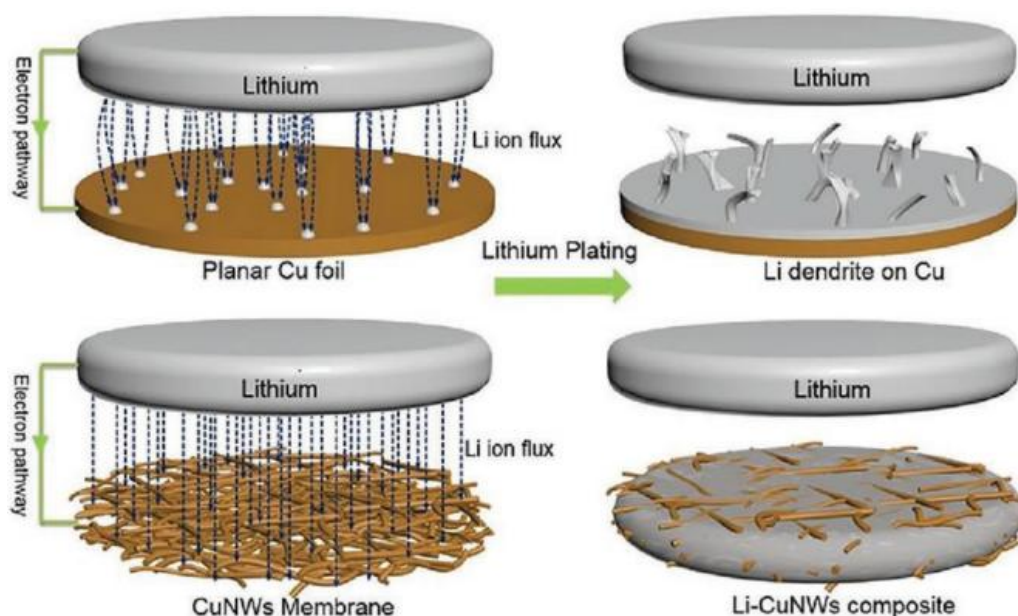


Figure 13. 3D porous copper mesh as a lithium plating substrate⁶⁷.

Aside from their promising performance advantages, however, most synthetic methods (like chemical dealloying, electrodeposition, and e-beam evaporation) are unsuitable for large scale production.

Carbon as the most versatile element is used in a wide variety of applications and exhibits a diverse range of characteristics. As a conductive agent carbon offers excellent electric/thermal conductivity, structural stability, light weight, and chemical inertness. Therefore, a carbon-based material can be used in both the anode and cathode. Hard carbon materials are inactive for intercalation of Li^+ at potentials > 0.5 V versus Li/Li^+ . Li^+ intercalation at the anode happens at potentials < 0.5 V. Thus, carbon current collectors like, e.g., carbon nanotubes, show negligible

Li intercalation. Moreover, the graphene surface of the carbon material allows absorption/desorption of Li. Also, when functionalized as a super capacitor device, such batteries are able to store additional electric energy.

One aspect that requires considerations when forming 3D CCs, is the type of chemical bonds connecting the carbon material, either covalent or non-covalent bonds. In 2011, Cheng et al. described a 3D graphene foam that was produced by CVD. Utilizing a nickel foam as the foundation, graphene flakes were deposited on its surface and covalently connected together. The resulting 2 mm-thick 3D graphene foam exhibits a density of 5 mg/cm³ with 99.9 % porosity⁶⁸. The application of such a current collector as an LFP cathode current collector revealed an extremely high areal capacity and a high mechanical stability. 3D carbon-based current collectors can also be assembled by weak Van-der-Waal forces. Carbon fibers, carbon nanotubes and graphene flakes are used widely for these purposes²⁰.

Overall, 3D current collectors feature superior electronic conductivity, a larger interface between the active material and the current collector, and an increase in mechanical stability. These characteristics benefit the electrode's energy density, power density, and cycling stability, which has led to a surge in research aimed at improving 3D current collectors.

It is also worth mentioning that researchers have observed a higher Li⁺ diffusion rate in these batteries. Yin et al²⁶ used copper nanowires as the current collector and found that with increasing amounts of nanowires dispersed in active material, a greater diffusivity value was measured by GITT. The given explanation is that the 3D network restricts the expansion of the active material and guarantees a lithium- ion pathway. Similarly, Muramatsu et al.⁶⁹ reported a novel electric double-layer capacitor design combining carbon and a 3D stainless steel current collector. They explain their finding that the ionic conductivity measured by EIS is enhanced with a change in the ion pathway tortuosity by the 3D current collector, which reduces the diffusive resistance. In this dissertation a 3-dimensional fleece made of ultrafine metal fibers is used as a current collector and an enhancement of ion diffusion is observed. I demonstrate that this 3D CC is able to accelerate ionic diffusion not only because of the change of the electrode's tortuosity, but rather because of the rapid surface diffusion of ions along the metal surface. As the 3D CC is filled with active material and electrolyte, a large interface between the current collector and the electrolyte is created. During the charging/discharging process, as voltage is applied to the 3D CC, an electrical double layer is generated at this interface. The ions within the electrical double layer display ultrahigh diffusivity, resulting in an overall enhanced diffusion within the electrode's pores.

2.7 MATHEMATICAL MODELING OF LIBS

Lithium-ion cells play an important role in the electrification of many industries. Computational modeling serves as a valuable tool for tailoring batteries to suit specific applications, as it enables the evaluation of cell performance during charging and discharging processes and provides deeper insights into the underlying mechanisms, thus allowing performance optimization. This, of course, requires models with high accuracy and low computational cost.

As explained in Chapter 2.5, the performance of LiBs is fundamentally determined by mass transport and charge transport within the active material and electrolyte. Within the electrolyte phase, the Nernst Planck equation governs the voltage and the concentration gradient variation, together with the law of electroneutrality. Within the electrode phase Fick's law governs solid-phase diffusion and Ohm's law governs electrical current and electrical potential level. At the interface between the solid and the electrolyte the overpotential is calculated based on the Butler-Volmer equation (**Table 1**). By coupling and solving these equations on a resolved cell geometry, the charging/discharging overpotential can be predicted at different current densities. This computational method is called microstructural simulation or direct numerical simulation, since it is solved based on the actual heterogeneous structure of the cell.

Table 1. Governing equations with relevance to a microscopic battery model

Electrolyte (e)	Variables and constants
Diffusion and Migration $\frac{\partial c^e}{\partial t} = \nabla \cdot \left[\left(D^e + K^e t_+ (1 - t_+) \frac{RT}{F^2} \frac{1}{c^e} \right) \nabla c^e + K^e \frac{t_+}{F} \nabla \varphi^e \right] \quad (1)$ Charge conservation and electroneutrality $0 = \nabla \cdot \vec{j}^e = \nabla \cdot \left[\left(K^e (1 - t_+) \frac{RT}{F} \frac{1}{c^e} \right) \nabla c^e + K^e \nabla \varphi^e \right] \quad (2)$	c^e: equilibrium Li concentration in e c^s: Li concentration in s φ^e: Electrochemical potential of e Φ^s: electrical potential of s j^e: Current density of all ionic charges in e j^s: Effective electronic current in s U_0: Open-Circuit Potential of AM vs. Lithium η_s: Interfacial overpotential c_{max}^s: Maximum Li concentration in AM K^e: Ionic conductivity of e K^{AM}: Electronic conductivity of AM D^e: Ionic diffusion constant of e D^s: Diffusion constant of s t_+: Li transference number k: Butler-Volmer rate constant T: Temperature F: Faraday constant R: Universal gas constant
Active Material (AM)	
Diffusion $\frac{\partial c^s}{\partial t} = \nabla \cdot [D^s \nabla c^s] \quad (3)$ Ohm's law $0 = \nabla \cdot \vec{j}^s = \nabla \cdot [K^s \nabla \Phi^s] \quad (4)$	
Interface between electrolyte and AM	
Butler Volmer Interface Current density $= k \sqrt{c^{s,surf} c^e} \left(1 - \frac{c^{s,surf}}{c_{max}^s} \right) 2 \sinh \left[\frac{F}{2RT} \left(\underbrace{\Phi^s - \varphi^e - U_0}_{=\eta_s} \right) \right] \quad (5)$	

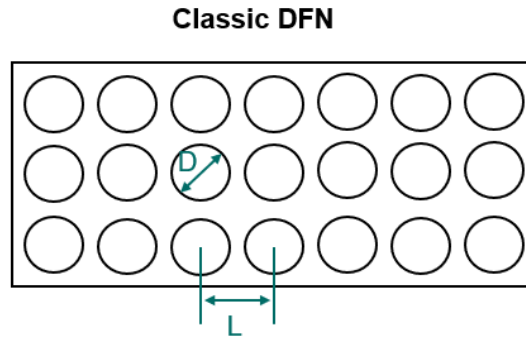
This electrochemical simulation model provides a spatially resolved solution for ion concentration distribution, potential gradient as well as current and ionic flux in the electrode and electrolyte phases. The obtained high accuracy calculation results are able to show the impact of employing heterogeneous materials to influence electrochemical performance. To achieve this, microstructural simulation requires a resolved geometry, in other words, a finite element method (FEM) or finite volume method (FVM) is employed. The computation time as well as the calculation effort per charging/discharging cycle is enormous due to the high number of parameters and, hence, impractical for industrial application and unsuitable for the optimization on a cell or battery module level.

Therefore, a model-based optimization or approximation is necessary to reduce the computational complexity and decrease the calculation time. This can be achieved by deriving a so-called

upscaling or macroscopic model, in this case a state-of-the-art macroscopic model known as the Doyle-Fuller-Newmann model (DFN model). This macroscale model is based on effective mass and charge transport equations. The model comprises two 1-dimensional calculations – one for the spherical active material particle and the other for the whole electrode. It separately calculates the solid-phase diffusion process at the microscale and the liquid-phase diffusion as well as conduction at the macroscale, and then couples these two calculations. For the 1-dimensional calculation along the electrode thickness direction, the effective electrical conductivity and ionic diffusivity is acquired using the Bruggmann correlation. The effective diffusivity can be expressed as **Equation 7**, ϵ is porosity and τ is ion path tortuosity within the pores. The DFN model approximates that all active material particles are identical spherical particles and are arranged as shown in **Figure 14**. Based on this geometry, porosity and ion path tortuosity can be calculated based on the Bruggmann correlation^{27,70}, and then the effective diffusivity can be obtained. For the 1-dimensional calculation at the single particle level, the ion concentration distribution within the solid active material particle is calculated based on Fick's second law (**Equation 8**). These two calculations are then coupled based on the Butler-Volmer equation. The AM particle surface ion concentration and electrolyte concentration are used to define the overpotential at the solid/liquid interface (**Figure 15**).

$$D_{eff} = D \times \frac{\epsilon}{\tau} \quad (7)$$

$$\frac{\partial c^s}{\partial t} = D^s \left(\frac{\partial^2 c^s}{\partial r^2} + \frac{2}{r} \frac{\partial c^s}{\partial r} \right) \quad (8)$$



$$\frac{D_{\text{eff}}}{D} = \frac{\varepsilon}{\tau}.$$

$$\tau = \begin{cases} \varepsilon^{-1/2} & : n = 2 \quad (\text{spheres}) \\ \varepsilon^{-1} & : n = 1 \quad (\text{cylinders}) \end{cases}$$

ε : porosity τ : tortuosity

Figure 14. Effective diffusivity calculation using the DFN model.

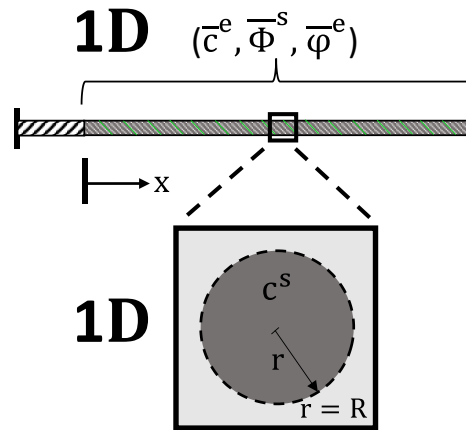


Figure 15. Calculations using the DFN model. Liquid-phase diffusion along the electrode thickness (x-direction), solid-phase diffusion, and charge transfer process are calculated on a single particle level (r-direction).

In conclusion, the macroscopic model mainly focuses on simplifying the geometry and structure of the electrodes. Thus, the prediction error of the DFN model is mainly a consequence of the heterogeneous structure of the electrode. **Figure 16** shows the true electrode geometry reconstructed from μ -CT scanning. Compared to the real structure, the DFN model neglects the particle size distribution and particle shape distribution as well as neglecting the conductive binder phase. Neglecting the particle size and shape distribution could lead to an inaccurate estimation of

the solid/liquid interface area and, thus, an underestimation or overestimation of the overpotential of the charge transfer process. Neglecting the conductive binder phase causes an underestimation of the diffusive resistance within the pores, leading to an imprecise prediction especially at high charge/discharge rates. The latter is the main reason that the DFN model is not suitable for predicting cycling at charge/discharge rates $>2C$ ⁷¹.

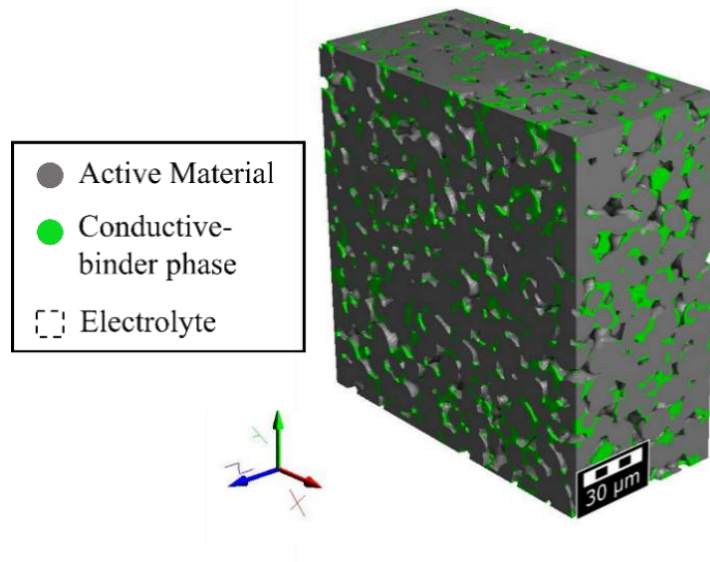


Figure 16. Reconstructed microstructure of a graphite electrode based on X-ray micro-computed tomography (μ -CT).

Hence, it is crucial to develop computational models which accurately depict the electrode's heterogeneous structure, while maintaining low computational complexity. To achieve this, the full homogenized macroscale (FHM) model has been proposed. This macroscale model is derived by Asymptotic Homogenization (AH) of the microscopic transport equations^{71,72}. The FHM model homogenizes the electron transport, ion diffusion, and the migration process within a small representative volume element (RVE). As a result, the FHM model is able to provide insight into the morphology of the real electrode and provides high geometric fidelity. On the downside, it underestimates the diffusion process within the solid phase and, therefore, underestimates the overpotential at high C-rates.

In this work, I developed an extension model based on the FHM model that combines the asymptotic homogenization of charge and mass transport with diffusion length theory. First, ion diffusion and electron transport is simulated in a small volume (RVE), after which it is homogenized at the macroscale. Next, the obtained calculation is coupled with another 0D microscale calculation that approximates the ion concentration gradient within an active material particle based on diffusion length theory. In this way, the calculation can preserve electrode

heterogeneity and at the same time include the solid-phase diffusion process in the simulation. This novel model offers higher prediction accuracy coupled with higher flexibility, which makes it useful for studying electrode structures with greater complexity, like electrodes with 3D CC. A more detailed discussion of the model can be found in Chapter 3.9.

III METHODS

This chapter describes the preparation of the novel LiB electrode containing a 3D metal fleece, the electrochemical tests carried out for electrode characterization, the design of a novel experimental set-up combining Raman microspectroscopy and microfluidic chips for studying the interaction between the metal surface and electrolyte, an ab-initio DFT simulation set-up to measure increased ion diffusion at the metal/electrolyte interface on a molecular level, and, finally, the development of a digital twin for fast predictions of the electrochemical performance of the developed electrodes.

3.1 ELECTRODE PREPARATION & CELL ASSEMBLY

For film electrode fabrication, an electrode slurry was prepared and doctor-bladed onto the current collectors (Cu foil and Al foil) with defined thickness. The anode slurry contained: 94 wt.% synthetic graphite (Targray, item number: SPGPT802), 1.5 wt.% carbon black (Alfa Aesar, 90+% trace metals basis, CAS: 1333-86-4), 2.4 wt.% CMC, and 1.6% SBR. The cathode slurry contained: 93 wt.% NMC 622 (Targray, item number: T61R), 2 wt.% Carbon Black (Alfa Aesar, 90+% trace metals basis, CAS: 1333-86-4), 2 wt.% natural graphite flakes (Targray, item number: T7R3), and 3 wt.% PVDF-HFP (Sigma Aldrich, CAS: 9011-17-0). The anode slurry was dispersed in water with a solid to liquid ratio of 1:1.1. The cathode slurry was dispersed in NMP with a solid to liquid ratio of 1:0.85. The dispersion was created with a Thinky mixer (SDR-500) at a rotation speed of 2000 rpm over 30 min. The slurry was coated on the foil current collector (12 μm -thick copper foil / 16 μm -thick aluminum foil) and dried at 80 °C in ambient condition. Afterwards, the electrode was calendared to the desired porosity at a speed of 5 m min⁻¹ at 160 °C. The electrode was vacuum-heated to 100 °C to get rid of H₂O and other residuals before being transferred to a glovebox.

To create fleece electrodes, fine metal ribbons were produced with a melt spinning technique. The width and thickness of the metal ribbons were approx. 40 μm and approx. 15 μm , respectively. The obtained fine ribbons were cut to ~7 mm length and were assembled into a fleece through dispersion in paraffin oil. Afterwards, they were thermally sintered to produce a mechanically stable fleece under inert gas (Argon). The areal loading and the thickness were calculated geometrically to achieve a certain mean mesh diameter within the fleece. With this method, a metal fleece containing interconnected and isotropically distributed metal fibers was fabricated. The percolation network formed by the fleece showed 3D distribution and, thanks to the fibrous structure, 99.9% of the void space is in the open pore-network structure.

Sintered fleeces were filled with the slurry described above. The metal fleece was dipped into the slurry for 60 s. Ultrasound (VWR Ultrasonic Cleaner) treatment was used to get air bubbles out and achieve optimal filling of the fleece with active material slurry. The coated fleece was dried in hot air (40 °C) and afterwards compressed to the desired porosity using a uniaxial compression machine at 10 KN/cm². The electrode was vacuum-heated to 100 °C to get rid of H₂O and other residuals before being transferred to a glovebox.

For half-cell testing, round electrodes (film and fleece electrodes) were punched out from the original electrode material (14 mm in diameter). The electrodes were soaked in electrolyte for 30 min (1 M LiPF₆ in EC: DMC at a volumetric ratio of 50:50; Sigma Aldrich, Germany). For one half of the cells, a metallic lithium coin acted as the anode and lithium source, separated by a glass fiber separator (Whatman 934-AH). All cells were assembled into state-of-the-art coin cell set-ups (MTI Corp.) with wave springs and separators were fitted to the size of the electrodes. Afterwards, the cells were sealed with an electrical coin cell crimper, stored for 24h at room temperature to achieve electrolyte wetting, and then prepared for testing. For full-cell testing, electrodes of 14 mm diameter (anode and cathode) were punched out, both electrodes soaked in the electrolyte for 30 mins, and then assembled with a PP separator (Celgard 2500).

Prior to electrochemical tests, the assembled coin cells were stored in a 40 °C oven for 12 hours, allowing the electrolyte to fully wet the electrode and separator.

3.2 SEI FORMATION & ELECTROCHEMICAL TESTS

Cell testing was performed in a coin cell using an SP-150 Potentiostat (Bio-Logic). After assembly, the half-cell underwent three SEI formation cycles with CC-CV charging and discharging at C/10 each in a voltage window between 12mV-1.5V (anode half-cell). The initial efficiency was calculated by dividing the 2nd formation discharge capacity by the 1st formation cycle discharge capacity. The rate capability tests were run at CC-CV charging and CC discharging conditions within the same voltage window.

Solid-phase diffusivity was determined using the GITT measurement. Towards this end, the anode/cathode half-cell was charged/discharged at C/20 for 12 mins, followed by a 2h relaxation period. This pulse/relaxation cycle was repeated 100 times until the cell was fully charged/discharged. A detailed description of the effective solid-phase diffusivity calculation is given in Chapter 3.3.

Potentiostatic electrochemical impedance spectroscopy was performed to determine the film resistance, the charge transfer resistance, and the Butler-Volmer exchange current density. The applied frequency ranged from 0.1 Hz to 1 MHz with an amplitude of 5 mV. Data fitting with an equivalent circuit model was carried out in MATLAB. The calculation of the Butler-Volmer exchange current density and the reaction rate are described in Chapter 3.3. The charging/discharging protocol, GITT and EIS protocol are given in **Appendix I**.

The Van-der-Pauw method was used for measuring the dry electrode's electrical conductivity. The dry electrode layer was peeled off from the copper foil and measured with a 4-point source meter (Keithley 2615 A Source meter).

3.3 GITT, MICRO-CT RECONSTRUCTION & IMPEDANCE MEASUREMENTS

The galvanostatic intermittent titration technique (GITT) is a method that provides kinetic and thermodynamic information about an electrochemical system. We used GITT to investigate the solid-phase diffusion process within the half-cell. During the measurement a series of current pulses ($C/20$), each followed by a relaxation time of 2h, is applied to the anode half-cell. During the relaxation phase the open circuit voltage (OCV) can be determined as a function of the state of charge (SoC). We chose 100 pulses during both charging and discharging to obtain a more accurate OCV and more detailed information concerning diffusion process variations at different SoCs. The relaxation periods were chosen to be sufficiently long to ensure the establishment of equilibrium conditions at the lithium-ion concentration gradient within the electrolyte. **Figure 17** shows the GITT curve. The OCVs for lithiation and delithiation can be extracted by plotting the relaxation-phase voltage. By comparing the pulse phase and the relaxation phase, the solid-state diffusivity was calculated utilizing **Equation 9**. I is the charging current during the pulse phase, V_m is the molar volume of the active material, F is the Faraday constant, S is the active material/electrolyte interface area, and y , which ranges from 0 to 1, indicates the SOC.

$$D = \frac{4}{\pi} \left(\frac{IV_m}{FS} \right)^2 \left(\frac{dE_s/dy}{dE_t/dt^{\frac{1}{2}}} \right)^2 \quad (9)$$

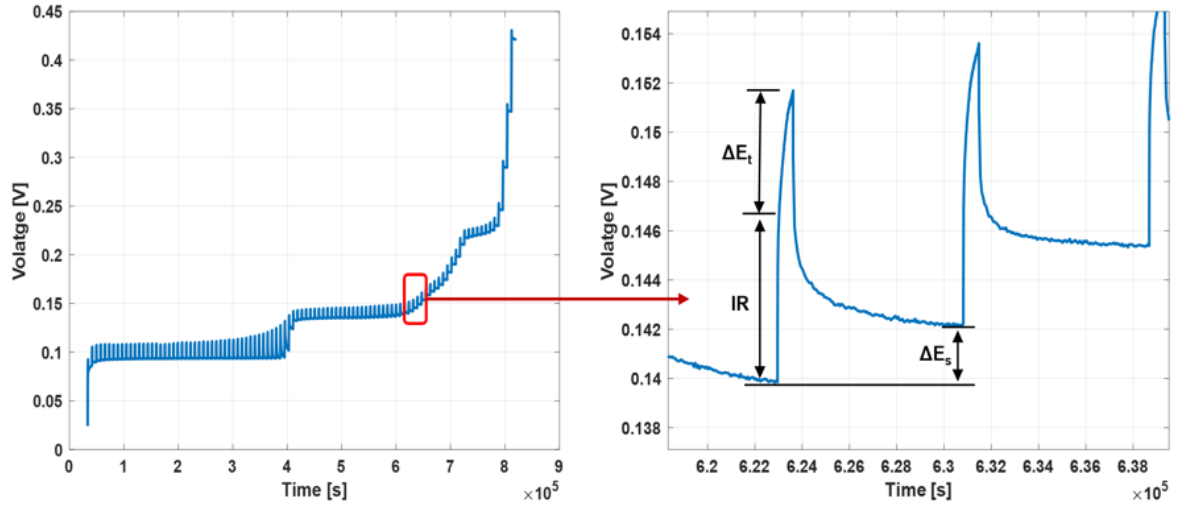


Figure 17. GITT measurement of an anode half cell.

In order to perform a reliable GITT measurement, two key points must be kept in mind: (1) the separation of overpotential caused by electrical resistance and diffusive resistance and (2) an accurate estimation of the active material/electrolyte interface area.

References in literature^{73–76} have described different methods to separate the pulse overpotential. According to Figure 8 the time scale of electron transport is ultrafast compared to the diffusion, thus, the most straightforward way is to define time constants for separating these two processes. However, charge transfer processes overlap between the two and the time constant of these processes is highly dependent on the electrode geometry. Therefore, from a practical standpoint, separating the processes by time is not a good way to proceed. In our case we are solely interested in the solid-phase diffusivity. Therefore, the E vs $t^{0.5}$ during the pulse phase, which is taken from strict linear behavior, is adequate for an accurate determination of the diffusion coefficient (**Figure 18**). Specifically, the second derivative of $dE_t/dt^{0.5}$ is calculated and a threshold value ($5E-6$) is used to define the ‘strict linear behavior’. It is worthwhile mentioning that E_s is not calculated directly from $I=0$ but also averaged after E_s is stabilized (**Figure 19**). This ensures that an accurate OCV can be determined, which is then used to determine the $dE_s/dSOC$.

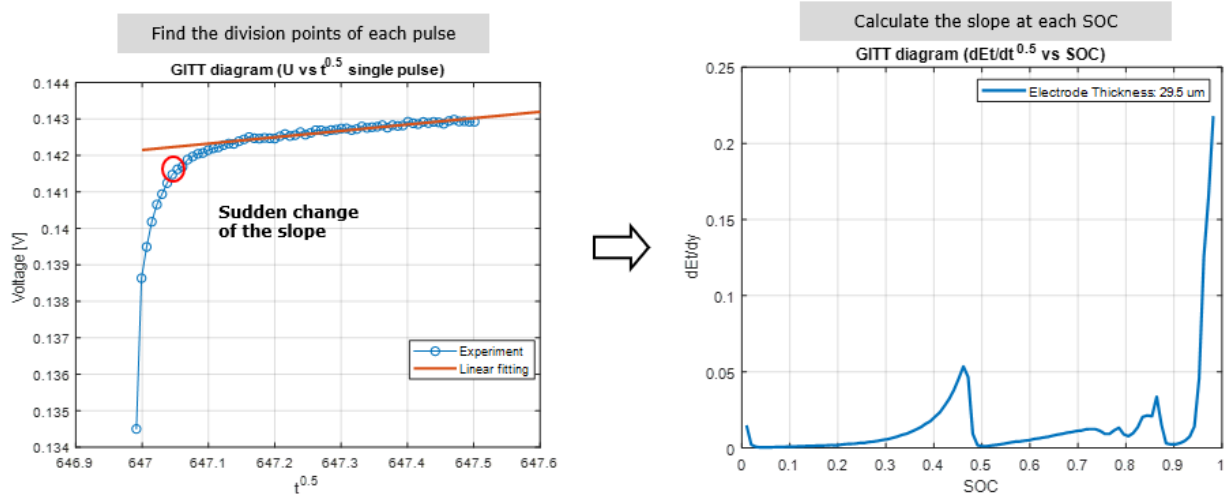


Figure 18. Determination of the $dEt/dt^{0.5}$ from GITT measurements.

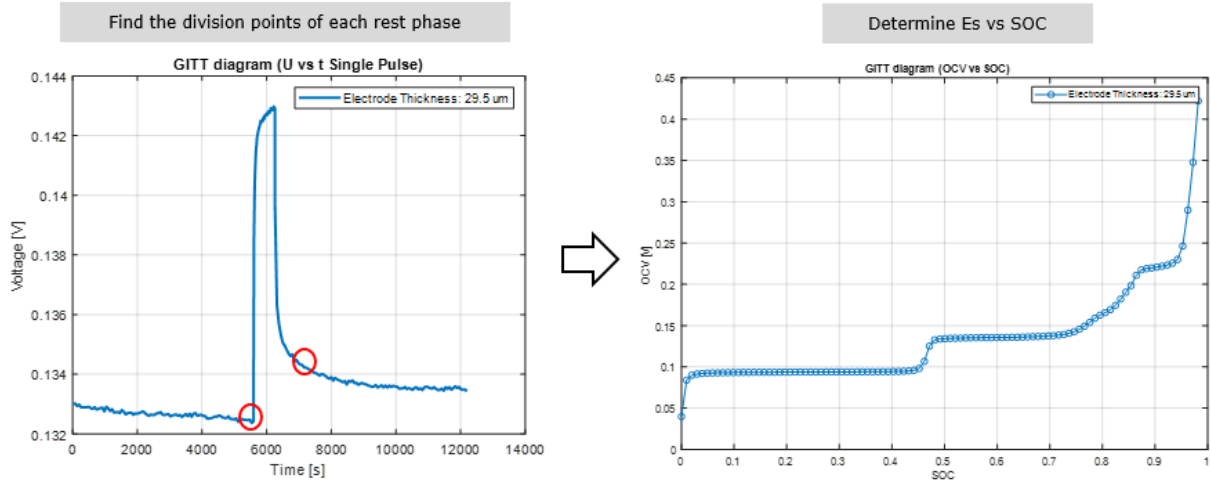


Figure 19. Determination of the $dEs/dSOC$ from a GITT measurement.

The interfacial area between the active material and the electrolyte was calculated with the aid of a micro-CT reconstructed 3D structure. Specific interface area estimation methods were employed for different active material particles. For NMC or LFP particles, which have a bimodal particle size distribution, Verma et al⁷⁷ calculated the area by approximating the NMC particles as a spherical particle with a certain ‘roughness’ (shown in **Figure 20**). In the case of the graphite anode, ‘smoother’ battery-grade graphite particles,⁷⁸ which are derived from natural graphite flakes with different crystalline orientations, are used. Because the particle shape cannot be approximated as round or elliptical, the estimation of the anode active material as well as the electrolyte interface is more challenging.

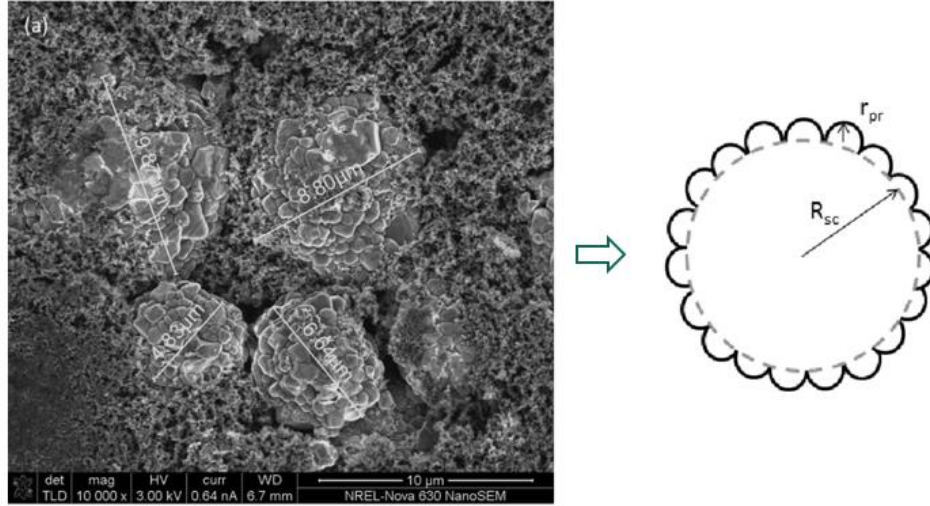


Figure 20. NCM cathode active material surface area estimation.

We directly utilized μ -CT 3D reconstruction as the preferred method for identifying particle size, particle size distribution, and shape. This allows greater resolution and accuracy than both BET and estimation by particle size distribution. 3 mm diameter electrode discs were punched out from the anode & cathode material sheet and mounted on a special pinhead sample holder. Next, they were scanned using a lab-based X-ray μ -CT system (Skyscan 1272, Bruker, Germany). An X-ray source with 70 kV source voltage and an 85 μ A source current were used with 586 ms exposure time. A 360° rotation scan using 0.2° rotational steps was carried out for the 3-dimensional reconstruction of the electrode. A voxel size of 0.5 μ m 3D volume of the electrode was reconstructed and then imported into a voxel-based analyzing commercial software package (Geodict, Math2Markt, Germany). Multiphase segmentation was carried out based on the Otsu algorithm. The interfacial area between pores and active material was calculated and used for galvanostatic intermittent titration technique (GITT) measurements. **Figure 21** shows a 3D reconstruction of the anode.

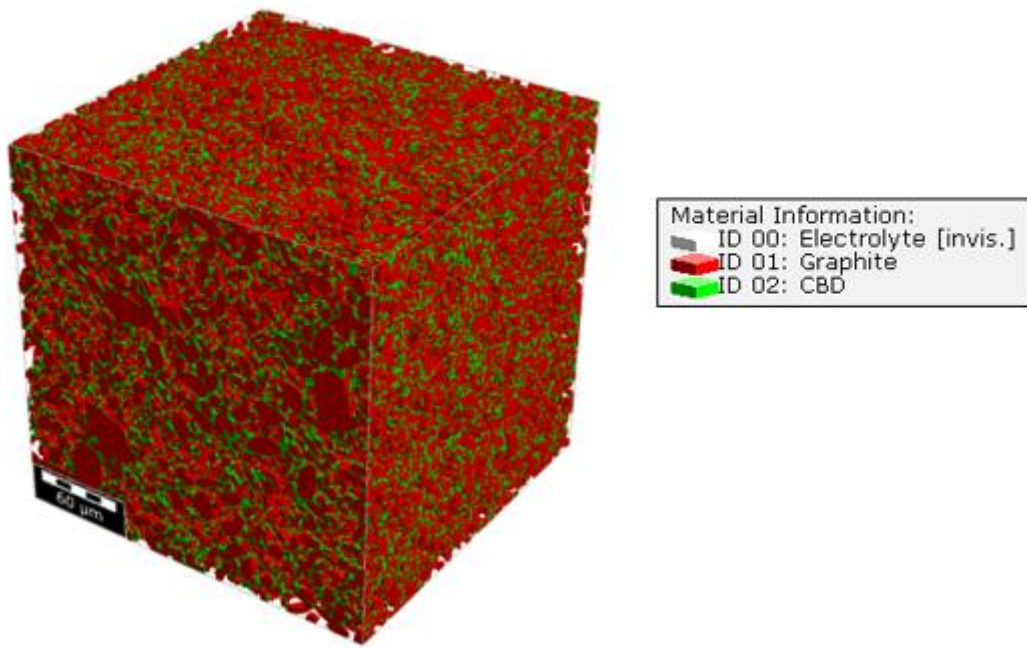


Figure 21. μ -CT reconstruction and segmentation of a graphite anode.

The charge transfer and ion migration between the electrolyte and the active material are described by the kinetic reaction rate and the exchange current density at the interface. The reaction rate and exchange current density can be obtained by impedance measurements at open-circuit voltage. The Butler-Volmer equation (**Equation 10**) is used to quantify the relation between interface overpotential and the exchange current density.

$$j = j_0 \left(\exp \left[\frac{(1-\alpha)F\eta}{RT} \right] - \exp \left[\frac{-\alpha F\eta}{RT} \right] \right) \quad (10)$$

In EIS measurements the overpotential is small, thus the equation can be linearized to:

$$j = j_0 \frac{F\eta}{RT} \quad (11)$$

Here the overpotential reflects the charge transfer resistance:

$$\eta = jSR_{ct} \quad (12)$$

Thus, the exchange current density can be derived if the charge transfer resistance and overpotential are characterized by EIS measurement. **Figure 22a** shows EIS measurements at different SOC. Data is fitted using the equivalent circuit shown in **Figure 22b**.

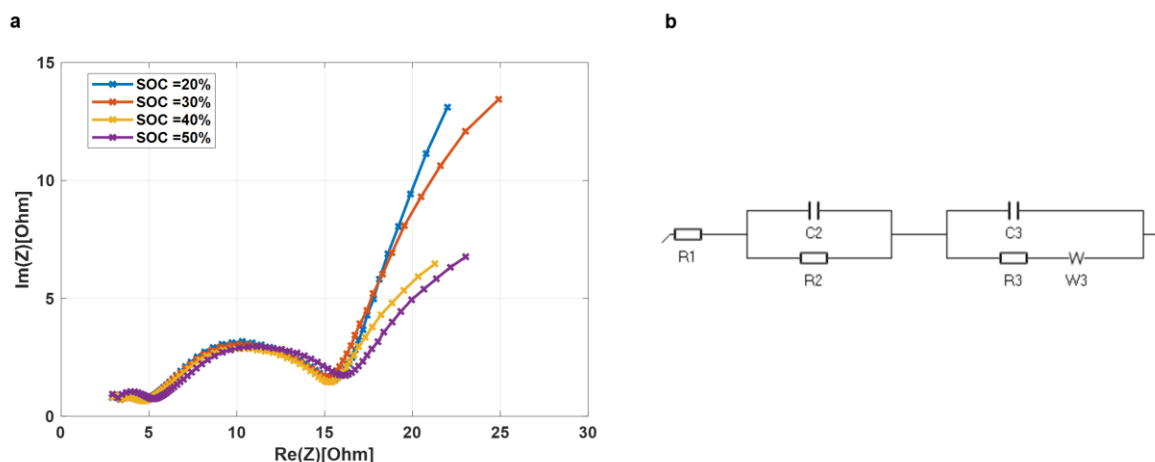


Figure 22. (a) EIS data of a half-cell anode at different SOC values; (b) The equivalent circuit to fit the EIS curve.

3.4 ELECTROLYTE DESCRIPTION & PFG-NMR

Ultra-pure LiPF_6 (99.8%, Sigma Aldrich, Germany) and electrolyte solvent (Ethylene carbonate (EC): Dimethyl carbonate (DMC) 50:50, Sigma Aldrich, Germany) were mixed in an argon atmosphere glovebox with low H_2O and O_2 content (< 0.1 ppm). LiPF_6 was baked at 80°C for 48 h under vacuum. Glassware was cleaned with $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ at a ratio of 1:3, washed with deionized water in an ultrasonic bath, and dried under vacuum for 24 h. LiPF_6 was dissolved to a concentration between 0-2 M in the binary solvent and then stored in aluminum bottles.

The characteristics of lithium-ion electrolytes were obtained by pulsed field gradient NMR (PFG-NMR). These measurements were performed with a Bruker AVANCE III 400 MHz spectrometer and a Bruker wide-bore magnet. The shape of the gradient pulses was given by a half-sine function and the diffusion time between the two gradient pulses of a pulse sequence was fixed at 10 ms. The amplitude of the gradient pulses G was varied in 16 steps up to 10.55 Tm^{-1} for the bulk electrolyte. With PFG-NMR, the ionic conductivity, lithium-ion diffusion coefficient, and transference number were determined.

3.5 MICROFLUIDIC DEVICE ASSEMBLY & WORKING PRINCIPLE

In order to quantitatively study Li^+ mobility on a current collector surface we developed a microfluidic experiment utilizing Raman spectroscopy. **Figure 23** illustrates the design of our electrochemical set-up. A 5-nanometer-thick adhesive layer of chromium was deposited onto a Si-wafer, followed by a 100-nanometer thick layer of copper. To assemble the microfluidic Y-shaped channel, photoresist was applied on the copper surface and selectively removed to form the walls of the microfluidic channel. A thin layer of PDMS was bonded onto the photoresist to seal the

channel. The diffusion experiment was based on two laminar co-flows with different ion concentrations generated in the microchannel, as described by, e.g., Peters et al⁷⁹. Two electrically grounded laminar flows of electrolytes, one with and one without Li^+ ions, were injected in the two arms of the Y-shaped channel. As the flows reach the Y-junction, they come into contact with one another and equilibration by diffusion follows.

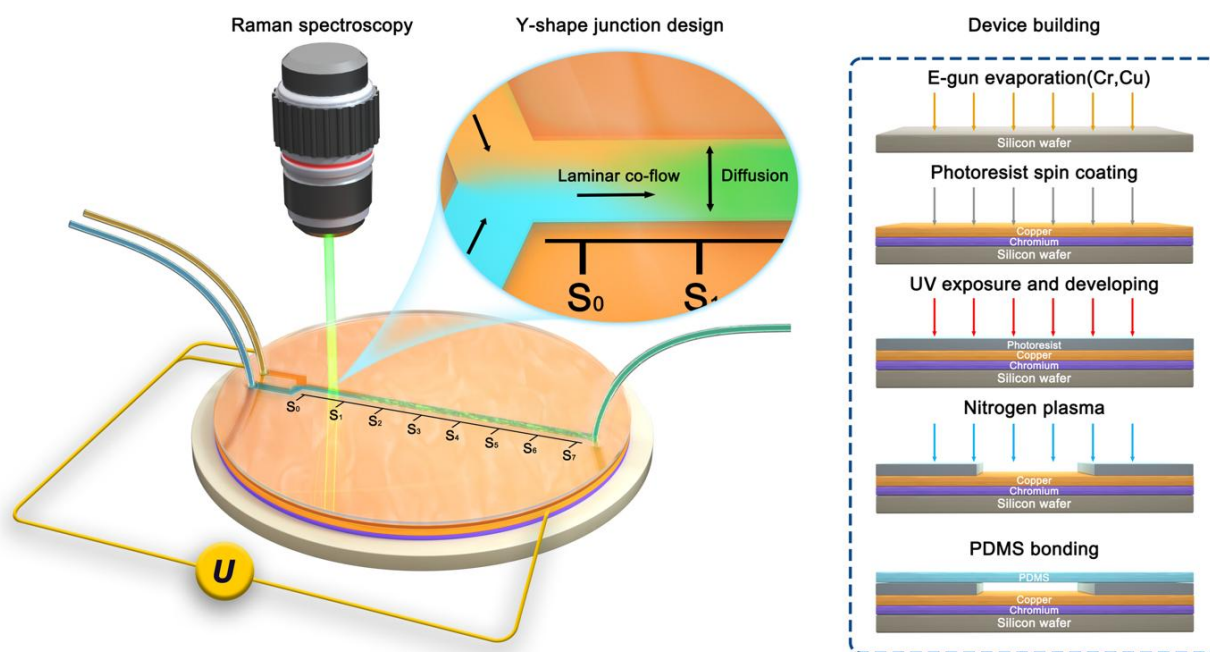


Figure 23. μ -CT reconstruction and segmentation of a graphite anode.

To construct the device, first, a chromium and then a copper layer were deposited onto the silicon wafer by E-beam evaporation. Microfluidic channels were constructed by micropatterning a layer of negative photoresist (SU-8 3000 series) using direct writing laser lithography. The resulting channels were sealed at the top through chemically bonding a thin PDMS sheet activated by nitrogen plasma treatment. PDMS-based tubing connectors were bonded onto the inlets and outlets. Finally, a copper wire was soldered onto the wafer's copper surface to allow for the application of an electrical potential. The procedure is described in greater detail below:

Step 1: Copper deposition on 4" silicon wafers by E-beam evaporation

Copper deposition on 4-inch silicon wafers was performed using an E-beam evaporation process (E-beam evaporator Pfeiffer Vacuum Classic 500). The wafer was assembled in the evaporation chamber, argon plasma applied to clean the surface, and the whole chamber was evacuated to 1.18 e-7 mbar. Afterwards, 5 nm chromium and then 100 nm copper were deposited on the Si-wafer at a rate of 2 Å/s.

Step 2: Spin Coating of the SU-8 3000 photoresists

Copper-coated Si-wafers were cleaned using acetone and isopropanol. The wafers were heated to 110°C and cleaned with nitrogen gas. The hot wafers were completely covered with SU8 photoresist and spin-coated (Laurell Technologies Corp., USA) to accomplish specific channel thickness. Each spin coating run consisted of a spread cycle at 500 rpm for 10 s (100 rpm/s acceleration) and spin cycles at various speeds for 30 s (excluding acceleration time at 300 rpm/s) (see **Table 2**). Coated wafers were soft-baked for 3 min at 65°C and 5 min at 95°C. This procedure maximizes photoresist adhesion to the copper surface.

Table 2. Parameters of spin coating protocol.

Height [μm]	SU8-3000 photoresists	Speed [rpm]
10	SU8-3010	3000
20	SU8-3025	4000
30	SU8-3025	2700

Step 3: Micropatterning by laser lithography

Microfluidic devices were designed using the QCAD-pro application of RibbonSoft (Switzerland) and transferred into the photoresist layer on the coated wafers by laser lithography using the μPG 101 Micro Pattern Generator (Heidelberg Instruments, Germany) in writing mode IV at a maximum power of 70 mW with 100%-pixel pulse duration and 1x2 energy mode settings. The post-exposure bake was conducted for 1 min at 65°C followed by 5 min at 95°C. The wafer was allowed to cool down to room temperature and unpolymerized photoresist was removed using the mr-DEV 600 developer (micro resist technology, Germany) for 12 minutes, during which the developer solution was exchanged once. Remaining traces of developer solution on the wafer were removed with isopropanol.

Step 4: Preparation of PDMS sheets

A thin PDMS (Sylgard 184, Dow Corning, USA) sheet was prepared by mixing the oligomer and the curing agent at a 10:1 (w/w) ratio, followed by degassing. To ensure uniform sheet reproduction with regards to thickness, a 3D-printed casting frame with a cross-sectional area of 50 cm² was taped to a petri dish and filled with 1 ml of the PDMS mixture and subsequently cured at 70°C for at least 2 hours. This resulted in a sheet thickness of 1-2 mm. The PDMS sheet was removed from the petri dish, cleaned using 70% ethanol spray, dried with pressurized air, and protected from both sides with tape to avoid any dust contamination. After the sheet was cooled to room temperature, inlets and outlets were punched into the sheet with a 0.75 mm biopsy puncher (Darwin Microfluidics, Germany).

Step 5: Sealing microfluidic channels by PDMS sheet bonding

To seal the microfluidic channels, the previously prepared PDMS sheet was chemically bonded to the SU-8 photoresist layer. To this end, the tape from the bottom side of the PDMS sheet was removed and the surface activated by exposure to low-pressure ultra-pure nitrogen plasma (200 W, 0.4 mbar, 60 s; PVA TePla 100, PVA TePla, Germany). The sheet was positioned on the photoresist layer, such that the inlet and outlet holes aligned, and bonded for 30 min at 100°C. To improve bonding, weights were applied on the PDMS sheet.

Step 6: Bonding of tubing connectors

To facilitate the connection to appropriate tubing, thicker PDMS blocks (4-5mm) were produced and equipped with inlets and outlets. The top PDMS surface of the PDMS-wafer composite as well as the PDMS tubing connector were exposed to low-pressure oxygen plasma (200 W, 0.5 mbar, 30s; PVA TePla 100, PVA TePla, Germany) and bonded together (2h, 80 °C).

Step 7: Soldering of copper wires to the wafer's copper surface

Copper wires were soldered to the copper surface of the microfluidic device with a low melting alloy (51IN-32.5BI-16.5SN, Indium Corporation of America, USA) to allow the application of an electrical potential.

The microfluidic device design also included two leakage indicator channels alongside the main channel (**Figure 24**), which fill with liquid droplets in the case of leakage. A ruler is placed next to the leakage indicator channel to facilitate reproducible measurements.

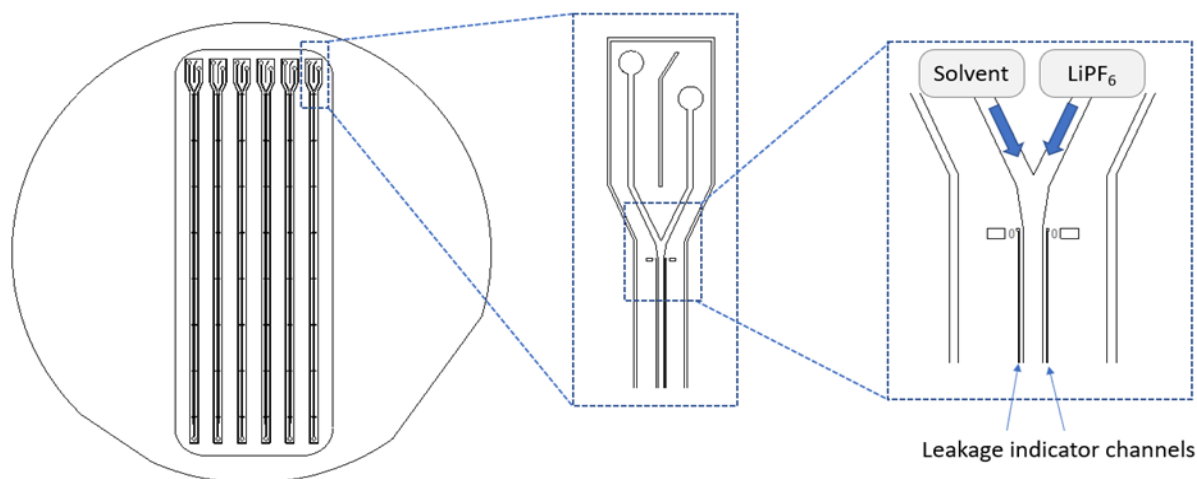


Figure 24. Microfluidic chip design.

3.6 RAMAN SPECTRUM ACQUISITION, CONCENTRATION CALIBRATION & NOISE REDUCTION

Confocal Raman Spectroscopy was used to spatially and temporally measure the quantitative ion concentration perpendicular to the flow direction. In the electrolyte (1 M LiPF_6 in 50:50 ethylene carbonate (EC): dimethyl carbonate (DMC)), the dissolved Li^+ associates with solvent molecules to form solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and aggregates. This process is mediated by ion-dipole-interactions which impact the solvent molecule bond vibration frequencies, thus leaving a trace in the solvent molecules' Raman spectrum. Specifically, we focused on the Li^+ and EC ion-solvent association. As a Li^+ ion impacts the oxygen-carbon-oxygen bond (O-C-O) vibrational frequency of EC at 720 cm^{-1} it shifts it towards 733 cm^{-1} . Meanwhile, P-F stretching is observed at 744 cm^{-1} , indicating an increased amount of anions (PF_6^-). By eliminating fluorescence noise, normalizing, and comparing the intensity of the original O-C-O peak and the P-F peak, Li^+ ion concentration was visualized in real-time with resolution in space.

A scanning near-field confocal Raman microscope (AlphaSNOM, Witec, Germany) equipped with a 532 nm laser (max. power: 40 W) and a glass objective with 50x magnification corrected for aberrations (Zeiss 50x/0.55 DIC LD, Zeiss, Germany) provided a $\sim 1.2\text{ }\mu\text{m}$ spot size at 9 mm working distance. Small calibration chambers were designed and built from photoresist deposited onto the copper-covered Si-wafer (SU-8 3025). Also, a thin sheet of PDMS was bonded to seal the channel. Different electrolytes with a Li^+ ion concentration between 0-2 M were injected and spectra recorded at 50% laser power. Each separate measurement consisted of an average of 10 spectra, each one collected using 0.5 s exposure. Measurements were repeated 5 times. A MATLAB script was used for background removal. Fluorescence background noise was too loud

to be negligible, because the lithium salt in the solvent evokes greater fluorescence. First, measurements were calibrated by normalizing the Rayleigh peak intensity to account for slight differences in laser intensity between measurements. In a second step, data were normalized by comparing the spectra intensities between the Raman bands at 720 cm^{-1} and 733 cm^{-1} . These represent the O-C-O bonding in the presence of or without the presence of Li^+ , thereby resulting in the visualization of different lithium concentrations.

Laminar flow is a prerequisite to characterizing the diffusion coefficient. Thus, the selection of the flow rate is crucial for this measurement. On the one hand, the flow rate should be slow enough to guarantee a laminar flow condition and should allow enough time for the diffusion process to take place within the main channel. On the other hand, the flow rate should be fast enough that (i) convection flow is much greater than diffusive flow and (ii) a clear interface between different lithium-ion concentrations is generated at the Y-junction. The Reynolds number is calculated as:

$$Re = \frac{\mu L}{\nu} \quad (13)$$

Re is the Reynolds number, L is the characteristic length, μ is the flow speed and ν the kinematic viscosity. Considering that the main channel width is much larger than the channel height, the characteristic dimension L is equal to the channel height.

Meanwhile, the flow rate should be large enough that diffusive flow along the x-direction is negligible. The Péclet number should be much larger than 1.

$$Pe_L = \frac{L^2/D}{L/\mu} \quad (14)$$

Pe_L is the Péclet number and D is the diffusion coefficient. With this calculation we determined that the flow rate should be $1\text{ }\mu\text{L/min}$, $2\text{ }\mu\text{L/min}$ and $3\text{ }\mu\text{L/min}$ for channels with a height of $10\text{ }\mu\text{m}$, $20\text{ }\mu\text{m}$ and $30\text{ }\mu\text{m}$, respectively. **Figure 25** shows the concentration gradient at $2\text{ }\mu\text{L/min}$ flow rate in a channel of $20\text{ }\mu\text{m}$ height. These parameters generate a clear concentration gradient at s0 while maintaining a low Reynolds number and also establish a clear interface at the Y-junction.

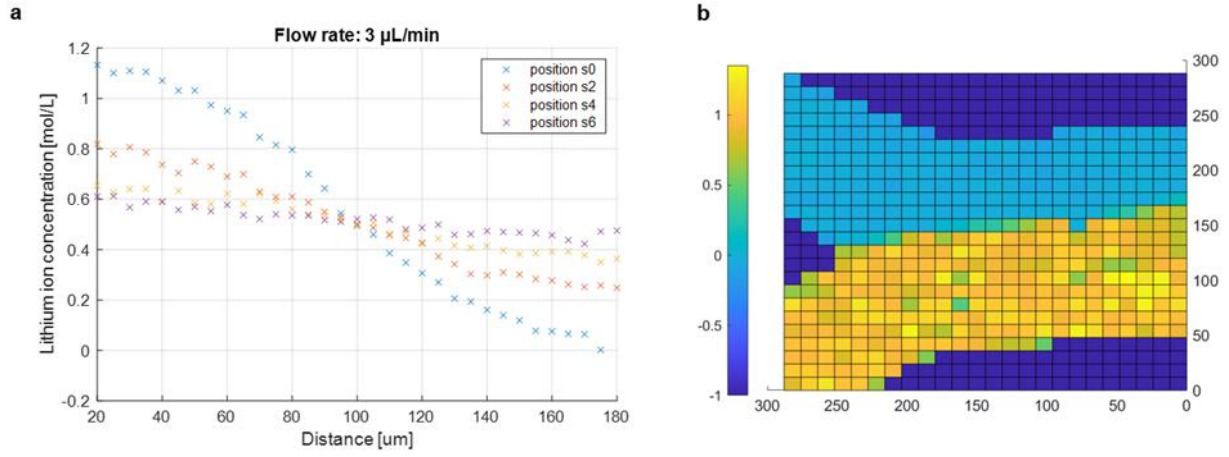


Figure 25. (a) The lithium-ion concentration gradient at 2 μL/min in a channel with a height of 20 μm. (b) 2D Raman scan of the Y-junction. The legend on the left indicates the lithium-ion concentration in mol/L (-1 indicates the PDMS wall).

For quantifying the diffusion process, a convection-diffusion model was applied to determine the apparent diffusion coefficient. The convection-diffusion model describes multicomponent diffusion between two laminar co-flowing liquids in the microchannel.

When the two channels join together, the two flows come into contact with each other and diffusion starts at the interface of the laminar co-flow. The convection laminar flow velocity profile in the rectangular duct along the y-axis can be described as

$$v(y) = \left(\frac{n+1}{n}\right) \left[1 - \left(\frac{y}{W/2}\right)^n\right] \bar{v} \quad (15)$$

$\bar{v}$ is the mean velocity calculated by flow rate, W is the width of channel, and the exponent n depends on the channel dimensions.

$$n = 1.7 + 0.5\left(\frac{H}{W}\right)^{-1.4} \quad (16)$$

H is the height of the channel and the non-slip boundary condition is applied to the channel wall. Since the Péclet number is larger than 100, the diffusion along the x-axis is negligible. Diffusion along the y-axis is described by Fick's second law.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \quad (17)$$

c is lithium-ion concentration, D is diffusivity, and t is time. Here the diffusion time t can be substituted by

$$t = \frac{x}{v(y)} \quad (18)$$

$v(y)$ is the convection flow velocity along the channel calculated by Equation S5 and x is the flow distance along the x -axis. Therefore, Fick's second law can be re-written as

$$v(y) \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \quad (19)$$

In this convection-diffusion model the second partial differential term $\frac{\partial^2 c}{\partial y^2}$ is key for the measurement. Also, a sufficiently small Δy is required. Therefore, the Raman line scan along the y -axis is implemented in 4 μm steps to accurately calculate the diffusion coefficient.

3.7 MICROFLUIDIC DEVICE OPERATION & OPERANDO RAMAN LINE SCAN MEASUREMENT

To conduct diffusion measurements between a lithium-ion rich phase and a lithium-ion poor phase, a 1 mol/L LiPF_6 solution in 50:50 EC/DMC as well as a 50:50 EC/DMC solution without LiPF_6 were prepared. The solutions were loaded into gas tight glass syringes (SKU:HM-1001 Darwin microfluidics, Germany), which were connected to a needle (0.4 x 19 mm, BD Microlance 3, Spain) and polytetrafluoroethylene (PTFE) tubing (OD x 0.32 mm, Darwin microfluidics, Germany). After priming of the tubing, the syringes were connected to the microfluidic device via the PDMS inlet holes. The laminar flow was controlled by a syringe pump (Pump II Pico Plus Elite, Harvard Apparatus, USA) and the flow rates of both solutions were set at the same value. The flow rate was selected based on the Reynolds number and diffusion rate. After the entire channel was wetted, the leakage indicator channels were checked to exclude any leakage at the PDMS-bonded seals. For experiments where an electrical potential was applied to the copper surface by a source meter (Keithley 2615 A Source meter), grounding electrodes were connected to the needles of the syringes, whereas the active electrode was connected to the copper wire on the copper substrate. The source meter applied a constant voltage during the entire measurement. To avoid any electrochemical reactions, the voltage range we chose was between -500 mV to 500 mV. **Figure 26** shows the experimental set-up.

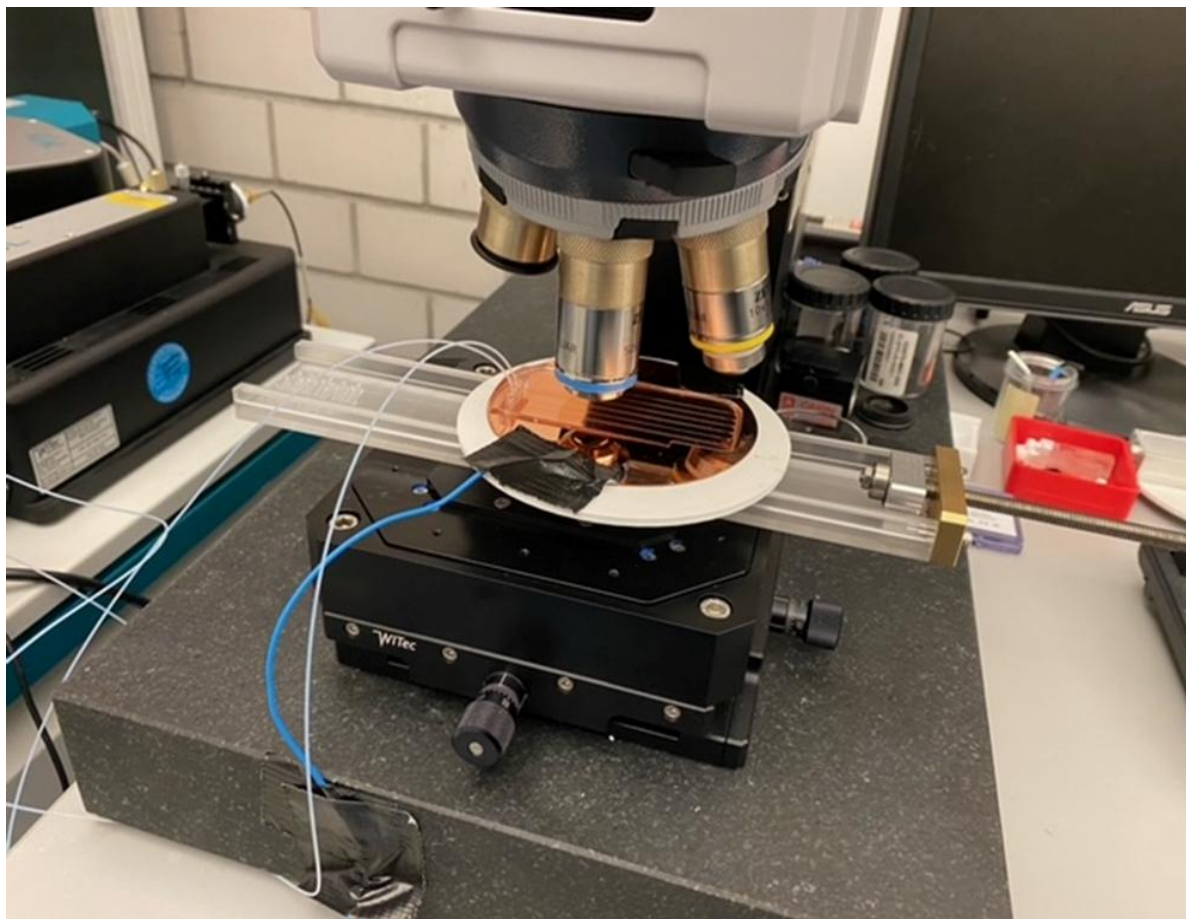


Figure 26. The experimental set-up: The microfluidic channel was built on the copper-coated wafer. The organic solvent with or without lithium salt was connected to a grounding electrode and injected. An offset voltage was applied to the copper.

The whole device was fixed on a piezoelectric stage to ensure that the microfluidic channels were in the horizontal plane. A test line scan along the z-axis was carried out to locate the PDMS and copper surface. Next, the focus point was fixed to the central line of the channel. Afterwards, a 1-D line scan along the y-axis was carried out with the same settings for calibration purposes. Due to the presence of laminar flow, the impact of the laser power on electrolyte degradation and temperature was negligible, thus allowing the adoption of a higher output power. Raman spectra were obtained in a line scan along the channel width at 40 different points with 5 μm distance between the points. The number of independent Raman measurements at each point was on average 10 per sample. A Confocal Raman microscope uses a pinhole aperture to get rid of out-of-focus signals, thereby enabling the collection of volume information with defined depth. The microfluidic device design also featured a ruler next to the leakage indicator channel, in order to locate the line scan starting and end points and thus ensure accuracy during repeated measurements. After calibrating the device as described above, the concentration was visualized and the apparent Li^+ diffusivity was calculated based on Fick's law.

3.8 MD SIMULATION

To explore ion surface diffusion and establish a profound understanding of it on a molecular level, full scale ab-initio molecular dynamic simulation (MD simulation) based on density function theory (DFT) is carried out to study ion movement at the interface between the electrolyte and charged metal surface. First, the bulk electrolyte is modeled and a preset negative surface charge density is assigned to the copper surface. Due to the surface charge, the ions are redistributed along the surface and an electrical double layer (EDL) is formed. For the simulation, the ion mobility within the EDL is calculated based on the time evolution of its trajectory within the bulk electrolyte and on the surface ($< 20 \text{ \AA}$).

MD simulation is implemented using the Material Studio (MS) software. The COMPASS III force fields were used to optimize the atoms and charges. Simulations of bulk electrolytes were calculated at room temperature (293 K) assuming constant particle numbers and a constant volume. The electrolyte volume was $35.70 \text{ \AA} \times 35.33 \text{ \AA} \times 50.0 \text{ \AA}$, with 30 Li^+ , 30 PF_6^- , 225 EC molecules and 178 DMC molecules. This is equivalent to 1 M LiPF_6 in EC: DMC (50:50 v: v) electrolyte with a density of 1.195 g/cm^3 . The electrode consists of 5 layers of copper atoms along the [111] direction and the surface area equals $35.70 \text{ \AA} \times 35.33 \text{ \AA}$ (**Figure 27**).

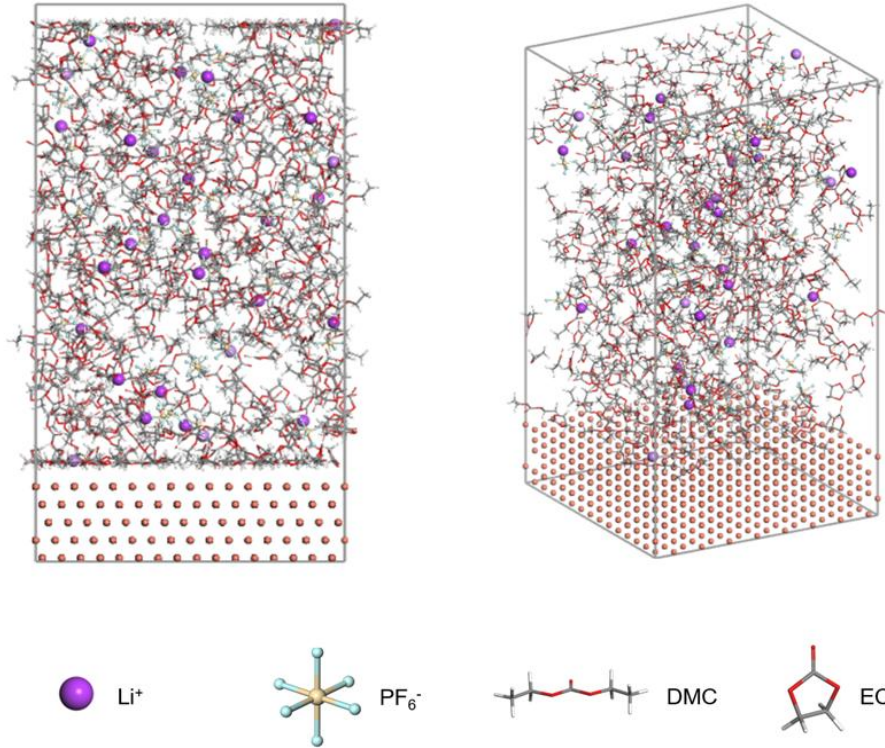


Figure 27. Solid electrolyte interface used for the molecular dynamic simulation.

The COMPASS II force field together with atom-based Ewald electrostatic and van der Waals summation methods with convergence tolerance were selected for DFT calculations. The explicit solvent (DFT-CES) was applied. First, an equilibration run for 2 ns at room temperature with zero charge density conditions on the electrode (1 fs time step) was performed, followed by a production run using the NVT ensemble for another 2 ns for a statistical analysis of the concentration distribution of each species. For the charged surface, 4 ns using the NVT ensemble at room temperature was performed to obtain the equilibrium state. When the species' concentrations were calculated at ~ 3 ns, the electric double layer (EDL) was converged.

The electrical double layer (EDL) is the result of the variation of electric potential near a surface. The relationship between the interfacial potential and the surface charge can be expressed by the Grahame equation, which is derived from the Gouy-Chapman theory under the assumption of electroneutrality conditions:

$$\sigma = \sqrt{8c_0\varepsilon\varepsilon_0k_B N_a T} \sinh\left(\frac{ze\varphi_0}{2k_B T}\right) \quad (20)$$

σ is the surface charge density, c_0 is the bulk electrolyte density, ε and ε_0 are the relative dielectric and vacuum dielectric constant, k_B is the Boltzmann constant, and φ_0 is the interfacial potential.

During MD simulation, 50 mV was set as the interfacial potential. Thus 0.8 e/nm^2 was assigned as the charge density on the copper surface.

These ions were selected within the EDL and tracked over time for diffusivity calculations. The mean square displacement (MSD) of their trajectory was calculated for 700 ps. The diffusion coefficient was calculated using the Einstein relation:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\sum_i^N (r_i(t) - r_i(0))^2 \right] \quad (21)$$

D is the diffusion coefficient, r_i is the center-of-mass position vector of particle i , N the total number of particles, and t is the time. Given a sufficiently long time the mean square displacement starts to be proportional to the time according to the Fickian regime. The diffusion coefficient can be extracted by linear fitting.

3.9 MICROSCOPIC SIMULATION

For the purpose of building a digital twin of the LiB and in order to perform reliable predictions, a microscopic electrochemical simulation was carried out to calibrate the macroscopic model and the microscale model was designed to include heterogeneities and the microstructural morphology of the electrodes. Towards this end, X-ray micro computed tomography (μ -CT) has emerged as an effective technique for the reconstruction of the electrode microstructure in 3D.

For the phase separation of the reconstructed structure, first, SEM images of the anode were analyzed and an estimation of the particle shape and particle size distribution was carried out. Using this dataset and a grain-fitting algorithm, it was then possible to distinguish pores, active material (AM) phase, and the conductive-binder (CB) phase in the μ -CT reconstructed structure (**Figure 21**).

It should be mentioned that the conductive binder phase, which in reality has a nano-porous structure, is here segmented as a single and continuous phase. Therefore, we developed a mathematical modeling technique to model the nanostructure of the conductive binder phase, which determines the effective conductivity and diffusivity of this phase⁸⁰.

The microscale model is based on the governing equations for an isothermal battery cell developed by Latz et al.⁸¹(**Table 1**). The Nernst Planck equation and the electroneutrality law govern the voltage and variations in the concentration gradient in the electrolyte phase. Solid-phase diffusion and Ohm's law govern the lithium concentration and the electrical potential level within the

electrode. The overpotential at the solid-liquid interface is calculated based on the Butler-Volmer equation. The CB phase is modeled as an inactive porous structure that allows lithium-ion flow and electronic flow simultaneously. Geodict from Math2Market is used as the simulation software. Hereinafter, the microscale model is referred to as the DNS (direct numerical simulation) model.

3.10 EXTENSION FHM MODELING, PARAMETERISATION & VALIDATION

As described in Chapter 2.7, the FHM model employs the asymptotic homogenization (AH) technique for microscale model reduction. The idea of this method is to transfer the influences of the heterogeneous microscale to a homogeneous macroscale. The influences of the heterogeneous microscale are analyzed within a so-called unit cell. The unit cell is a microscale domain Y that represents the properties of the macroscopic domain Ω_ε . The ratio of the characteristic length of the unit cell to the length of the macroscopic domain is defined by the so-called scale separation parameter:

$$\varepsilon = \frac{l}{L} \ll 1 \quad (21)$$

The condition for the validity of the AH technique is a sufficiently small-scale separation parameter. The smaller ε is, the lower the heterogeneity at the microscale. As shown in **Figure 28**, for the limiting case $\varepsilon \rightarrow 0$ we get a homogenous domain Ω consisting of a periodic sequence of infinitesimally small unit cells.

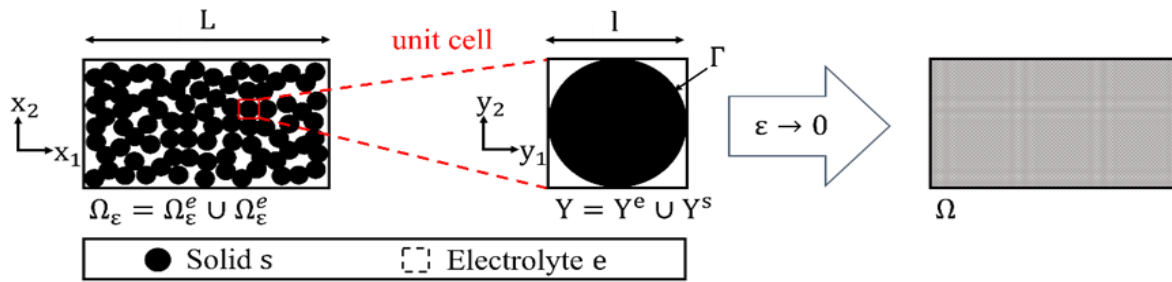


Figure 28. Concept of the Asymptotic Homogenization.

Here, the AH of the microscopic variables is based on the two-scale expansion approach:

$$u_\varepsilon(\vec{x}, t) = \sum_{n=0}^{\infty} \varepsilon^n \cdot u_n(\vec{x}, \vec{y}, t) = u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + O(\varepsilon^3) \quad (22)$$

The transport variable u_ε behaves periodically in the microscale. The index n defines the order of the different scales. The case $n=0$ corresponds to the macroscale. Starting from this scale, smaller and smaller scales with higher order are considered.

The variables of the different scales u_n depend both on a microscale spatial variable $\vec{y}$ and on a macroscale spatial variable $\vec{x}$. The two spatial variables are related by the scale separation parameter.

$$\vec{y} = \frac{\vec{x}}{\varepsilon} \quad (23)$$

In the limiting case $\varepsilon \rightarrow 0$, the homogeneity of the domain results in transport dynamics which no longer depend on $\vec{y}$, but rather only on $\vec{x}$ and time.

In this work the theory of the AH technique was applied to microscale model transport equations (**Table 3**). As shown in **Figure 29**, the macroscale region, and hence the unit cell, is divided into a solid, active material phase (s) and an electrolyte phase (e). The Y-periodic transport variables are the concentration and the potential. This results in a separate set of homogenized transport equations for each battery section with the corresponding porosity η^e and the AM volume fraction η^s .

Table 3. Transport equations of the FHM model.

Variables	Solid s with $j = \{p\}$	Electrolyte e with $j = \{sep, p\}$
concentration c	$\eta_j^s \frac{\partial \bar{c}_j^s}{\partial t} = \frac{\partial}{\partial x} \left(D_j^{s,eff} \frac{\partial \bar{c}_j^s}{\partial x} \right) \underset{\approx 0}{- \frac{1}{F} a_j^s \bar{i}_{se,j}}$	$\eta_j^e \frac{\partial \bar{c}_j^e}{\partial t} = \frac{\partial}{\partial x} \left(D_j^{e,eff} \frac{\partial \bar{c}_j^e}{\partial x} + \frac{\mathbb{R}T t_+ \lambda}{F^2} K_j^{e,eff} \frac{\partial \ln(\bar{c}_j^e)}{\partial x} + \frac{t_+}{F} K_j^{e,eff} \frac{\partial \bar{\Phi}_j^e}{\partial x} \right) + \frac{1}{F} a_j^s \bar{i}_{se,j}$
potential Φ	$0 = \frac{\partial}{\partial x} \left(K_j^{s,eff} \frac{\partial \bar{\Phi}_j^s}{\partial x} \right) - a_j^s \bar{i}_{se,j}$	$0 = \frac{\partial}{\partial x} \left(\frac{\mathbb{R}T t_+ \lambda}{F} K_j^{e,eff} \frac{\partial \ln(\bar{c}_j^e)}{\partial x} + K_j^{e,eff} \frac{\partial \bar{\Phi}_j^e}{\partial x} + a_j^s \bar{i}_{se,j} \right)$
$\bar{i}_{se,p} = k_p \underbrace{\sqrt{\bar{c}_p^e \bar{c}_p^s \left(1 - \frac{\bar{c}_p^s}{c_{max,p}^s} \right)}}_{\approx \bar{i}_{0,j}} \cdot 2 \sinh \left(\frac{F}{2\mathbb{R}T} \left[\bar{\Phi}_p^s - \bar{\Phi}_p^e - U_{0,p}(\bar{c}_p^s) \right] \right) \text{ and } \bar{i}_{se,sep} = 0$ with $a_p^s = \frac{ \Gamma_p }{ \Upsilon_p } \frac{1}{l_p}$ and $a_{sep}^s = 0$		

Using the AH technique the transport equations of the three-dimensional microscale model are reduced to a set of one-dimensional homogenized transport equations. A detailed description of how to perform the AH technique on microscale transport equations can be found in the literature⁸².

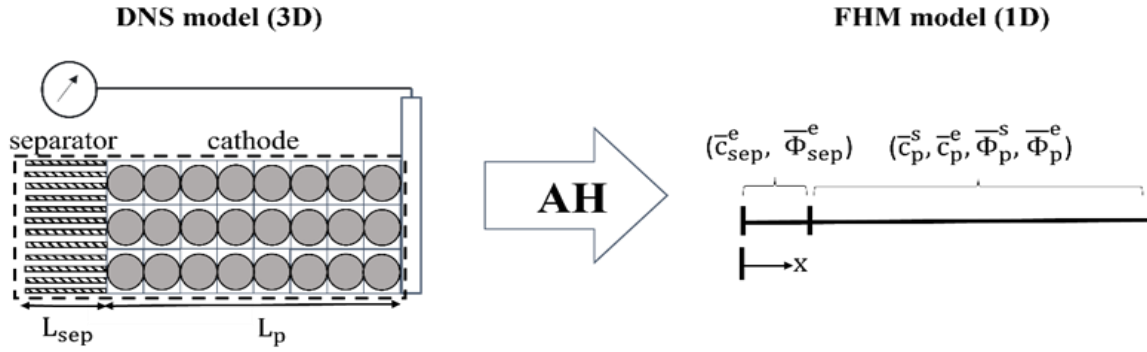


Figure 29. Conceptual comparison between DNS and FHM model.

The geometrical properties of the separator and electrodes differ. Therefore, the cell problem must be solved separately for each unit cell of the respective battery section. The unit cell should be selected so that **Equation 23** can be satisfied. The macroscopic length L corresponds to the thickness of the respective battery section shown in **Figure 29**.

In this way the electron transport and mass transport through the electrode can be derived. However, the classical FHM model assumes that the time constant of lithium diffusion into the active material (solid- phase diffusion) is much larger than liquid-phase diffusion. But because lithium diffusion into the AM particle is neglected an accurate calculation for high charge/discharge rates is impossible. At high current densities, which represent a reaction limited transport regime, the mass and charge transport parameters are comparatively high. The solid phase lithium ion concentration and potential gradients on the microscale cannot be negligible. Consequently, steep concentration gradients form near the interface Γ (**Figure 30**). The resulting concentration profiles can no longer be covered by the homogenized value. The resulting deviation between the surface concentration $c_{s,surf}$ and the homogenized concentration reveals that the FHM model is not applicable to diffusion-limited battery processes (in other words, a high charge/discharge rate situation).

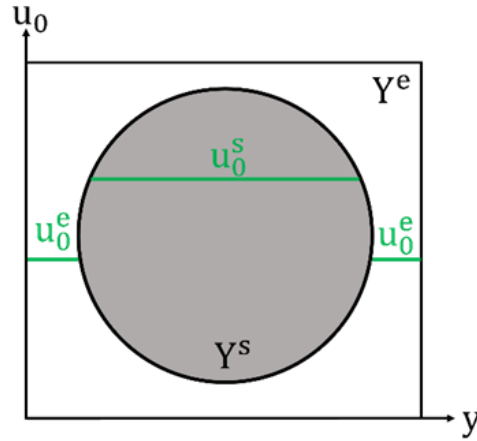


Figure 30. Steep concentration gradients observed in the FHM model.

Therefore, in order to depict the solid-phase diffusion process and calculate the ion concentration distribution within the active material, we applied the diffusion length theory^{83,84} in the AM microstructure, which, using boundary layer theory, divides the particle phase into a bulk phase and a diffusion layer.

Within the microscopic unit cell, first the conductive binder as well as the size and shape distribution are considered when calculating the effective conduction and diffusion parameters. The ionic concentration distribution within the AM is approximated as a constant value in the bulk phase and a linear fitting is performed for the surface layer (see **Figure 31**).

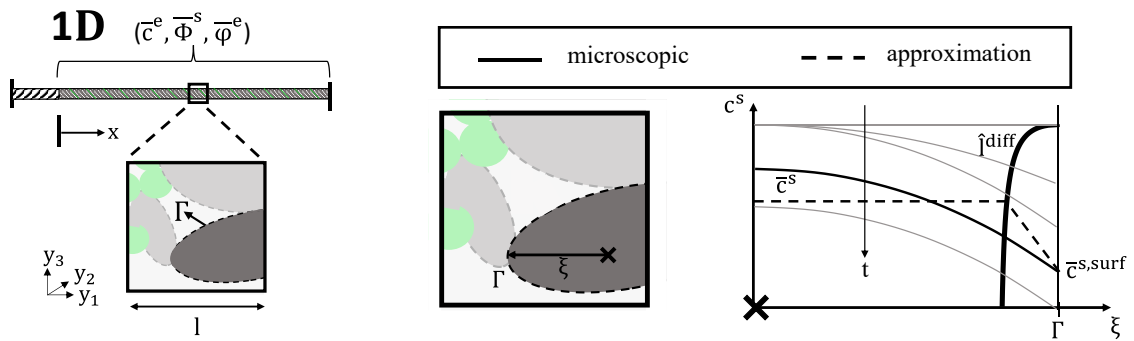


Figure 31. Schematic of the extended FHM. Unit cells were defined based on the symmetries in the existing microstructure, the real microstructure was considered, and diffusion layer theory was applied within the AM.

As shown in **Figure 31**, the bulk concentration $c_{s,bulk}$ corresponds to the homogenized concentration $\bar{c}^s$ as defined by the classical FHM model. The correlation between c_s and $c_{s,surf}$ is defined by the thickness of the diffusion layer l^{diff} . The thickness l^{diff} is a time-varying quantity that reveals the following dimensionless behavior based on the analysis of the microscale:

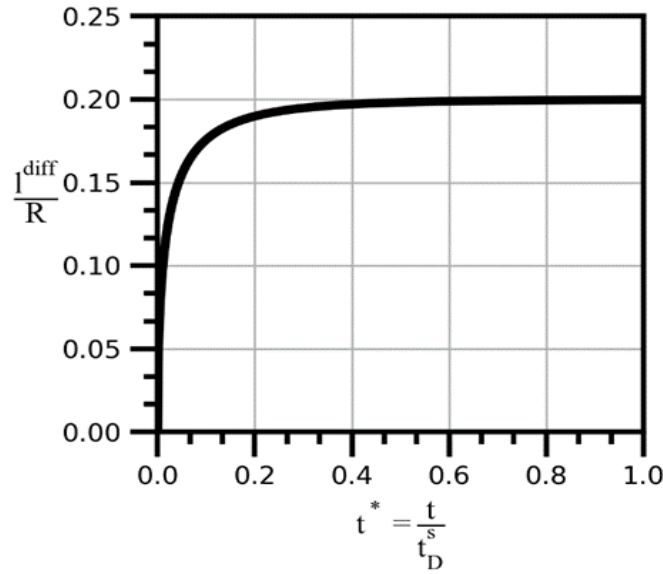


Figure 32. Temporal development of the dimensionless diffusion layer thickness.

As illustrated in **Figure 32**, the dimensionless time t^* is related to the characteristic time of solid diffusion. R is the particle radii. l^{diff} therefore can be expressed as:

$$l^{\text{diff}}(\tau) = l^{\text{diff},\infty} \cdot (1 - \delta(\tau)). \quad (24)$$

The time function $\delta(\tau)$ defines the dynamic of the diffusion layer and $l^{\text{diff},\infty}$ is the thickness of the diffusion layer at a stationary state. To determine the stationary diffusion layer thickness $l^{\text{diff},\infty}$ and its decaying time function $\delta(\tau)$, we need the data of a single microscopic simulation on the considered electrode geometry.

Moreover, instead of considering single particles, the solid-phase diffusion function was extended to all particles within the unit cell. **Table 4** lists the equations of this new approximation method with k as the particle index:

Table 4. Added interface conditions for the surface concentration.

Volume averaged concentration $\bar{c}^s$	$\eta_k^s \frac{\partial \bar{c}_k^s}{\partial t} = -\frac{1}{\mathbb{F}} a_k^s \bar{i}_{\text{se},k} (\bar{c}^e, \bar{c}_k^{\text{s,surf}}, \bar{\varphi}^e, \bar{\Phi}^s)$
Surface averaged concentration $\bar{c}^{\text{s,surf}}$	$\frac{\bar{c}_k^{\text{s,surf}}(\tau)}{c_{\text{max}}^s} = \frac{\bar{c}_k^s(\tau)}{c_{\text{max}}^s} - \text{Da}_k \cdot l_k^{\text{diff}}(\tau)$
reaction source term $\bar{J}_{\text{Li}}$	$\bar{J}_{\text{Li}} = \sum_{k=0}^{N_p} [a_k^s \cdot \bar{i}_{\text{se},k} (\bar{c}^e, \bar{c}_k^{\text{s,surf}}, \bar{\varphi}^e, \bar{\Phi}^s)]$

The concentration gradient $\nabla c^s(r = R) \approx \frac{\bar{c}^s - c^{s,\text{surf}}}{l_{\text{diff}}}$ is approximated by the diffusion layer theory. With this continuity condition the surface concentration $c^{s,\text{surf}}$ can be derived and included in the Butler-Volmer equation.

The boundary conditions as well as the initial conditions of the transport variables are given in **Table 5**.

Table 5. Boundary conditions of the FHM model.

Variables	$x = 0$	$x = L_{\text{sep}}$	$x = L_{\text{sep}} + L_p$
$\bar{c}^s$	-	no flow	no flow
$\bar{c}^e$	$-D_{\text{sep}}^{\text{e,eff}} \frac{\partial \bar{c}^e}{\partial x} = \frac{I_{\text{app}}}{F A_{\text{cell}}}$	continuity	no flow
$\bar{\Phi}^s$	-	no flow	$K_p^{\text{s,eff}} \frac{\partial \bar{\Phi}^s}{\partial x} = \frac{I_{\text{app}}}{A_{\text{cell}}}$
$\bar{\Phi}^e$	$\bar{\varphi}^e = 0$	continuity	no flow

A_{cell} represents the cross-sectional area parallel to the current collector and I_{app} is the applied current. A flux source boundary condition is proposed for the particle concentration $\bar{c}^s$ at the position $x = L_{\text{sep}}$. The diffusion and migration flux of the electrolyte at $x = 0$ is defined as:

$$\dot{N}^{\text{e,eff}} = - \left[D^{\text{e,eff}} \frac{\partial \bar{c}^e}{\partial x} + \frac{RT t_+^2 \lambda}{F^2} K^{\text{e,eff}} \frac{\partial \ln(\bar{c}^e)}{\partial x} + \frac{t_+}{F} K^{\text{e,eff}} \frac{\partial \bar{\varphi}^e}{\partial x} \right] \quad (25)$$

The model was established on COMSOL and the model parametrization was based on a series of above-mentioned experimental set-ups (μ -CT reconstruction, GITT, EIS etc.). The model validation was based on a comparison of the simulation result and the experimental data as well as microscopic simulation. Details are described in Chapter 4.5.

IV RESULTS AND DISCUSSION

As discussed in Chapter 2, sluggish Li^+ ion transport kinetics and limited electrical conductivity in the active material of electrodes are critical bottlenecks for a satisfactory lithium-ion battery performance. The ultimate solution for enhancing Li^+ ion diffusivity and electrical conductivity of electrodes would be to insert a compound into the electrode material that can provide paths with little electrical resistance and fast ion transport while at the same time not occupying additional space or adding additional weight to the electrode. In this work we report on replacing the traditionally applied copper foil of a graphite anode in a Li^+ ion half-cell with an ultrafine copper fiber fleece inserted into the active material (**Figure 33**), providing a material density of $\sim 1.3 \text{ g/cm}^3$ that is, thus, comparable to copper foil-based electrodes. The copper fleece infiltrates the active material and is, therefore, in direct contact with the active material and the electrolyte. Since the fleece is made of ultrafine copper fibers it also provides more surface area in contact with the electrolyte and the active material. Overall, the fleece provides both mechanical stability and reduced contact resistance for Li^+ ion and electron mobility. Microfluidic experiments and MD simulations were used to confirm and quantify this enhanced diffusivity along the copper surface. Moreover, a digital twin we developed as a mathematical tool to optimize this new type of electrode.

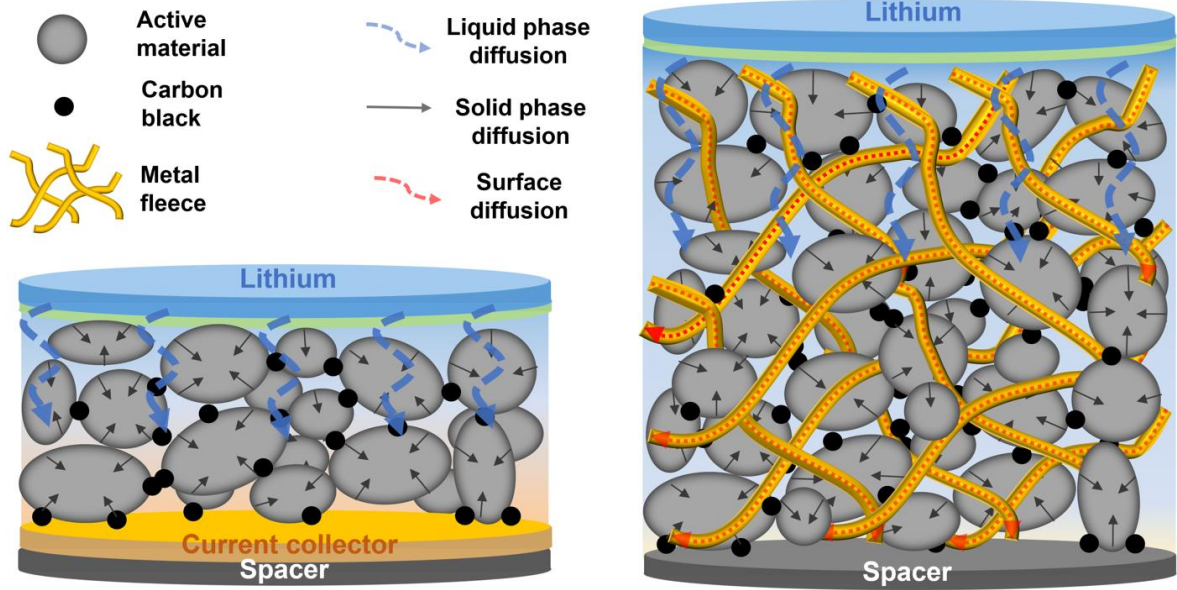


Figure 33. Schematic of a copper foil-based film anode (left) and a fleece anode (right). Solid-phase and liquid-phase diffusion pathways are shown in both electrodes. Only the copper fleece-based anode additionally features surface diffusion along the metal surfaces.

4.1 FLEECE ELECTRODE FABRICATION & CHARACTERIZATION

The ultrafine copper fiber is fabricated by a melt-spinning process. **Figure 34a** shows the optical image of the fibers and **Figure 34b** shows the SEM image of the fibers. As shown in **Figure 34b**, the fabricated fiber has a ribbon-shape, the average width of the fiber is $\sim 38 \mu\text{m}$ and the average thickness of the fiber is $\sim 12 \mu\text{m}$.

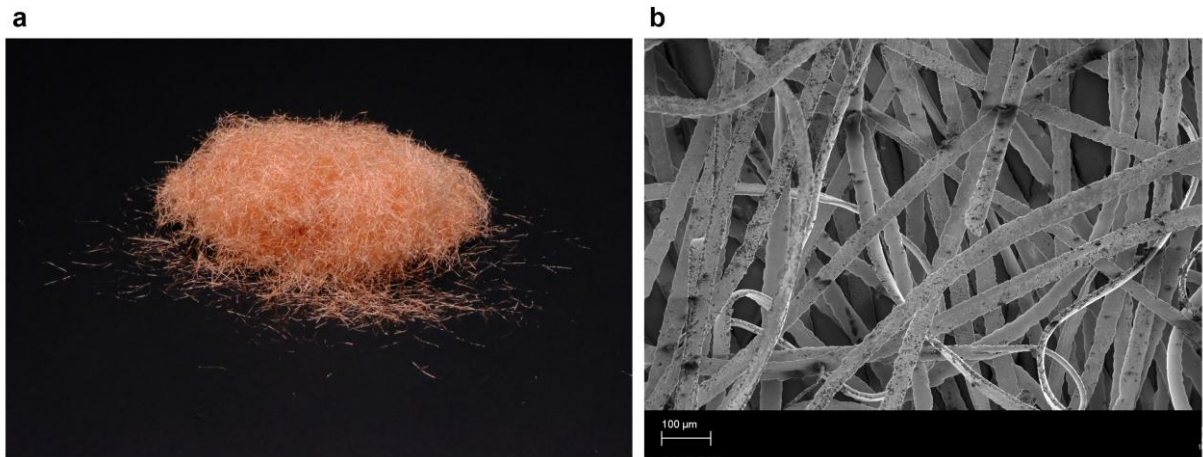


Figure 34. (a) Optical and (b) SEM images of melt spun copper fibers.

After fiber dispersion and thermal sintering, the resulting ribbon-like fibers had a cylindrical shape and a diameter of $\sim 20 \mu\text{m}$. Copper fibers are connected by copper atom diffusion. **Figures 35a and b** show the optical and Micro CT reconstruction of the 3D fleece (1 mm thick, 95% porosity).

Figure 35c shows the SEM image of a sintered fleece, the ribbon-shaped fibers turn to a round shape during thermal sintering. The sintered fiber diameter distribution is calculated based on a Micro-CT scan of the fleece using the software Geodict 2024 from Math2Market (result shown in **Figure 35d**). The radius of the fibers was distributed within a narrow range with an average value of 11 μm .

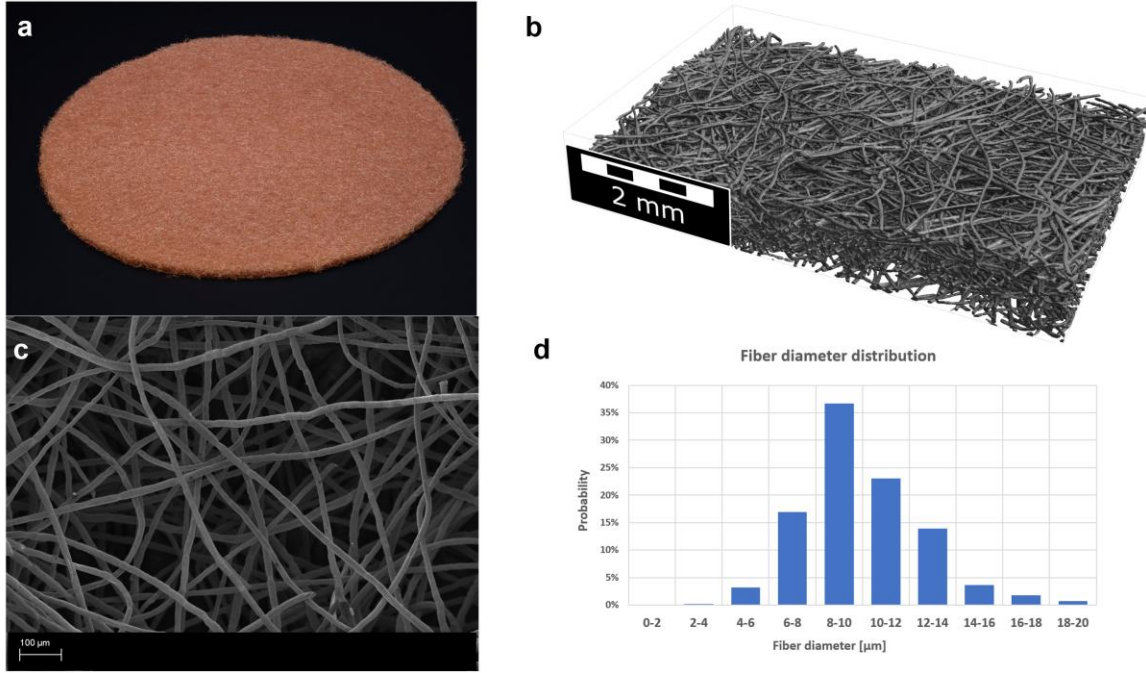


Figure 35. The sintered copper fleece and its parameters: (a) optical image, (b) micro-CT 3D reconstruction, (c) SEM image, and (d) round fiber diameter distribution.

Figure 36 depicts the pore size distribution of the fleece. The mean pore diameter is $\sim 160 \mu\text{m}$ (**Figure 36a**) and the pore size distribution is controlled by fiber density, shape, size, and dispersion parameters. We fabricated the fleece with 95% porosity to ensure a high amount of active material filling and chose the mean pore diameter to be about 160 μm so that the maximum distance between active material particles and fibers is less than 80 μm , which represents the typical film electrode thickness. **Figure 36b** shows the visualized pore size distribution and **Figure 36c** shows the density map of the fleece in the XZ-plane. The fiber distribution is relatively homogeneous and therefore the pore size distribution is relatively narrow, only some surface pores are larger than 200 μm . **Table 6** shows the characteristics of the fleece.

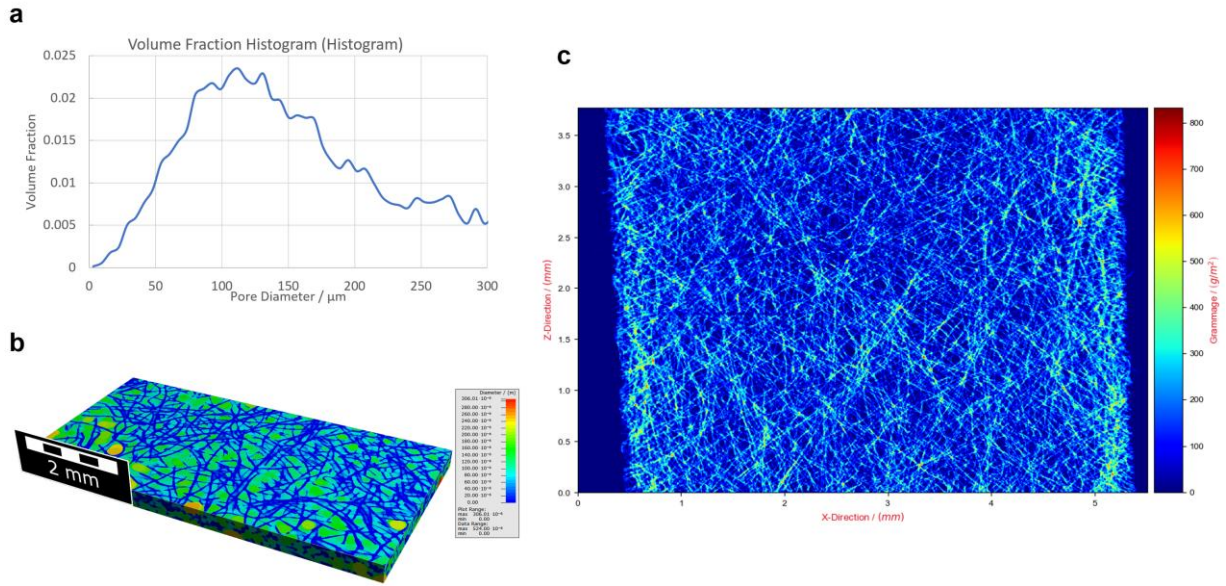


Figure 36. Copper fleece pore size and density: (a) and (b) pore size distribution, (c) density map.

Table 6. Copper fleece properties.

Fiber diameter	10~12 μm
Fleece thickness	400 ~ 2500 μm (before active material filling)
Fleece porosity	4.8% ~ 5.5%
Fleece density	442 ~ 450 mg/cm^3
Mean Pore diameter	148 ~ 167 μm

The slurry is then filled into the fleece, and the dry fleece electrode is compressed with a uniaxial hot compression machine to achieve the desired active material density. Compared to doctor blading, the filling of the 3D fleece requires a re-adjustment of the slurry viscosity (see details in Chapter 3.1). Here, the additive provided by BYK is added to the slurry to decrease the viscosity of the slurry so that it can nicely penetrate the 3D CC. **Figure 37a** shows optical images of the fleece electrode, **Figure 37b** shows the μ -CT reconstruction of the fleece electrode.

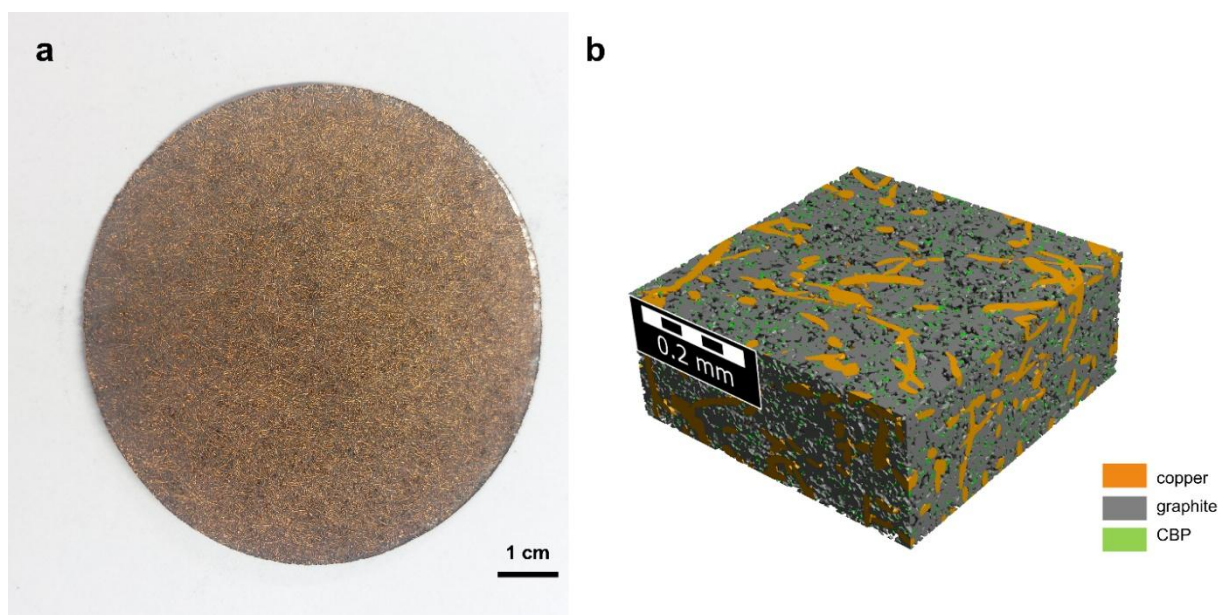


Figure 37. (a) Optical image and (b) Micro-CT reconstruction of the copper fleece anode.

To check the filling quality of the electrode, the electrode is embedded into resin and polished to check the cross sections of electrode. **Figure 38** shows the cross section and the surface of a fleece electrode with 350 μm thickness. As shown in the figure, the copper fleece fills homogeneously and the amount of required filling is comparable to a conventional electrode featuring ultra-high areal capacity.

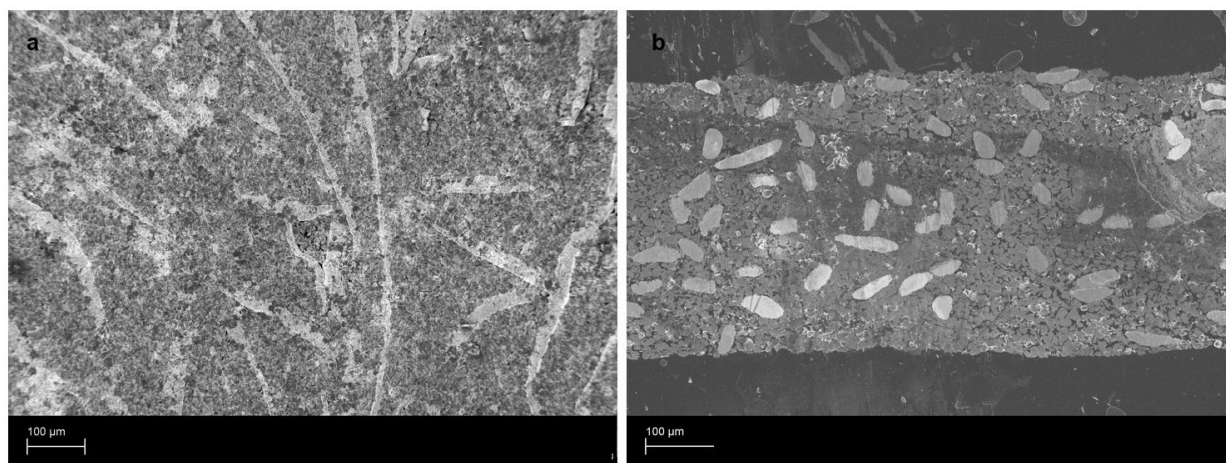


Figure 38. SEM images of the fleece electrode: (a) surface and (b) cross-section.

The mass load of the active material depends on the fleece thickness and the slurry composition. In addition, conventional foil electrodes with various coating thicknesses were built as control samples. The areal mass load, active material density, electrode thickness and theoretical areal capacity of foil and fleece electrodes are shown in **Table 7** and **Table 8**.

Table 7. Copper foil electrode parameters.

Electrode thickness [um]	Theoretical areal capacity [mAh/cm ²]	Active material load [mg/cm ²]	Active material density [g/cm ³]
29.5	0.79	2.26	0.85
39.16	1.00	2.86	0.82
73.8	1.79	5.12	0.77
112.1	2.54	7.27	0.72
154.3	3.62	10.36	0.745
284	7.16	20.48	0.80
457.2	12.10	34.61	0.84
50	1.65	4.73	1.05
94	3.20	9.15	1.08
121	3.51	10.03	0.92
150	4.58	13.11	0.97
160	5.54	15.86	1.1
220	7.62	21.81	1.1

80	2.90	8.29	1.15
108	4.02	11.49	1.18
129	4.92	14.07	1.21
200	7.50	21.45	1.19
215	8.67	24.80	1.28
252	9.37	26.80	1.18

Table 8. Copper fleece electrode parameters.

Thickness [μm]	Theoretical areal capacity [mAh/cm^2]	Active material load [mg/cm^2]	Active material density [g/cm^3]
472	8.70	24.85	0.65
760	15.52	44.33	0.72
870	17.27	49.34	0.7
1220	22.83	65.24	0.66
1706	33.86	96.75	0.7
335	9.50	27.14	1

450	12.12	34.64	0.95
500	15.60	44.56	1.1
1030	27.75	79.28	0.95
1278	35.15	100.44	0.97
370	13.12	37.45	1.25
450	15.44	44.12	1.21
550	19.18	54.81	1.23
812	26.48	75.66	1.15
900	30.63	87.50	1.20
1120	37.48	107.08	1.18

4.2 ELECTROCHEMICAL CHARACTERIZATION OF FLEECE AND FOIL ELECTRODES

Electrical conductivity

The electrical conductivity of the electrode is significantly enhanced with the metal fleece embedded into the graphite anode. The 3-dimensionally distributed metal fibers form a percolation network for electron transport and greatly decrease the potential gradient within thick electrodes. **Figure 39** shows the sintering points between fibers. Such sintering points are commonly observed within electrodes, a sign of the formation of the interconnected percolation path. Next, a quantitative study was carried out to characterize the electrical conductivity of the fleece and film electrodes.

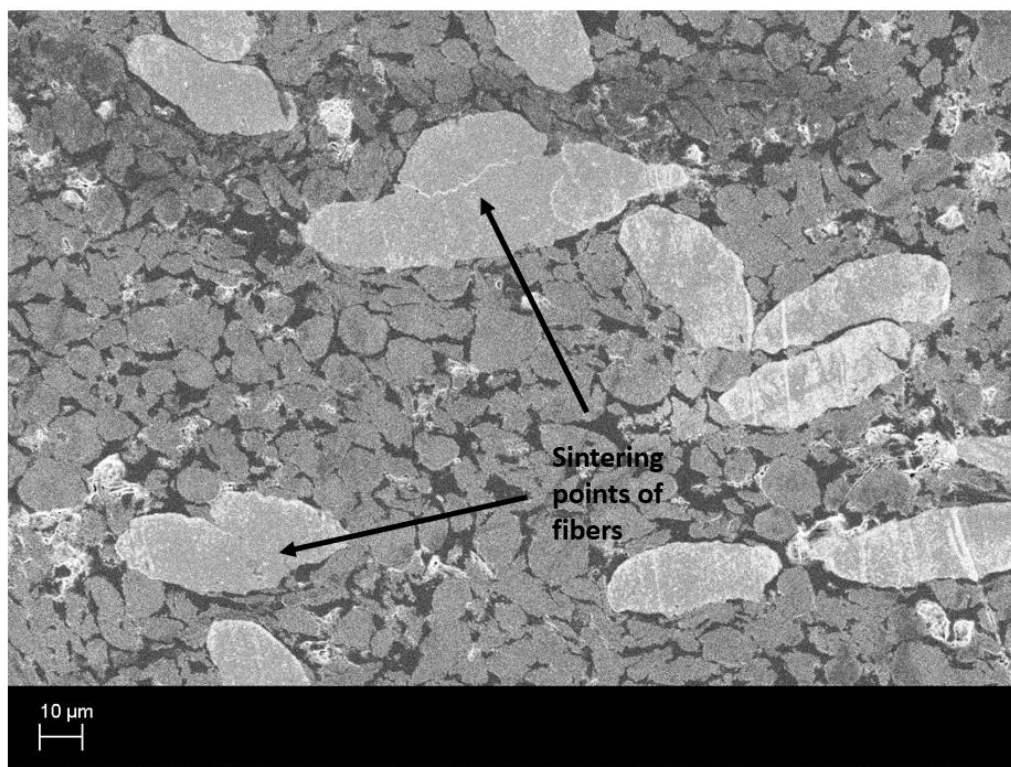


Figure 39. Sintering points between copper fibers.

In the conventional foil electrode the conductive filler combined with the polymer forms a conductive binder phase which provides not only the mechanical connection between active material particles but also an electrical connection between particles. The electrical conductivity of the film electrode is largely dependent on the ratio of conductive filler to polymer as well as the absolute amount of the conductive filler. To characterize the conductivity the 4-point measurement and the Van-der-Pauw method are most commonly used. Both, however, are not applicable to fleece electrodes. Due to the existence of the fiber network, the current would be short-circuited by the metal fibers. During normal battery operation the current flows through the network to the active material particles, accomplishing charge transfer at the particle surface and transforming to ionic flow within the electrolyte. Therefore, we implemented electrochemical impedance measurement (EIS) for characterizing the electrical conductivity of the foil and fleece electrodes.

In EIS measurements serial alternative currents with various frequencies are applied to the electrode. The electrical resistance, charge transfer resistance, and diffusive resistance can be separated by calculating the impedance of the electrochemical system. In our system the working electrodes are the fleece or foil electrodes and the counter electrode is made from metallic lithium (**Figure 33**). For example, **Figure 40** shows electrochemical impedance measurements of a film electrode with 86 μm thickness and a fleece electrode with 276 μm thickness. Both cells feature a

similar internal resistance of 5 Ohm at high frequency (1 MHz). This resistance reflects the electrical resistance of the cell set-up. In this experiment both cells have the same resistance value because they were both designed as coin cells. Next, we dropped the AC frequency to ~10 KHz and measured the film impedance. Film impedance reflects the electrical resistance and capacitance within the porous electrodes and gives an estimation of the quality of inter-particle connection. In this experiment the film electrode showed higher film impedance than the fleece electrode, which indicates that the metallic fiber network provides a percolation pathway for electrons and greatly enhances the electric conductivity of the electrode. By applying an equivalent circuit fitting, the ohmic resistance R_{film} was calculated using **Equation 26** to obtain the electronic conductivity:

$$R_{film} = \frac{1}{\sigma S} \quad (26)$$

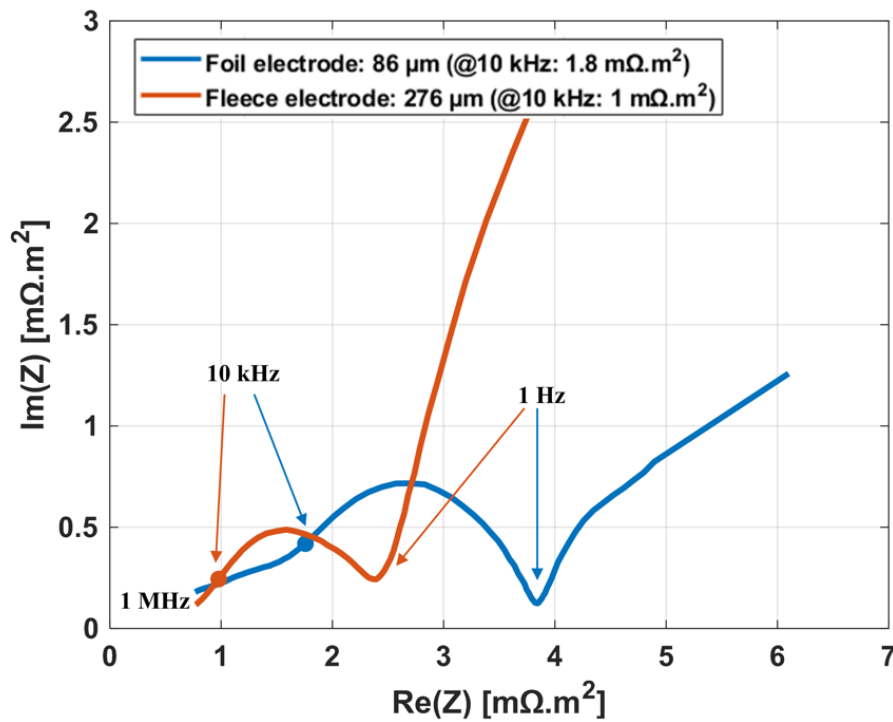


Figure 40. EIS measurements of a film and of a fleece electrode.

Here σ is the conductivity, l is the thickness of the electrode and S is the area of the electrode. It is worthwhile mentioning that with EIS, the crystal structure of graphite is modified during lithiation/de-lithiation and thus the conductivity varies, meaning that we measure SOC-dependent electronic conductivity (**Figure 22**). **Table 9** shows the results of our electronic conductivity measurements at 150 mV open circuit voltage.

Table 9. Electrical conductivity of foil and fleece anodes.

Electrode design	AM Density (g/cm ³)	Electrical Conductivity (S/m)
foil	~0,8	350.632 ± 17.81
foil	~1,0	373.120 ± 12.34
foil	~1,2	392.150 ± 20.76
fleece	~0,7	603.1309 ± 40.38
fleece	~0,9	721.4436 ± 67.19
fleece	~1,2	1130.942 ± 80.28

Electrical conductivity is significantly higher in electrodes containing the 3D copper fleece. This is due to the highly effective percolation path, which provides sufficient electrons to surrounding AM particles. Unlike in foil electrodes the electrical resistance of the fleece electrodes is independent of electrode thickness. Instead it depends on the fleece mesh size. AM density also has a significant impact on both foil and fleece electrodes, as an increase in AM density effectively decreases the inter-particle electrical resistance.

Areal capacity and initial Coulombic efficiency

The 3D copper fleece works not only as a 3D CC, but can also be functionalized as a substrate as well as providing mechanical stability. This allows the realization of ultra-thick electrodes with high areal capacity. After coating the copper foil and filling the fleece with active material slurry, SEI formation cycles at 0.1C are carried out. **Figure 41** depicts the 1st cycle (SEI formation cycle) and the 5th cycle of a film electrode of 86 µm thickness and a fleece electrode of 276 µm thickness. Both cells reached their theoretical capacity with decent initial Coulombic efficiency: 95.3% and 91.6% in the film and fleece electrode, respectively. The initial Coulombic efficiency is a bit lower in fleece electrodes, because the interface area between the active material/electrolyte is larger, thus, causing more SEI formation. At low cycling rates, the film electrode with 86 µm thickness

and the fleece electrode with 276 μm thickness perform similarly. This is due to the fact that in both cases mass electrolyte transport is sufficient, despite the fact that the fleece electrode provides 3 times higher areal capacity.

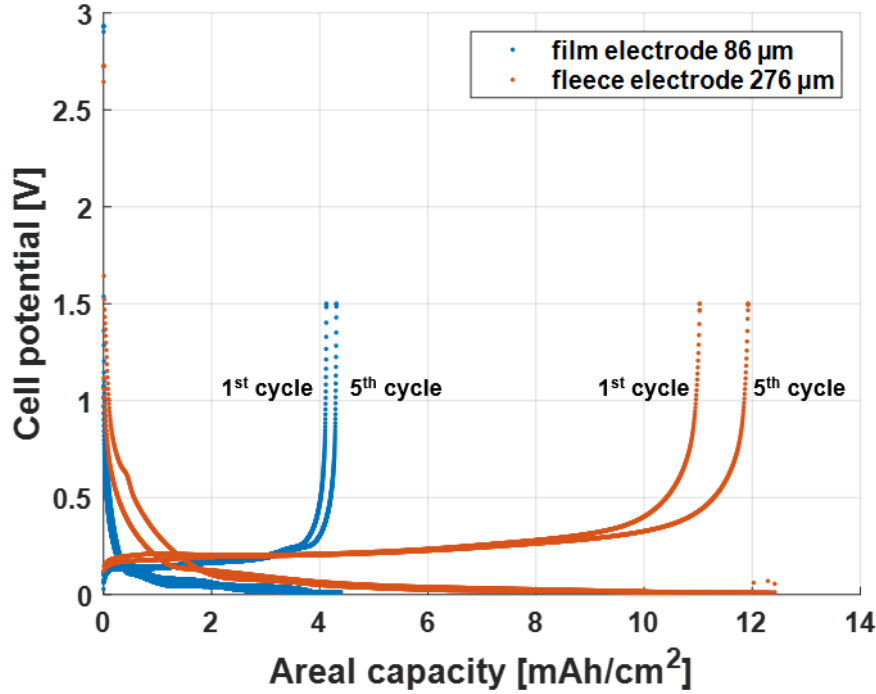


Figure 41. Voltage-capacity curve of 1st cycle (SEI formation cycle) and 5th cycle of the foil and fleece electrode, cycling rate: 0.1C.

If, however, the thickness of the film and fleece electrodes is further increased, the film battery starts to fail. **Figure 42** shows the comparison between the electrode's areal capacity at 0.1C and the theoretical areal capacity (listed in **Table 7** and **Table 8**). For thick film electrodes, the theoretical capacity cannot be fully reached even at 0.1C. If the graphite is densified, this additionally hinders reaching it, because both the increase of electrode thickness and decrease of porosity negatively impact lithium-ion flow path establishment and electron transport. In contrast, the fleece electrodes are able to be fully lithiated/delithated at 0.1C regardless of electrode thickness or porosity.

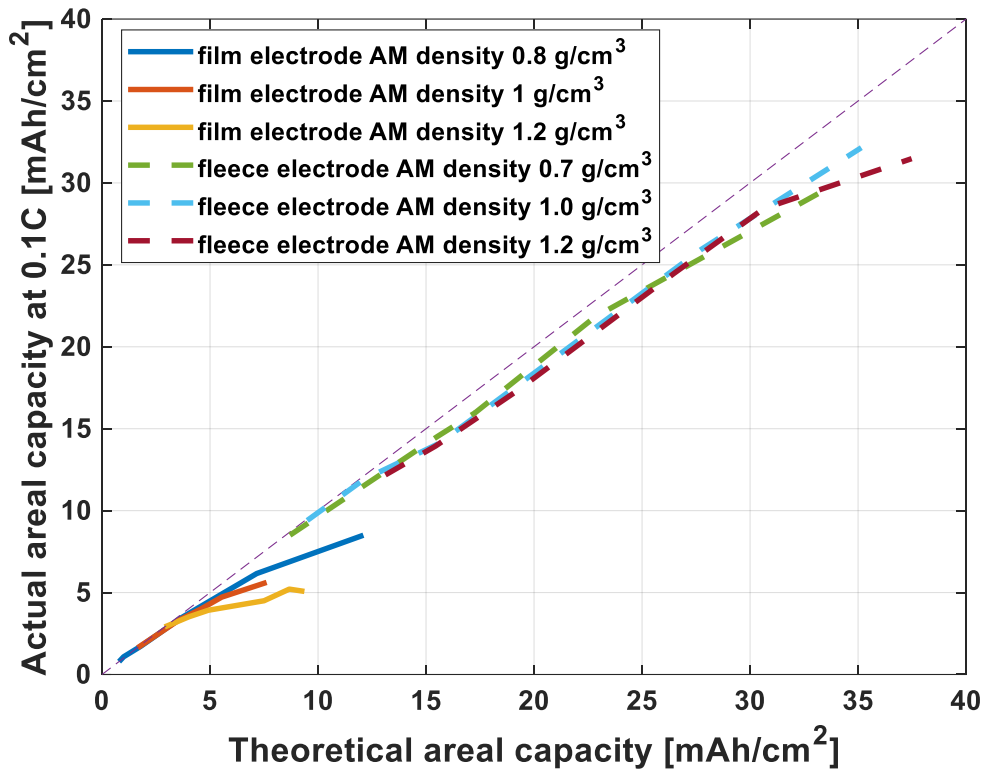


Figure 42. Theoretical areal capacity vs. actual areal capacity at 0.1C.

Volumetric and gravimetric energy density

Another advantage of the fleece electrodes is the energy density. As above-mentioned, the volume fraction of the metal content is set to 4.8% ~ 5.5%. As a comparison, in commercial cell anode (LGM 50), the copper foil volume fraction is 11.8%, the fleece electrodes use half of the copper amount and therefore provide higher volumetric and gravimetric energy density.

Besides, in foil electrode, increase the active material thickness or decrease the electrode's porosity cannot directly enhance the energy density, due to the increased electrical and diffusive resistances. However in fleece electrodes, thanks to the metal fleece, both electrical and ionic conductivity are enhanced, thus the utilization of active material is quite high and, almost independent to the electrode thickness. **Table 10** shows the volumetric and gravimetric energy density of fleece and foil electrodes with various porosity and thickness.

Table 10 . Energy density of foil and fleece anodes.

Foil electrodes					
Electrode thickness [μm]	Electrode density [g/cm ³]	Areal capacity @ 0.1C [mAh/cm ²]	Electrode mass including CC [mg/cm ²]	Volumetric energy density including CC [mAh/cm ³]	Gravimetric energy density including CC [mAh/g]
39.5	0.85	0.785	11.41	158.59	38.65
49.2	0.82	1.08	12.08	182.43	51.48
83.8	0.77	1.72	14.59	183.37	73.23
122.1	0.72	2.41	16.98	182.44	93.13
164.3	0.745	3.42	20.41	196.21	116.68
294	0.8	6.16	31.66	202.63	151.89
467.2	0.84	8.5	47.36	178.12	151.10
60	1.05	1.63	14.16	232.86	70.70
104	1.08	3	19.07	263.16	107.27
131	0.92	3.28	20.04	232.62	113.32
160	0.97	4	23.47	235.29	123.58
170	1.1	4.72	26.52	262.22	133.25
230	1.1	5.62	33.13	234.17	133.70
90	1.15	2.9	18.11	290.00	107.36
118	1.18	3.52	21.67	275.00	115.16
139	1.21	3.92	24.53	263.09	117.25
210	1.19	4.5	32.73	204.55	108.09
225	1.28	5.12	36.46	217.87	112.89
262	1.18	5.07	38.68	186.40	106.56

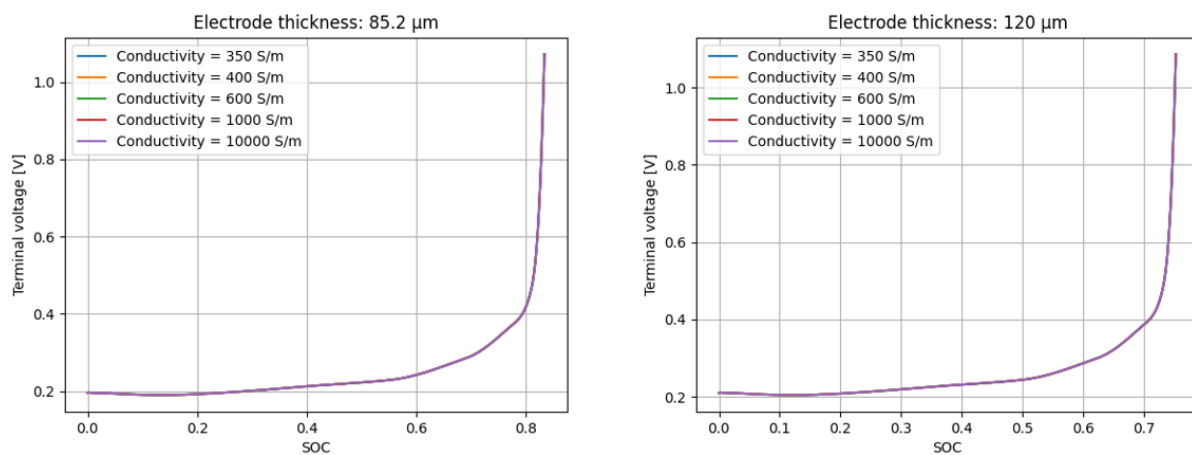
Fleece electrodes					
Electrode thickness [μm]	Electrode density [g/cm ³]	Areal capacity @ 0.1C [mAh/cm ²]	Electrode mass including CC [mg/cm ²]	Volumetric energy density including CC [mAh/cm ³]	Gravimetric energy density including CC [mAh/g]
472	0.65	8.5	45.85	180.08	185.37
760	0.72	14.52	78.15	191.05	185.80
870	0.7	15.97	88.06	183.56	181.36
1220	0.66	21.83	119.53	178.93	182.63
1706	0.7	29.86	172.67	175.03	172.93
335	1	9.4	42.22	280.60	222.67
450	0.95	11.9	54.89	264.44	216.80
500	1.1	14.1	67.06	282.00	210.26
1030	0.95	25.95	125.63	251.94	206.56
1278	0.97	32.15	157.95	251.56	203.55
370	1.25	12.18	54.47	329.19	223.61
450	1.21	13.94	64.82	309.78	215.06
550	1.23	17.28	80.11	314.18	215.70
812	1.15	24.48	113.01	301.48	216.61
900	1.2	28.43	128.90	315.89	220.56
1120	1.18	31.48	158.60	281.07	198.49

The result shows that:

- In foil electrodes with high porosity, increase the AM layer thickness is able to achieve higher energy density, but there is a limitation;
- In foil electrodes with low porosity, increase the AM layer thickness cannot achieve higher energy density, due to the tortuous morphology, the diffusive resistance is too high and the AM utilization is low.
- In fleece electrode, the energy density is higher because of low metal content, besides there the utilization of AM is high and independent of the electrode thickness.

Electronic conduction or ionic diffusion?

The reason for this difference could be that the fleece works as a 3D percolation network for electron transport and reduces the electrical potential gradient within the electrode. Thus, all the graphite particles are at the inter/deintercalation potential of Li into graphite. However, various studies have shown that in the case of graphitic anodes increasing the electrode thickness is not limited by electrical resistance but rather ionic resistance. Here we carried out a series of simulations based on a microscopic model to study the influence of electrical conductivity on electrochemical performance. **Figure 43** shows the simulation results of anode half cells. Increasing the graphite anode electrical conductivity did not improve electrode performance. Besides, despite very good electrical conductivity, charging and discharging at 1C was impossible at electrode thicknesses above $\sim 120\ \mu\text{m}$. At $160\ \mu\text{m}$ anode thickness only $\sim 35\%$ percent of theoretical capacity could be reached at 1C.



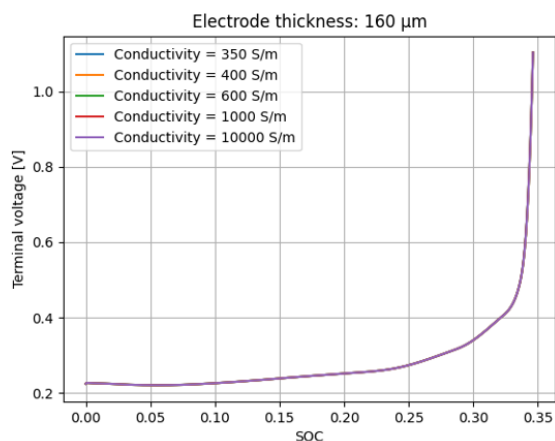


Figure 43. Half-cell anode simulation.

Simulation results revealed that electrical conductivity is not the bottleneck, as both the graphite particles and conductive binder were able to transfer electrons effectively. Instead, lithium-ion diffusion is the rate-limiting factor in thicker electrodes. However, the fleece electrode seems to work properly regardless of lithium-ion diffusion. In order to understand why the ultra-thick fleece electrode can still be electrochemically active, EIS measurements were carried out to analyze internal resistance with respect to characteristic frequencies in various electrochemical systems. **Figure 40** shows electrochemical impedance measurements of the film electrode (86 μm thickness) and the fleece electrode (276 μm thickness) in half cells as an example. Both half cells have a similar internal resistance (5 Ohm) at high frequency, because they both have a coin cell configuration. However, in contrast to the fleece electrode's film impedance of 1 MHz, the fleece electrode only has a film impedance of 10 kHz. This indicates that the metallic fiber network provides a percolation pathway for electrons and greatly enhances the electric conductivity of the electrode. Besides, the fleece electrode also has a lower charge transfer resistance (between 10 kHz to 1 Hz). We speculate that the enhanced diffusion and better conductivity help to form thinner and more homogeneous SEI and, therefore, decrease the charge transfer resistance. At low frequencies (between 1 Hz to 0.01 Hz), there is a difference in the 'tail' slope between the film and fleece electrodes. This indicates that, although the fleece electrode is 3 times thicker than the film electrode, the ion diffusion rate is significantly higher in the fleece electrode pores than in the film electrode.

GITT-measurements of solid-phase diffusivity

The EIS data indicates that in the case of the metal fleece the ionic resistance within the electrode is decreased. However, as mentioned above, diffusivity values obtained by EIS are known to be

very sensitive to differences in the experimental set-up, electrode heterogeneity, and solid electrolyte interface (SEI) resistance. Due to these limitations in quantitative reproducibility, EIS is usually only used for relative comparisons between different electrodes. Therefore, we chose the galvanostatic intermittent titration technique (GITT) to measure the effective diffusion rate of lithium into graphite particles.

The determination of Li^+ diffusivity values within electrodes is complex. In a typical Li^+ battery anode with graphite as the lithium insertion compound the Li^+ diffusion values that are reported differ, ranging from $10^{-5} \text{ cm}^2/\text{s}$ to $10^{-12} \text{ cm}^2/\text{s}$.^{8,12,75,85,86} These large variations indicate that there are several simultaneous transport mechanisms for Li^+ in the multiphase compound of an electrode. Scaling up from a nano- to a macroscopic perspective, the diffusion pathways of Li^+ ions within a graphitic carbon electrode are as follows (**Figure 44**): starting at the separator Li^+ undergoes (i) liquid (electrolyte)-phase diffusion within the porous electrode, (ii) solid-phase diffusion into the interlayers of graphite particles, and (iii) solid-phase diffusion within the crystal structure of the graphite until they finally accomplish intercalation. We applied the galvanostatic intermittent titration technique (GITT) to measure the effective diffusion rate of lithium into graphite particles (solid-phase diffusion processes (ii) and (iii)). These are affected by the local Li^+ concentration in the graphite particles' surroundings after the liquid-phase diffusion (process (i)). Liquid-phase diffusion is usually neglected in GITT measurements since it is ~ 1000 times faster than solid-phase diffusion, provided a sufficient supply of lithium is available for the graphite particles. These conditions can be achieved in very thin ($< 30 \text{ }\mu\text{m}$) electrodes. However, if the electrode is quite thick, liquid-phase diffusion restricts the supply of lithium to the solid graphite particles, which in turn affects the GITT-measured solid-phase diffusion values. Therefore, GITT provides solid-state diffusion values which are strongly affected by electrode thickness and electrode porosity. Literature reports thickness-dependent diffusion values obtained with GITT for foil-based electrodes¹².

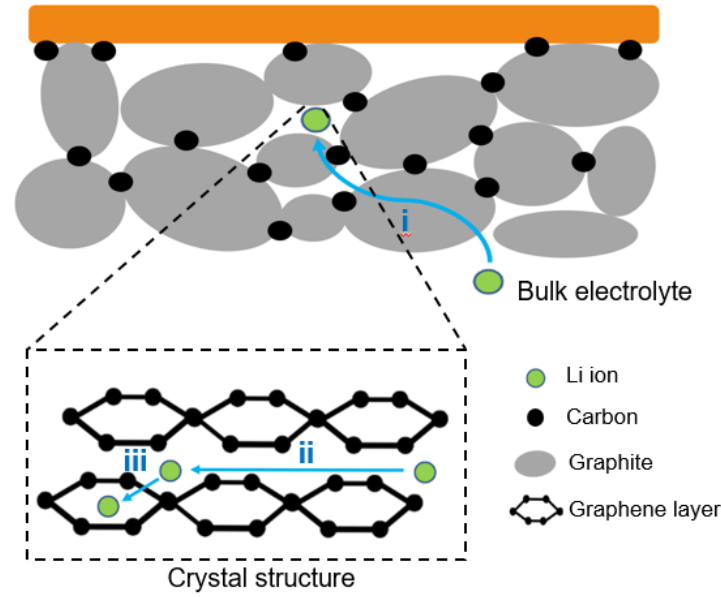


Figure 44. Lithium-ion diffusion path within a graphite anode.

As described in Chapter 3.3, the solid-phase diffusivity is calculated based on **Equation 9**. **Figure 45** describes the solid-state diffusivity as a function of the OCV during lithiation and de-lithiation processes. Two gaps, one at approximately 90 mV and one at approximately 140 mV, were observed. This is because intercalation limits the diffusion rate according to E. Deiss⁷³. Here we employ the mean value of diffusivity at the plateau phase at around 180 mV. **Figure 46** shows several fleece and foil electrode solid-phase diffusivities plotted against the OCV.

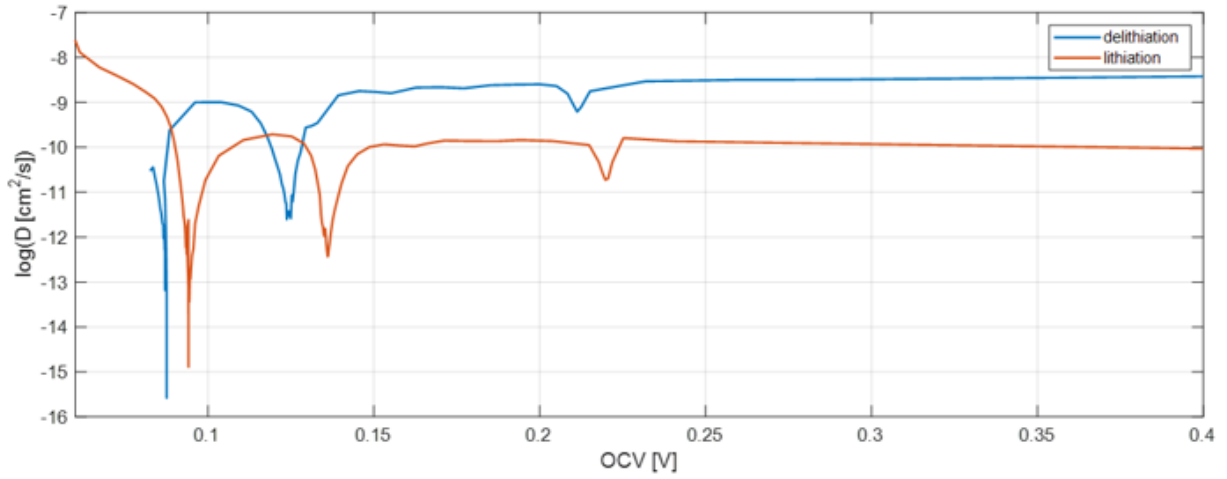


Figure 45. Solid-phase diffusivity plotted against the OCV during lithiation and de-lithiation processes (anode half-cell).

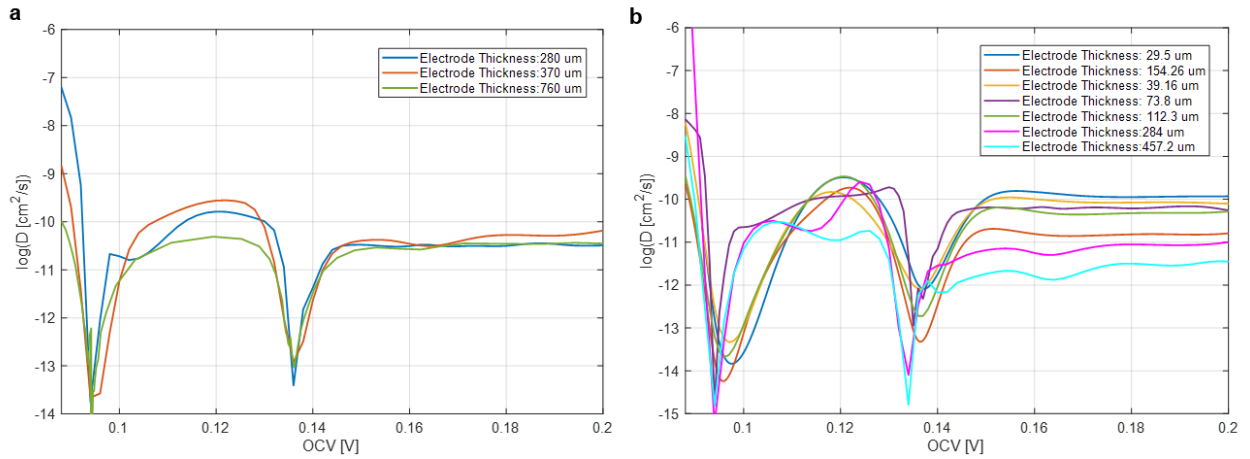


Figure 46. The diffusion coefficient plotted against the OCV of batteries with varying electrode thicknesses: (a) batteries with a fleece electrode and (b) conventional batteries.

In anodes the Li^+ ion diffusivity shows a dependency on electrode thickness and AM porosity. **Figure 47a** shows the GITT-measured diffusivity of foil electrodes and fleece electrodes differing in thickness and porosity. The electrodes were fabricated with thicknesses ranging from 29 to 457 μm for foil anodes and 280 to 1706 μm for fleece anodes. In all cases the electrode composition was identical: 90 wt.-% synthetic graphite, 3 wt.-% carbon black, and 7 wt.-% PVDF-HFP. The copper fleece density (445 mg/cm^3) and calculated diameter of the ultrathin mesh wires (approx. 160 μm mesh size) was identical for all fleece anodes.

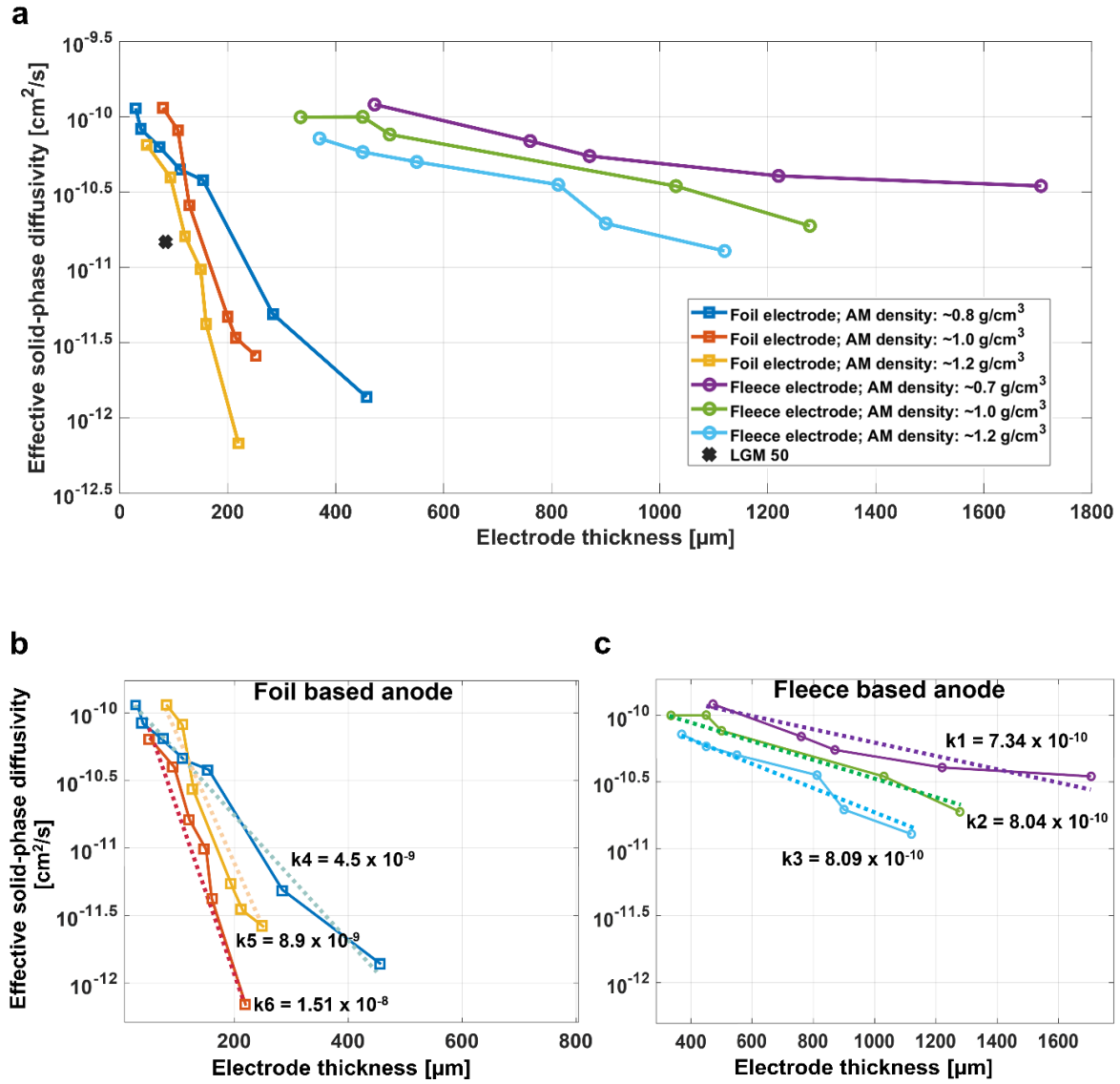


Figure 47. (a) GITT measurements of effective solid-phase diffusivity of foil (square data points) and fleece (round data points) anodes of different thicknesses; (b) effective solid-phase diffusivity of foil anodes differing in thickness and density from (a), and its linear fitting; (c) effective solid-phase diffusivity of fleece anodes differing in thickness and density from (a), and its linear fitting.

Figure 47a shows GITT measurements performed on graphite half-cells to determine the effective solid-phase diffusion constant of electrodes differing in thickness (29 - 1706 μm). Because the insufficient Li^+ ion supply through the pores of the thick electrodes (liquid-phase diffusion) directly affects solid-phase diffusion, in this study we use the term “effective solid-phase diffusivity” to refer to this electrode-thickness-dependent solid-phase diffusion constant. The effective solid-phase diffusivity is plotted in logarithmic scale against the thickness of the anode in **Figure 47a**.

For foil anodes the effective solid-phase diffusivity drops linearly with increasing electrode thickness (square dots). The slope of the linear drop increases with material density. For electrode thicknesses above 120 mm the effective solid-phase diffusivity dropped below 10^{-11} cm²/s. In the case of fleece electrodes (round dots) the logarithmically plotted effective solid-phase diffusivity also drops linearly, but much less steeply. At higher material densities the plotted lines exhibit a parallel shift to lower effective solid-state diffusivity values. The thickest anode we tested was 1.7 mm thick with an electrode density of 0.8 g/cm³. Also, with an electrode density of 1.2 g/cm³ the effective diffusivity does not drop below 10^{-11} cm²/sec at a thickness of ca. 1.2 mm. Remarkably, the extrapolation of the fleece electrode data suggests that thinner fleece electrodes act like foil electrodes. This occurs when the thickness of the fleece electrode reaches half the diameter of the mesh size at about 80 mm. For comparison, the solid-phase diffusivity of an LGM 50 cylindrical cell with an electrode thickness of approximately 85 mm and an effective diffusivity of 1.48×10^{-11} cm²/sec is included in **Figure 47a**⁷⁰.

In thick electrodes a long diffusion path and small electrode porosity hinders Li⁺ liquid-phase diffusion and impacts the local availability of Li⁺ ions in the vicinity of active material particles, as described by Kremer et al. and Gao et al.¹² This affects solid-phase diffusivity within the graphite particles. The GITT data in Figure 2a show that the impact of anode thickness on effective solid-phase diffusion in foil and fleece anodes differs greatly. In foil anodes, liquid-phase diffusion is the only pathway for Li⁺ to reach all graphite particles within the active material. The fact that effective solid-phase diffusivity is much greater in fleece electrodes that have the same material density but are thicker suggests that fleece anodes must offer a second, highly effective path for assisting Li⁺ distribution throughout the active material and Li⁺ supply to graphite.

The ion flux, $\frac{\partial N(x,t)}{\partial t}$, through the active material under the influence of a spatial ion concentration gradient and an electric field is described by the Nernst-Planck equation⁸⁷:

$$\frac{\partial N(x,t)}{\partial t} = -D \left(\frac{\partial N(x,t)}{\partial x} + \frac{qN(x,t)}{k_B T} \frac{\partial \phi(x)}{\partial x} \right) \quad (27)$$

with D being the Diffusion constant, N(x,t) the ion concentration, q the charge, k_B the Boltzmann constant, T the absolute temperature, and $\phi(x)$ the electrical potential field.

In foil batteries Li⁺ ions are transported through the liquid-electrolyte-filled pores of the active material to the solid graphite particles. The liquid-phase transport of Li⁺ ions then changes to solid-

phase diffusion into the solid graphite particles (**Figure 44**). Adopting the steady state condition ($\frac{\partial N(x,t)}{\partial t} = \phi = \text{constant}$) the spatial distribution of the Li^+ ion concentration can be solved as

$$N(x) = N_0 * e^{-\frac{x}{A}} \quad (28)$$

with N_0 being the Li^+ ion concentration at the separator and A being the distance from the separator to the site in the electrode where $N=N_0/e$.

The electrical potential is solved as

$$\varphi(x) = \varphi_0 * \left(1 - \frac{x}{A}\right) \quad (29)$$

The potential is set to be 0 at site A and φ_0 is the potential of the electrode at the separator.

Then the Nernst-Planck equation becomes

$$\phi = -D_1 * \frac{e^{-\frac{x}{A}}}{A} \left(-N_0 - \frac{qN_0}{k_B T} \varphi_0\right) \quad (30)$$

Therefore, the ion flux ϕ which reaches the solid graphite particles becomes a function of electrode thickness. At distance x from the separator the ion flux is reduced by $\frac{e^{-\frac{x}{A}}}{A}$. The reduction of the ion flux that reaches the solid graphite particles causes a rate-limiting mechanism that governs the solid-phase diffusion within the solid graphite particles. Hence, the effective solid-state diffusivity D_s^{eff} scales with the liquid-phase diffusivity D_l and the electrode thickness x according to:

$$D_s^{\text{eff}} \sim D_l * \frac{e^{-\frac{x}{A}}}{A} \quad (31)$$

$$\ln(D_s^{\text{eff}}) \sim \ln\left(\frac{D_l}{A}\right) - \frac{x}{A} \quad (32)$$

The determination of the effective solid-phase diffusivity on the logarithmic scale as a function of electrode thickness x for foil anodes reveals a linear drop. Greater material density, in other words, reduced porosity decreases the intrinsic liquid-phase diffusivity D_l . The distance at which the ion concentration drops to N_0/e , i.e., A , is shorter for denser materials. Therefore, greater material

density when scaled logarithmically against anode thickness causes an increase of the slope of the straight lines, thus, confirming the experimental findings (**Figure 47b**).

In the case of the fleece anode the metal fleece infiltrates the active material, in other words, the entire fleece mesh is effectively filled with solid graphite particles and liquid electrolyte. We propose that major ion flux through the active material is governed by diffusion on the surface of the copper fleece (D_m). Li^+ ions diffuse mainly via the fleece and from there into the graphite, which begins with Li^+ ion flux by liquid-phase diffusion through the pores in the graphite followed by the entry of the Li^+ ions into the solid graphite particles. In this serially coupled ion flux prior to entry into the solid graphite particles that takes place from fleece to liquid, the diffusion constant in the Nernst-Planck equation (1) can be approximated to

$$D = \frac{D_l * D_m}{D_l + D_m} \quad (33)$$

This term is simplified with $D_m \gg D_l$. Furthermore, the mesh size of the fleece is small in comparison to the electrode thickness. Thus, the ion flux through the liquid-phase within the mesh (prior to reaching the solid graphite particles), does not depend on electrode thickness and variations in mesh size are negligible. As a result, the diffusion constant of the ion flux scales as follows:

$$\ln(D_{s,f}^{eff}) \approx \ln\left(\frac{D_l}{B}\right) - \frac{x}{B} \quad (34)$$

with B being the distance from the separator in the electrode, where $N=N_0/e$ and the potential drops to zero. Since the fleece is metallic and has a high Li^+ ion mobility we assume $B \gg A$. Therefore, the ion flux that reaches the solid graphite particles drops as a straight line on a logarithmic plot with increasing anode thickness x . Also, the slope of this drop is far less steep than in foil anodes because $B \gg A$ (**Figure 47a**). Since the ion flux through thick fleece electrodes is mainly governed by diffusion along the metal fleece and metal fleece parameters, such as mesh size, were not changed for the measurements in **Figure 47c**, the slopes of the straight lines for the three different graphite densities were approximately identical. Densifying graphite decreased D_l , whereas the metal fleece parameters D_m and B were kept constant. Therefore, the parallel drop of the straight lines as presented in **Figure 47c** for fleece anodes is obviously due to an increase in graphite density, whereas the steepness of the slope of the straight lines is determined by the copper fleece properties (which were identical in all experiments).

Rate performance

The electrical conductivity measurements and the solid-phase diffusivity measurements of the foil and fleece electrodes show that electron transport and ion transport in fleece electrodes are not limited by electrode thickness. Thus, the rate performance of the electrodes will not be impacted by electrode thickness. **Figure 48a** shows the rate performance of foil electrodes and **Figure 48b** shows the fleece electrode in half cell configuration (graphitic anode against metallic lithium). The charging protocol was CC-CV charging + CC discharging. The capacity retention was calculated based on the CC discharging capacity. The charging/discharging protocol consisted of 5 cycles each at 0.2C, 0.5C, 1C, followed by 0.2C.

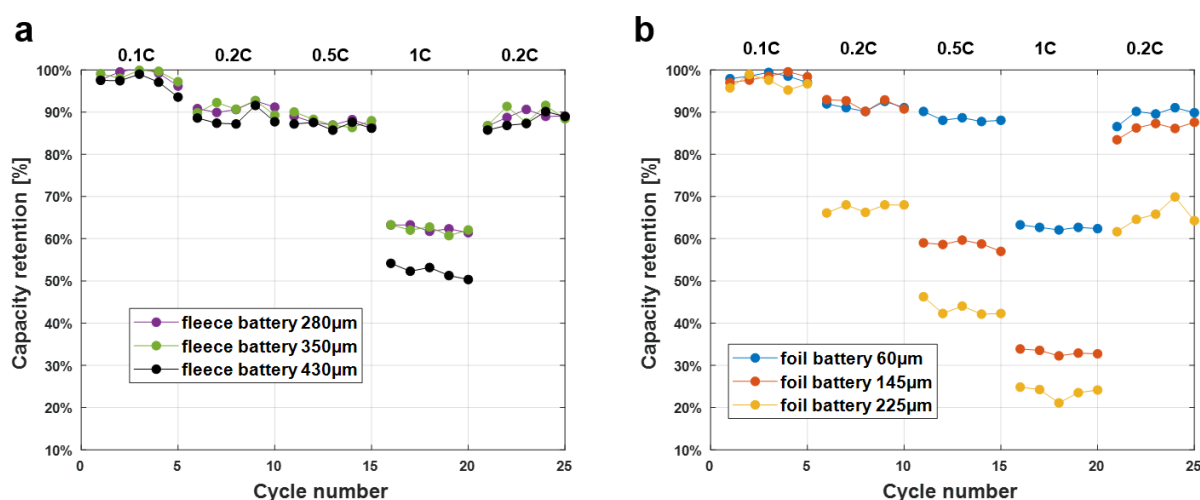


Figure 48. Rate performance of foil and fleece electrodes.

The thin foil electrode (60 µm) featured the highest capacity retention with high cycling rates, however a drastic drop of the reversible capacity was observed when the thickness of the film electrode was increased to 145 µm or 225 µm. In the case of the 225 µm thick electrode the capacity dropped to 0.5C, the electrode could only reach ~60% of its theoretical capacity, and during the final 0.2C cycling the capacity was still low. The latter suggests that the lithium plating on this electrode drastically increased the amount of dead lithium within the battery, causing permanent capacity loss. In the case of the 145 µm thick foil electrode the capacity dropped to 1C and could only reach ~43% of its theoretical capacity.

For fleece electrodes this correlation between electrode thickness and rate capability does not exist. Capacity retention at high C-rates was comparable to those in a film electrode with 50 µm thickness. This indicates that the mass and energy transport rate in the fleece electrodes is sufficiently fast and the performance rate not impacted by electrode thickness. For fleece

electrodes thicker than 430 μm (not shown here) the areal capacity was greater than 15 mAh/cm^2 . As a result, 1 C current density is higher than 10 mA/cm^2 and in this scenario the charge transfer resistance of the metallic lithium is enormous and becomes the bottleneck in rate capability tests. Because of the high overpotential of the metallic lithium, it is difficult to keep the graphite anode at the intercalation voltage at high C-rates.

The rate performance data shows that the metallic fleece is an outstanding electronic and ionic conductor, which fulfills energy and mass transport requirements and enables ultrathick electrode design. Besides, the GITT and rate performance measurements also reveal that in a fleece battery performance is decoupled from electrode thickness.

Full cell performance

Similarly, the fleece cathodes is able to be prepared with cathode active material infiltrated into a 3D aluminum fleece. After drying process the fleece cathodes are compressed to the target active material density. Here a NMC622 slurry is prepared together with carbon black, conductive graphite particles (KS-6) and PVDF binder, by adjusting the solvent (NMP) to solid ratio and temperature, the slurry is successfully filled into the aluminum fleece. **Figure 49** shows the cross section of a fleece cathode; the AM and conductive agent are homogeneously distributed into the fleece.

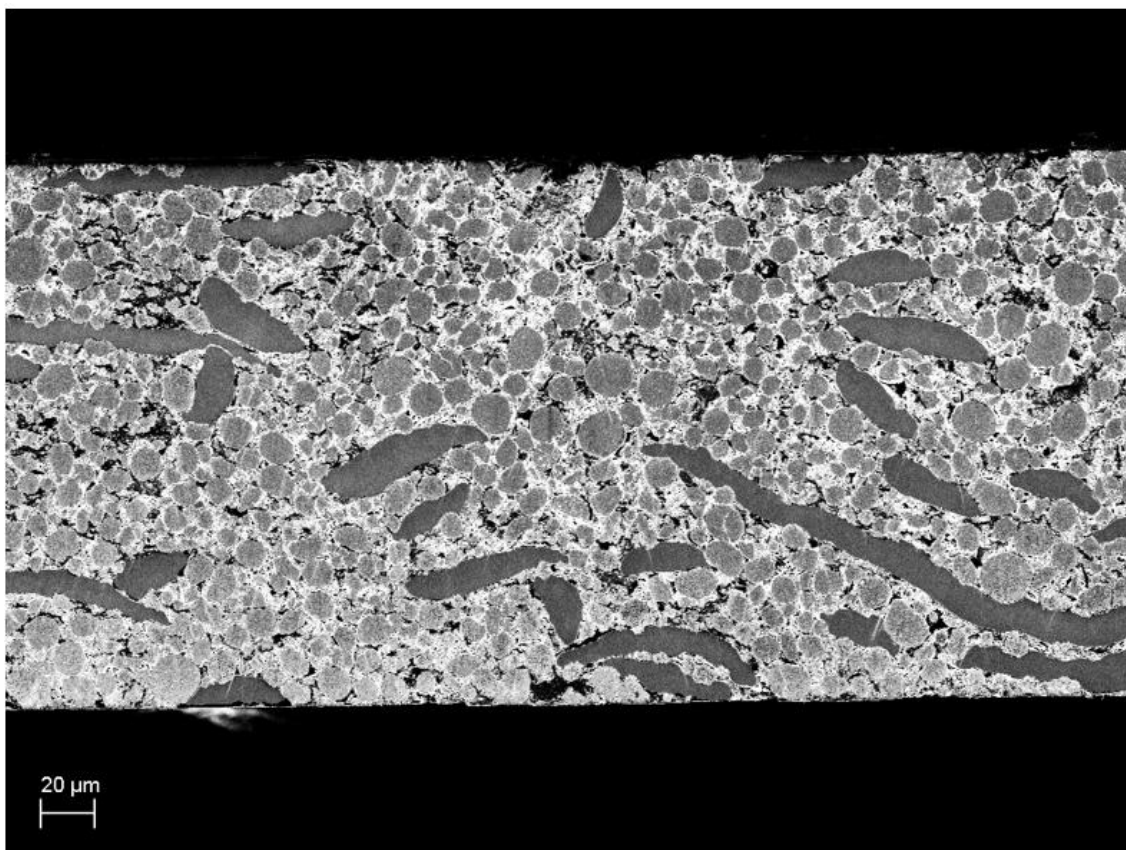


Figure 49. Cross section of fleece cathode

Assembled together with the fleece anode, a thick full cell with ultra-high areal capacity is fabricated, **Figure 50** shows the SEI formation cycles (0.1C), in the initial cycle, the full capacity is obtained (9.1 mAh/cm^2), means that the utilization of the AM is nearly to 100%. Normally in thick foil batteries, the utilization of the AM cannot reach 100% at initial cycle due to the high internal resistances. However, the initial coulombic efficiency is 88%, which is a bit lower than the industrial level (88% ~ 92%), this could due to the fact that for ultra-thick electrode, the electrolyte wetting is quite challenging, an inhomogeneous wetting leads to an inhomogeneous and thicker SEI formation and consumes more lithium at the beginning cycles. Further research on how to effectively wet the fleece electrodes is required in the future.

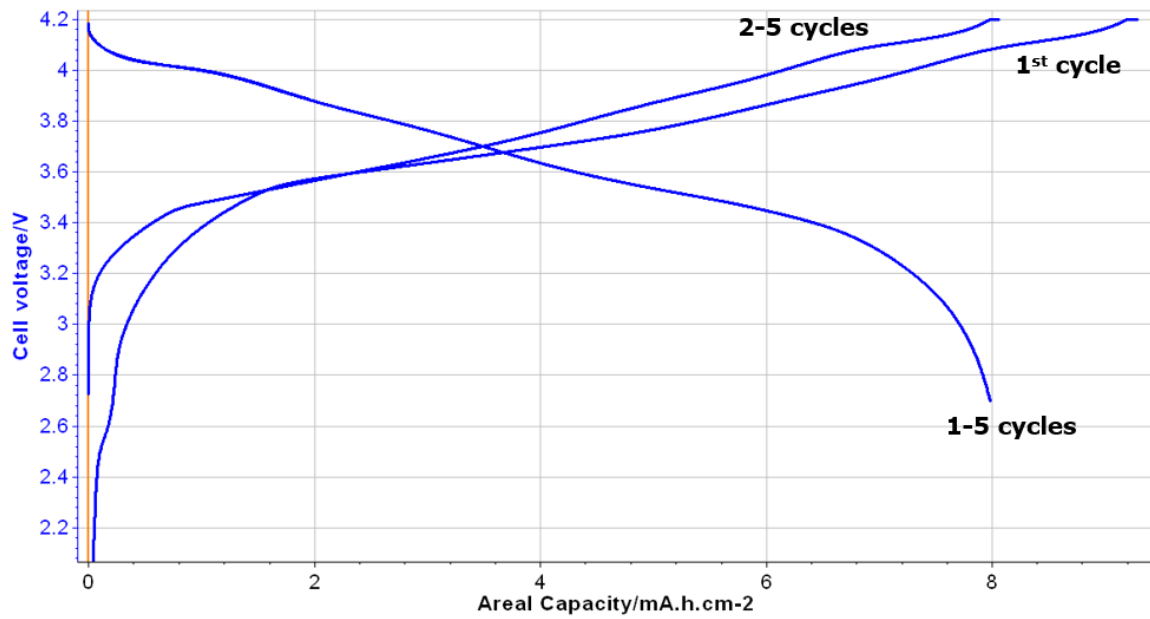


Figure 50. SEI formation cycles of fleece full cell.

Figure 51a shows the rate performance of the full cell, due to the enhancement of electron and ion transport, the full cell is able to provide considerable capacity with high charging discharging rate. To our best knowledge, this is the first time that a LiB full cell with such high capacity can be functional at such high charging discharging rate. **Figure 51b** shows the impedance measurement of the fleece full cell, unlike the half-cell EIS measurement, there is a semi-circle at high frequency range, this is because that the film resistance within anode and cathode are super positioned. Same in the range from 10 kHz to 1 Hz, that the charge transfer impedances of anode and cathode are overlaid with each other.

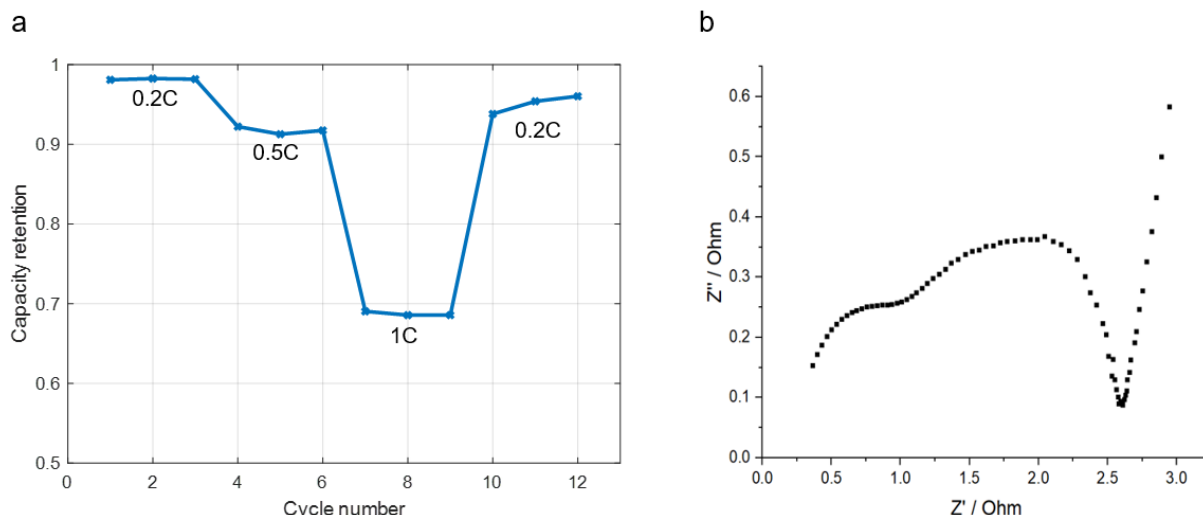


Figure 51. (a) rate performance of fleece full cell. (b) impedance measurement of fleece full cell

4.3 SURFACE DIFFUSION MEASUREMENTS WITH A MICROFLUIDIC DEVICE COMBINED WITH RAMAN SPECTROSCOPY

Although it appears logical that a copper fleece would improve the electrical conductivity of the electrodes, it is not so obvious that this would go hand in hand with greatly enhanced Li^+ diffusivity. Three assumptions are made to explain this phenomenon:

- Assumption 1: The fiber network creates a more open porous structure, which decreases the electrode's tortuosity and the length of the lithium-ion diffusion path;
- Assumption 2: The interaction between the metallic fiber surface and ions enables rapid ion diffusion along the fiber surface;
- Assumption 3: a combination of assumption 1 and assumption 2.

To investigate the first assumption, the geometry of the fleece electrodes was investigated via micro CT reconstruction on the basis of which the tortuosity of the electrodes was calculated. These experiments showed that the impact of the fiber network on electrode tortuosity is quite limited, since after the electrode was compressed to the desired density the gap between the fiber and active material particles was negligible. This is evidence that the ion path is not decreased by the structure of the network. **Table 11** shows the tortuosity calculation of a thick foil electrode and a fleece electrode with identical thickness and porosity. The calculation is based on a μ -CT reconstructed structure.

Table 11. Tortuosity calculation of a foil and a fleece electrode.

Electrode thickness	Foil electrode tortuosity	Fleece electrode tortuosity
210 $\mu\text{m} \pm 12 \mu\text{m}$	3.65	3.58
280 $\mu\text{m} \pm 15 \mu\text{m}$	3.71	3.74
360 $\mu\text{m} \pm 8\mu\text{m}$	3.90	3.83

To investigate the second assumption, we developed a microfluidic experiment utilizing Raman spectroscopy in order to quantitatively study Li^+ ion mobility on a copper surface. **Figure 23** illustrates the design of our electrochemical set-up. The diffusion experiment was based on two laminar co-flows with different ion concentrations generated in the microchannel. The two electrically-grounded laminar flows of electrolytes, one with and one without Li^+ ions, are injected into the two arms of the Y-shaped channel. As the flows reach the Y-junction they come into contact with one another and equilibration by diffusion follows. Confocal Raman Spectroscopy is used to spatially and temporally measure the quantitative ion concentration perpendicular to the flow direction. The detailed experimental set-up is described in Chapter 3.5.

In the electrolyte (1 M LiPF_6 in 50:50 ethylene carbonate (EC): dimethyl carbonate (DMC)), the dissolved Li^+ ions associate with solvent molecules and form solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and aggregates. The ion-solvent association is mediated by ion-dipole-interactions which impact the solvent molecule bond vibration frequencies, thus leaving a trace in the solvent molecules' Raman spectrum. **Figure 52** shows the Raman spectrum of the electrolyte at different lithium-ion concentrations.

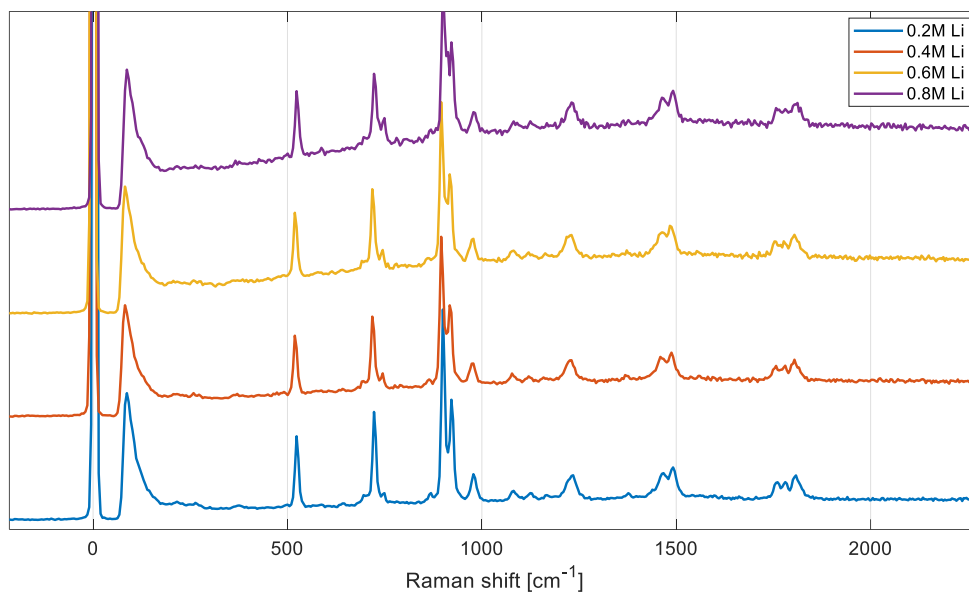


Figure 52. Raman spectra of electrolytes with different lithium-ion concentrations. The most significant Raman peaks were observed at 720 cm⁻¹ (O-C-O) and 744 cm⁻¹ (P-F).

It is worthwhile mentioning that a fluorescence noise was observed when increasing the lithium-ion concentration. To filter out the noise, all measurements were first calibrated by normalizing the Rayleigh peak intensity to account for slight differences in laser intensity between measurements and then the fluorescence noise was eliminated from spectra by applying an algorithm that removes the low frequency peak of the signal (**Figure 53**).

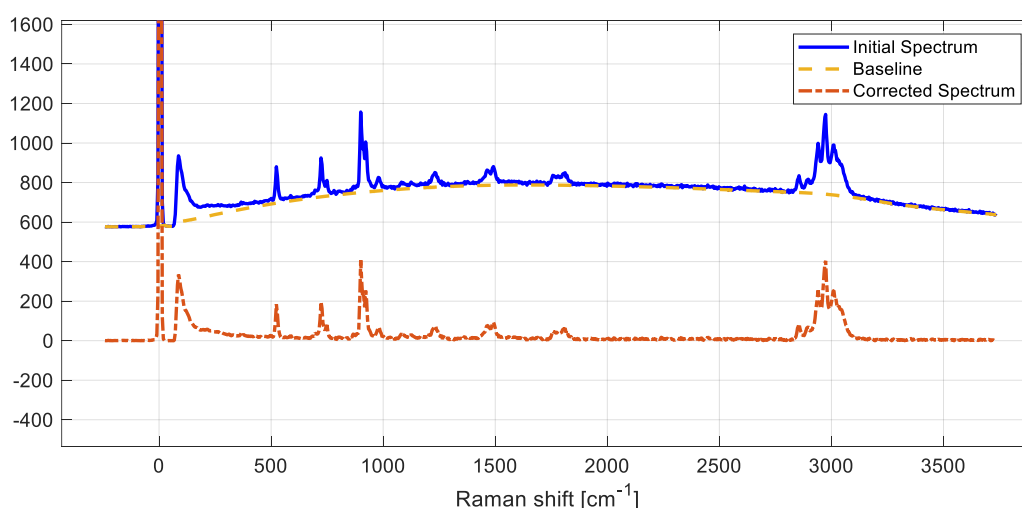


Figure 53. Fluorescence noise elimination.

We specifically focused on the Li⁺ ion and EC ion-solvent association. A Li⁺ ion impacts the oxygen-carbon-oxygen bond (O-C-O) vibrational frequency of EC at 720 cm⁻¹, and shifts it toward

733 cm^{-1} (**Figure 54a**). Simultaneously, P-F stretching is observed at 744 cm^{-1} , indicating an increase in anions (PF_6^-). By eliminating the fluorescence noise as well as normalizing and comparing the intensity of the original O-C-O peak and the P-F peak, Li^+ concentration is visualized spatially-resolved and in real-time (the applied algorithm is described in Supporting Information II). As mentioned before, the most significant effects of the lithium salt are O-C-O bond shifting and P-F bond stretching (**Figure 54a**). We observed that the integration of the two peaks is not linearly correlated to the lithium-ion concentration, but instead the ratio between the two peaks displays a linear relationship with the lithium-ion concentration. The ratio R is calculated as:

$$R = \frac{\int_{734 \text{ cm}^{-1}}^{754 \text{ cm}^{-1}} \text{CCD} - \int_{734 \text{ cm}^{-1}}^{754 \text{ cm}^{-1}} \text{CCD}_{\text{noise}}}{\int_{710 \text{ cm}^{-1}}^{730 \text{ cm}^{-1}} \text{CCD} - \int_{710 \text{ cm}^{-1}}^{730 \text{ cm}^{-1}} \text{CCD}_{\text{noise}}} \quad (35)$$

CCD is the Raman shift intensity of the initial spectrum and $\text{CCD}_{\text{noise}}$ is the fluorescence noise intensity. Using linear fitting (**Figure 54b**) the relationship between the integration ratio and ion concentration is described as:

$$c_{\text{lithium}} = 2.463 \times R - 0.00325 \quad (36)$$

Figure 54b shows the calibration of the normalized Raman spectrum ratio R as a function of the LiPF_6 concentration. Our experimental set-up with Raman spectroscopy allows the determination of the lithium-ion concentration during the microfluidic experiment and without disturbing it.

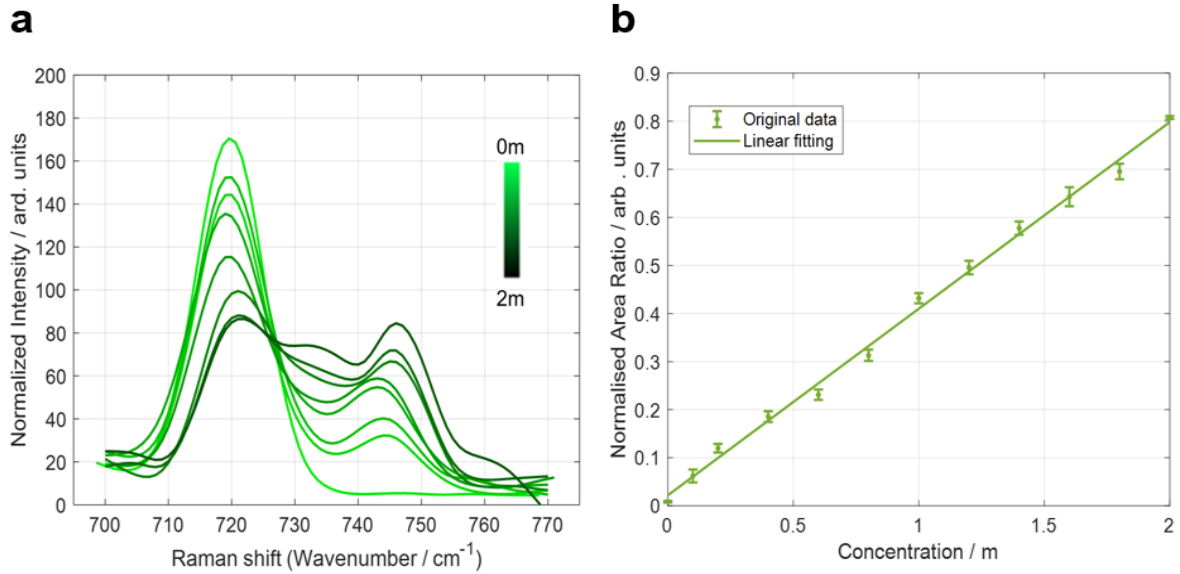


Figure 54. (a) Raman spectra of electrolytes with different lithium-ion concentrations. (b) Normalized signal intensity as a function of the lithium-ion concentration.

The ion concentration gradient from the lithium-rich to the lithium-poor phase is extracted from Raman spectroscopy line scans at 7 channel cross sections, each 10 mm apart (y-direction, **Figure 55**). Quantifying the concentration gradients at different cross sections, namely, positions S0 to S7 along the flow direction, can be interpreted as concentration gradients at different time points, since the liquid flow is well-defined.

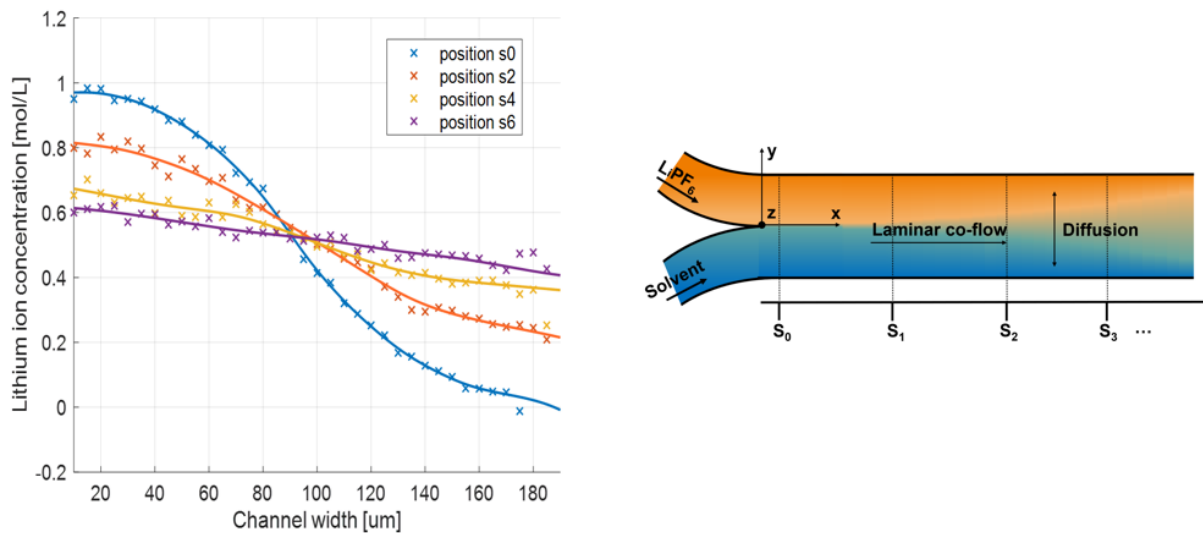


Figure 55. Ion concentration gradient within the Y-shaped microfluidic channel.

When the two laminar flows come into contact at the Y-junction (position S0) a clear concentration interface is established (**Figure 55**). The total width of the channel behind the Y-junction is 200 μm . At first the voltage is set to 0 V against zero charge potential. At the channel entry (position

S0), the concentration is 1 mol/L in one channel and 0 mol/L in the other channel. Measurements reveal that the concentration difference equilibrates once the Y-junction has been passed and with increasing distance to the channel entries. At position S6 the concentration difference across the channel is between 0.6 to 0.4 mol/L. Based on Fick's second law, the lithium-ion diffusion coefficient perpendicular to the flow direction is calculated to be $2.21 \times 10^{-10} \text{ m}^2/\text{s}$. At 0 V against zero charge potential this diffusion constant is independent of the channel height at which the spectra are taken. Therefore, surface diffusion does not overcome bulk diffusion. The measured diffusivity value is also quite similar to results obtained by PFG-NMR and the essential diffusivity value of a bulk electrolyte of $2.02 \times 10^{-10} \text{ m}^2/\text{s}$ found in literature⁴⁷.

In contrast, the diffusion rate increases substantially when an offset voltage is applied to the copper surface, regardless of whether the metal surface is positively or negatively charged (**Figure 56a**). Moreover, when the surface is negatively charged the Li^+ ion diffusivity is even greater than in the case of a positively charged surface. Measured diffusivity values also strongly depend on the height setting of the Raman microscope objective lens during spectra measurements as well as the applied voltage. When the measuring points are closer to the charged surface, higher diffusion rates along the channel width are observed. At -500 mV against zero charge voltage, the effective diffusion rate within the channel measured at 15 μm height from the copper foil is enhanced by a factor of 1.5. At lower objective lens heights this effect is amplified to approximately 2-fold at 10 μm and 3 times greater at 5 μm . These phenomena indicate that surface diffusion dominates the overall diffusion process near the charged surface and the acceleration of ion movement is more pronounced near the surface. In contrast, when the measuring points are far away from the surface the diffusion within the bulk electrolyte dominates the overall diffusion process. Also, the increase of electrical potential-related diffusion suggests that the formation of an electric charge at the surface causes faster diffusion. In the case of a positively charged surface the Li^+ diffusion rate also increases. In this scenario the anion mobility is enhanced due to the electroneutrality in the bulk electrolyte and the lithium-ions are pulled from the lithium rich to the lithium poor area. However, there is a saturation of the diffusion coefficient that can be observed at about +320 mV, since the enhancement of the diffusion process is limited by the essential mobility of the Li^+ ions in the bulk electrolyte. **Figure 56b** illustrates the diffusion process within the microfluidic channel when the surface is negatively charged: ions accumulate at the charged surface and an ion flow from lithium rich to lithium poor domains is followed by the release of Li^+ ions to the bulk solution.

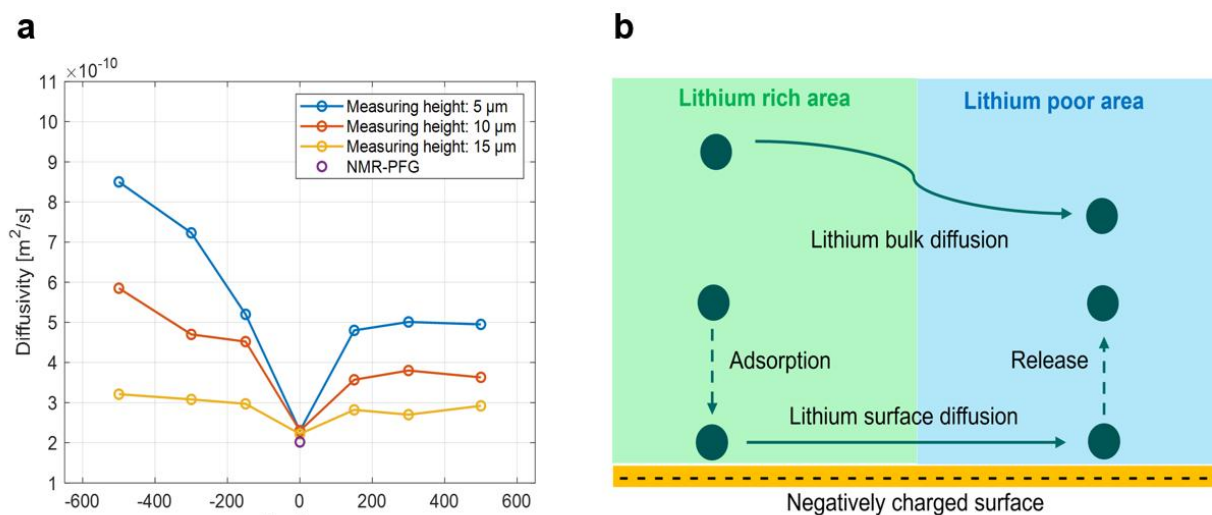


Figure 56. (a) Ion diffusivity in the Y-shape microfluidic channel at a charged surface. (b) Schematic of enhanced ion diffusion at charged surface.

Previous studies have also found that the ion diffusion process can be enhanced in the presence of a charged surface.^{85,88,89} But in contrast to our study, these measurements were either qualitative estimations or based on theoretical calculations and simulations. To the best of our knowledge, this is the first time that this phenomenon has been experimentally quantified.

4.4 BROWNIAN MOTION WITHIN THE ELECTRICAL DOUBLE LAYER

Although the microfluidic experiments illustrate that within the electrical double layer lithium-ions have greater mobility, it is still not clear why this is the case. To look into this, full-scale ab initio molecular dynamic simulations were carried out based on the density functional theory (DFT) (detailed information on the method is given in Chapter 3.8).

First, the bulk electrolyte was modeled and a preset positive surface charge density was assigned to the copper surface. Due to the surface charge, the ions are redistributed along the surface and the EDL is formed. **Figures 57a** and **57b** show the absolute and relative concentration profile of the ions and solvent molecules. Near the surface two peaks (increases) of cation concentration and a decrease of anions were observed. The first Li^+ peak indicates the position of the inner Helmholtz layer (IHL), whereas the second indicates the position of the outer Helmholtz layer (OHL). Li^+ , EC and DMC within the EDL are attached to the charged surface while anions are repelled and vanish.

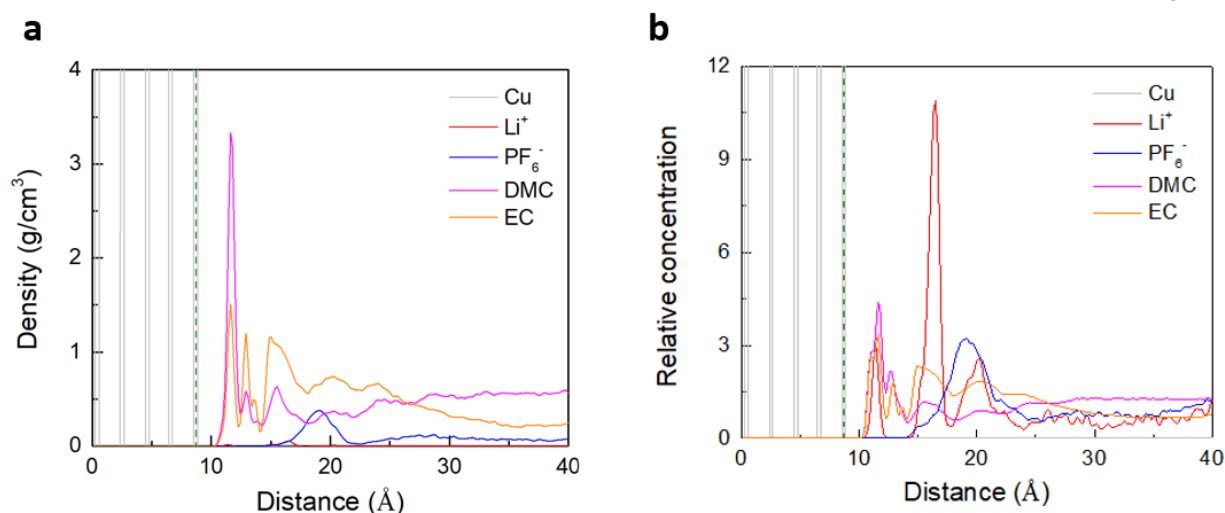


Figure 57. (a) Species density within EDL and (b) relative concentration of species in EDL.

Figure 58 shows the accumulation of free EC, free DMC and Li⁺-coordinated EC/DMC within the bulk electrolyte (IHL and OHL). Single-molecule counting was carried out in the EDL and the bulk electrolyte at the same time. Within the EDL large portions of free Li⁺ and solvent-associated Li-ions accumulated on the charged surface, whereas in the bulk electrolyte more solvent molecules were observed. In the bulk electrolyte all the Li-ions were coordinated with solvent molecules and formed SSIPs, CIPs, and aggregates. Within the EDL, in contrast, abundant free Li⁺ was observed as it was directly attached to the charged surface. This indicates that solvation shells or big aggregates of anions, solvent molecules, and cations were breaking up within the EDL. Also, the average association number of lithium-ions within the EDL is lower than in the bulk electrolyte. This break-up of the ion-solvent connection is obviously due to electrostatic forces.

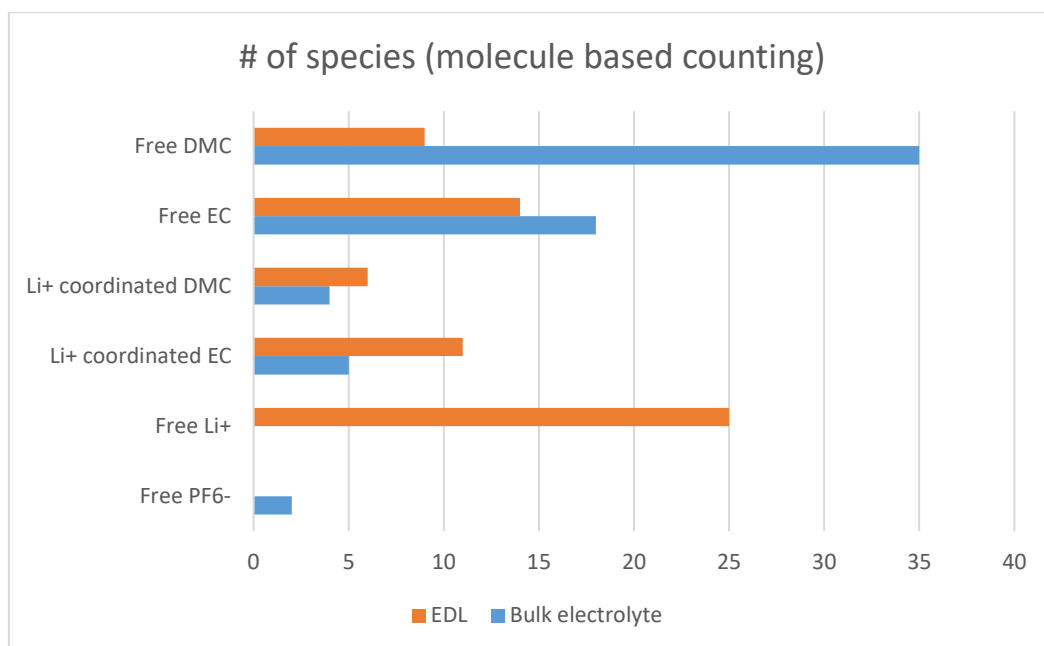


Figure 58. Number of species as determined by single-molecule counting in the bulk electrolyte and the EDL.

Afterwards, the diffusivity of Li^+ was calculated at this equilibrium state based on the time evolution of its trajectory in the bulk electrolyte and on the surface ($< 18 \text{ \AA}$). Details are given in Chapter 3.8. As **Figure 59** shows, the ions at the surface exhibited a much higher mobility than the ions in the bulk. Linear fitting of the mean square distance (MSD) and time revealed the diffusivity of surface ions to be $1.14 \times 10^{-8} \text{ m}^2/\text{s}$, which is about 56 times greater than Li^+ diffusivity in the bulk electrolyte.

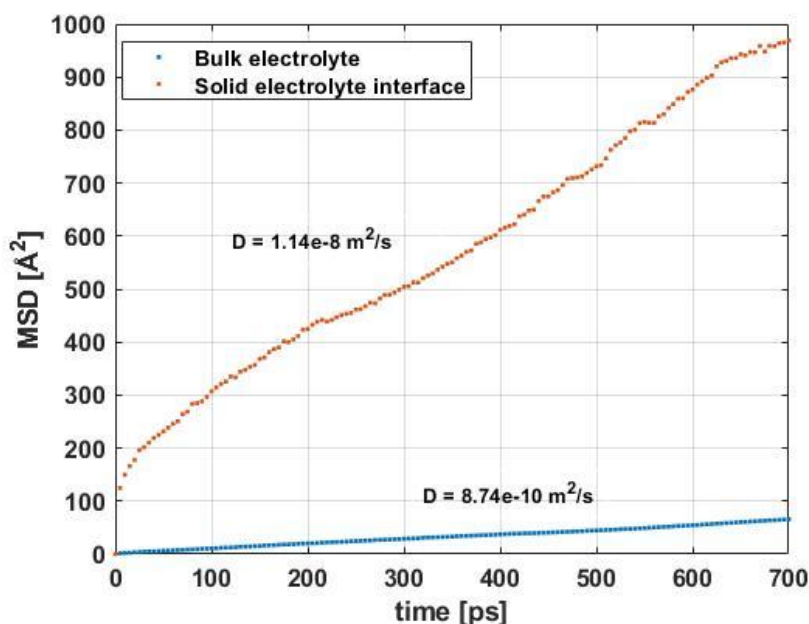


Figure 59. Li^+ diffusivity calculation based on MSD.

There is a difference between the diffusivity we calculated and the value given in the literature ($2.1 \times 10^{-10} \text{ m}^2/\text{s}$). This could be the result of an inaccurate force field calibration during simulation. Nevertheless, the ion and solvent molecule distribution revealed that in a liquid phase the ionic conductor (in this case the electrolyte) as well as the anions and cations always associate with the solvent molecule. This results in the formation of a solvation shell or big aggregates that contain anions, cations, and the solvent (**Figure 60a**). This phenomenon has been described previously, both theoretically^{90–92} and experimentally^{93,94}. Such associations, however, do not occur on a charged surface and instead ions and/or solvent molecules frequently interact directly with the charged surface via electrostatic forces^{28,95,96}. In an aqueous electrolyte the cation solvation shell is robust. In contrast, in carbonate-based Li^+ ion electrolytes our MD simulations and the literature⁹² indicate that Li-ions are prone to desolvate and adsorb on the charged electrode surface in ‘bare’ form. Our experiments and calculations reveal that the breakage of the ion-ion and ion-solvent interactions at charged interfaces free the ions from their ligand shells and thereby increase the mobility of the ions. As illustrated in **Figure 60b**, a Helmholtz layer (HL) is formed when the metallic surface is negatively charged. At the inner HL neither ion-solvent nor ion-ion pairing exist any longer and the large amounts of adsorbed ions form a compact HL at the surface. These bare ions interact with the excess electrons on the metallic surface and show ultra-high mobility. Also, the phenomenon is quite similar to job-sharing diffusion at interfaces in solid-state mixed conductors described by Chen et al.²⁸

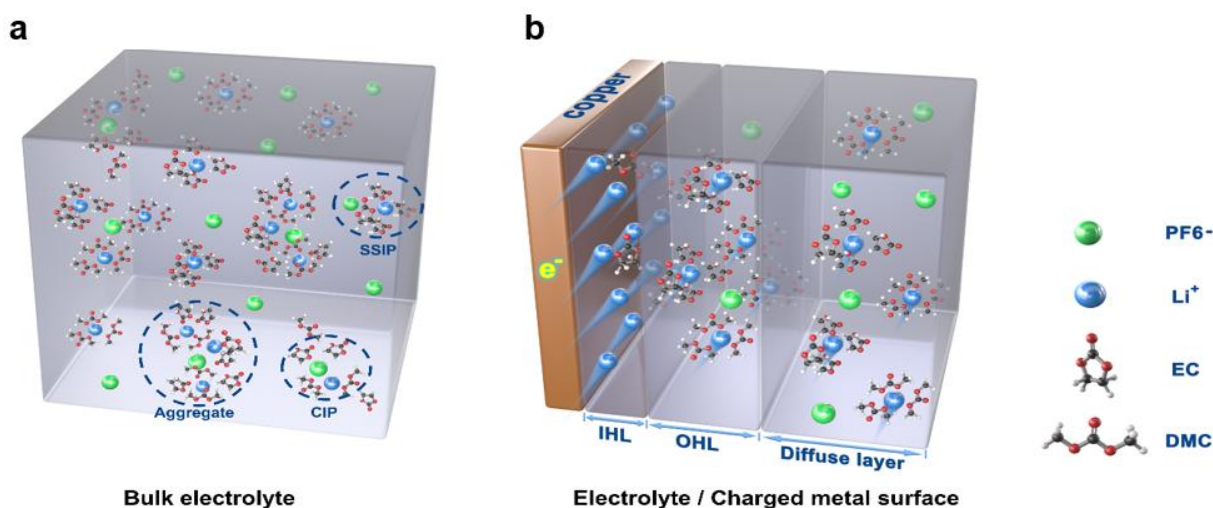


Figure 60. Schematic of diffusion processes in the bulk electrolyte and at a charged surface.

Based on the electric double layer (EDL) theory and computational calculations, the excess surface charge breaks the complexes between the Li^+ , EC, and DMC molecules. Instead, ion-electron pairs are established on the metal surface, thereby enabling much greater mobility than cation-anion contact pairs, solvent-separated ion pairs, or aggregates within the bulk electrolyte. As a higher polarized potential is applied at the surface, more ions accumulate at the surface and are ‘activated’ to have higher mobility, accelerating the mixing process within the microfluidic channel.

4.5 MODELING OF LITHIUM-ION BATTERIES

As mentioned above, the enhancement of energy transport and mass transport achieved by embedding the metallic fiber network into the active material enables us to build functional ultra-thick electrodes with high areal capacity. Towards further developing and optimizing this novel electrode, I performed a physical-based mathematical modeling study of the electrode with a battery digital twin, which provides deeper insights into underlying mechanisms and provides the means to evaluate and predict the battery’s charging/discharging performance, cycling stability, cell heat dissipation, and degradation behavior under various operational conditions. Building on this data a structural and morphological optimization of the electrode can be carried out, including the optimization of the geometry of the metal fibers, fleece density, fiber orientation, active material filling, and more.

As discussed in Chapter 2.7, the modeling of the electrochemical processes is categorized into macroscopic calculation and microscopic calculation. Latz et al. derived mass and charge transport equations describing the microscopic processes in the active material and the electrolyte of a lithium-ion battery cell. Solving this continuum model on a fully resolved 3D cell geometry

ensures accurate prediction that is comparable to experimental data. However, the computation time per charge cycle of such a microscopic model is very high and, hence, not suitable for an optimization, as optimization requires a high number of simulations. As a result, we switched to a state-of-the-art approximation of solid-state mass transport, the so-called Doyle-Fuller-Newman (DFN) model. In this model the shape of the active material is represented by spherical particles and the solid-state diffusion process is simplified from 3D to 1D in the radial direction. The resulting pseudo-two-dimensional coupling between the macroscopic 1D transport and the radial solid-state diffusion process is the most common and hence the classic form of the DFN model. As shown in **Figure 61**, the computation time of a microscopic model per charge cycle is very high and, hence, not suitable for an optimization, as optimization requires a high number of simulations. The 1D + 1D model (DFN model) lowers the computation accuracy but at the same time massively decreases both computation time and effort.

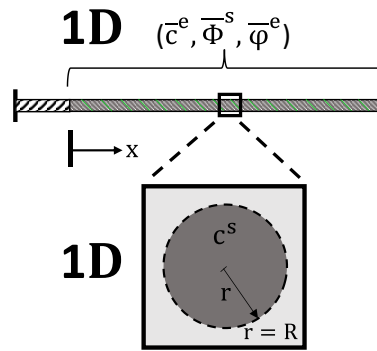


Figure 61. Concept of the DFN model.

However, there are also downsides to the DFN model, as it neglects the particle shape distribution and size distribution as well as only taking the active material and the electrolyte into consideration. Therefore, the DFN model is not suitable for fleece electrodes, as it lacks the flexibility to consider the metal phase and the surface diffusion mechanism. To solve this, I introduce a new approximation approach for solid-state mass transport which can be considered a compromise between the micro-macroscopic model and the DFN model (**Figure 62**). The model is designed to take the following phenomena into consideration: (i) non-spherical shape, (ii) impact of conductive phase (CBP or fleece), and (iii) overlap of non-spherical active material with different particle sizes. The detailed calculation and governing equations for this new approximation are described in Chapter 3.10.

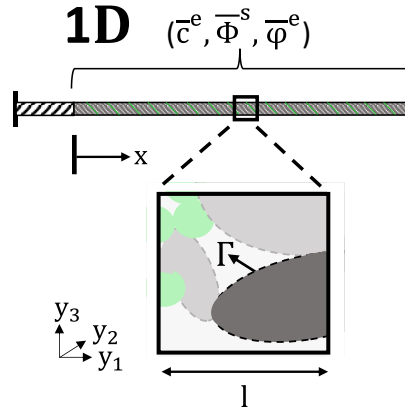


Figure 62. Concept of the new approximation approach.

Study 1: Considering the non-spherical shape of the active material

We chose the star-shaped geometry shown in **Figure 63** for the half-cell electrode to account for the non-spherical shape of the active material in testing the new approximation approach.

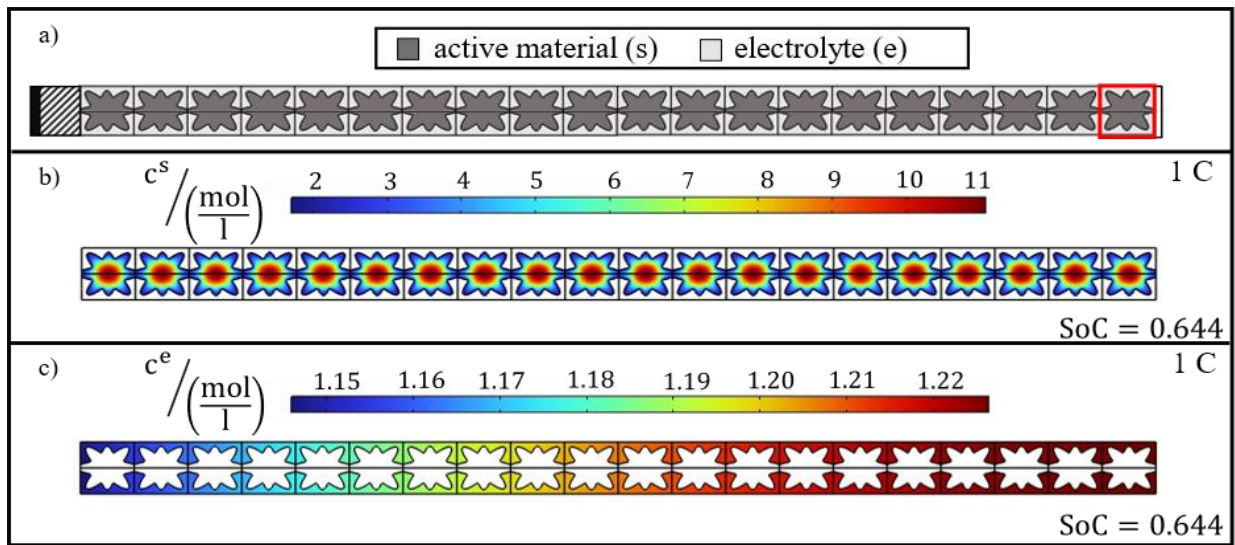


Figure 63. Choice of a star-shaped geometry to best represent the surface of the active material. (a) The lithium counter electrode and the separator are located on the left-hand side and the current collector of the half-cell electrode is on the right-hand side. (b) The microscopic concentration distribution within the active material at 1 C was SoC=0.644. (c) The microscopic concentration distribution within the electrolyte at 1 C was SoC=0.644.

As a first step, a microscopic simulation was done as a reference. Since the half-cell is charged, the lithium concentration within the active material of the cathode decreases over time. The depicted microscopic distribution of c^s shows the discussed quasi-stationary deviation between the inner concentration and the surface concentration depending on the Butler-Volmer rate. As the particles have a star-shaped geometry, this quasi-stationary deviation behaves highly non-

spherical. The de-intercalated Li-ions move from the interface through the electrolyte pore system to the separator and the lithium counter electrode. The resulting stationary profile of c^e , which depends on the charging rate of 1 C, is shown in **Figure 64**.

By applying the asymptotic homogenization and diffusion length theory (details in Chapter 3.10) the diffusion layer thickness can be extracted. This geometry had a stationary diffusion layer thickness of $l^{\text{diff},\infty}=0.09055$. The corresponding time function $\delta(\tau)$ is shown in **Figure 64**.

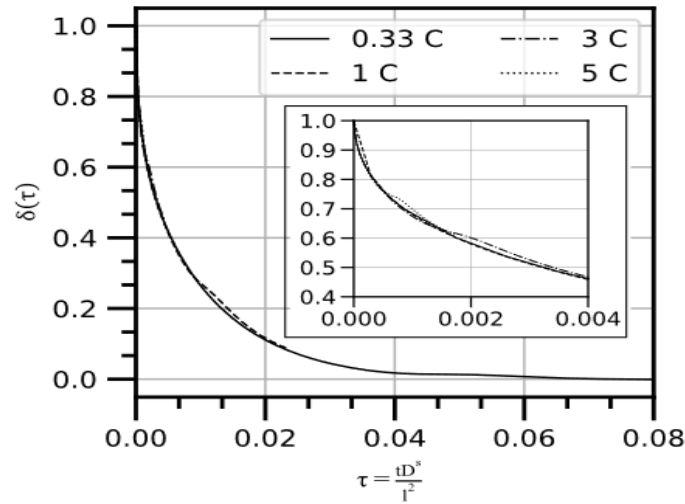


Figure 64. Decaying time function $\delta(\tau)$ of the diffusion layer at different C-rates assuming a star-shaped geometry for the active material.

As **Figure 64** shows, the decaying of the time constant $\delta(\tau)$ is independent of the charging rate. This means that the diffusion layer establishment only depends on the diffusion time constant and the geometry information of the AM particles. Thus, if the geometry information of the AM particle and the solid-phase diffusivity are well characterized, this new approximation model can be implemented to predict cell performance at different charging rates.

The higher the C-rate, the faster the simulation reaches the implemented stopping condition at 0.25 V. In the case of 1 C, 3 C and 5 C the simulations stopped before the time functions $\delta(\tau)$ decayed to zero, hence before the diffusion layer was fully developed.

The performance of the approximation model with the diffusion layer parameters was evaluated by comparing it with microscopic reference data and the DFN model. **Figure 62** shows the terminal voltage of the anode half-cell at different charging rates. To ensure a fair comparison of the macroscopic models, the radius of the DFN model was fitted to the microscopic cell voltage at 0.33 C. The diffusion layer parameters were determined using this charging scenario.

Since the DFN model cannot capture the solid-state diffusion limitations of random particle shapes, its error compared to the microscopic reference increased to over 20 % with higher C-rates (see **Figure 65d**). Meanwhile, the error of the proposed approximation model was continuously lower than this.

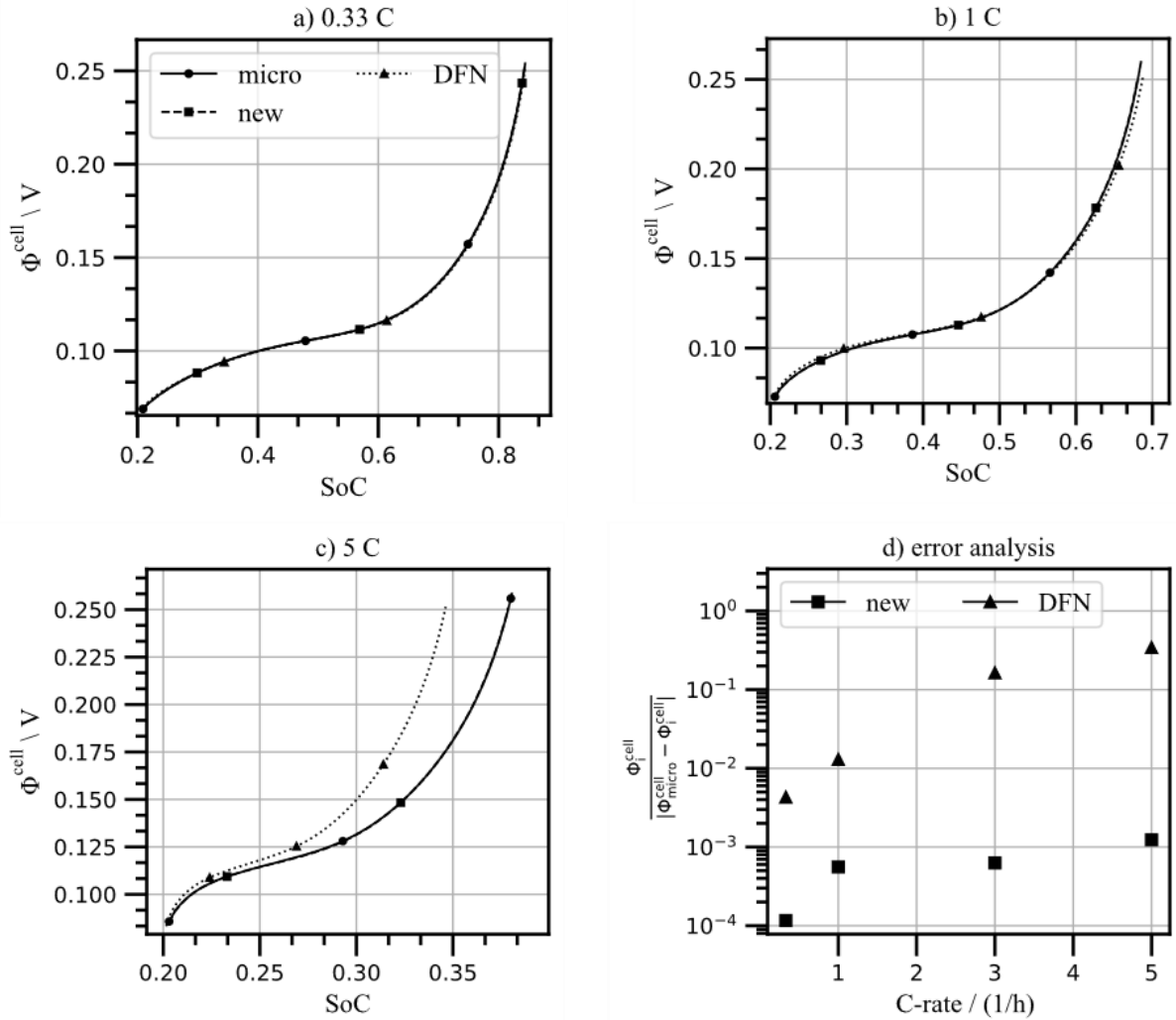


Figure 65. Comparison of the new approximation approach to the microscopic model and the DFN model after considering the non-spherical shape of the active material in the new approach. (a)-(c) Comparison of the predicted cell voltages over State of Charge (SoC) at different C-rates (0.33C, 1C, and 5C). The results of the microscopic model are displayed as a solid line with round markers, the new approximation model as a dashed line with square markers, and the DFN model as a dotted line with triangular markers. The markers are only used to distinguish the models and not to identify the data points. (d) Error at C-rates of 0.33 C, 1 C, 3 C, and 5 C.

Study 2: Considering the impact of the carbon-binder phase

The coverage by the carbon-binder phase leads to electrochemical inactivation of the interface, which results in differences in the concentration of lithium within the active material. To test the performance of the two macroscopic models for this microscopic phenomenon, we chose the

electrode geometry depicted in **Figure 66a** and **Figure 66b**. As in study 1, the half-cell was charged, and the Li-ions pulled out from the active material particles. **Figure 66c** shows that the concentration at the surface area, which is covered by the carbon-binder phase, was significantly higher because the Li-ions were unable to intercalate or de-intercalate from there.

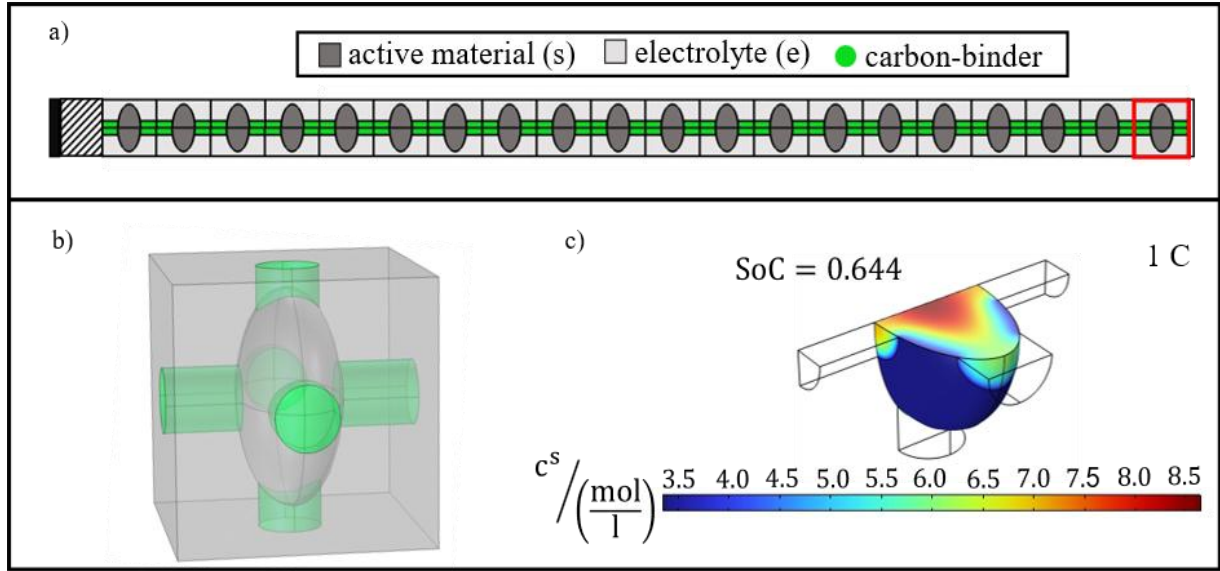


Figure 66. Electrode geometry chosen for considering the impact of the carbon-binder phase. (a) Simplified set-up of a lithium half-cell with active material covered by carbon-binder. (b) Unit cell of the electrode with ellipsoidal active material covered by cylindrical carbon-binder phase. (c) Microscopic concentration distribution within the active material at SoC=0.644 with 1 C.

As in study 1, we could determine the two diffusion layer parameters from the microscopic simulation at different charging rates. The active material ellipsoids covered by carbon-binder had a stationary diffusion layer thickness of $l^{\text{diff},\infty}=0.05525$. The decaying time function $\delta(\tau)$ is shown in **Figure 67**.

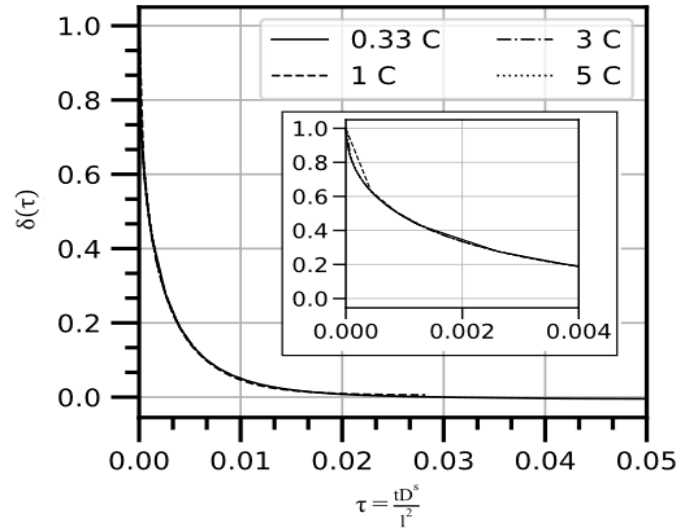


Figure 67. Calculation of the diffusion layer time constant in an electrode that takes the impact of the carbon-binder phase into consideration. Decaying time function $\delta(\tau)$ of the diffusion layer at different C-rates. The deviation of the time function of 0.33 C at the beginning is caused by larger time steps.

The calculation of the diffusion layer time constant is shown in **Figure 67**. Again, the diffusion layer variation depends only on the structural information that is given.

The comparison between microscopic simulation, DFN model and our model is shown in **Figure 68**. Due to limitations in the solid-state diffusion, the cell voltages increased faster at higher C-rates. The error between the macroscopic and the microscopic cell voltages grew with higher C-rates but remained small compared to the error measured in study 1. The error of the DFN model was low at 2 %, but the new approximation approach still had an overall higher predictive accuracy considering the computational cost of the DFN model.

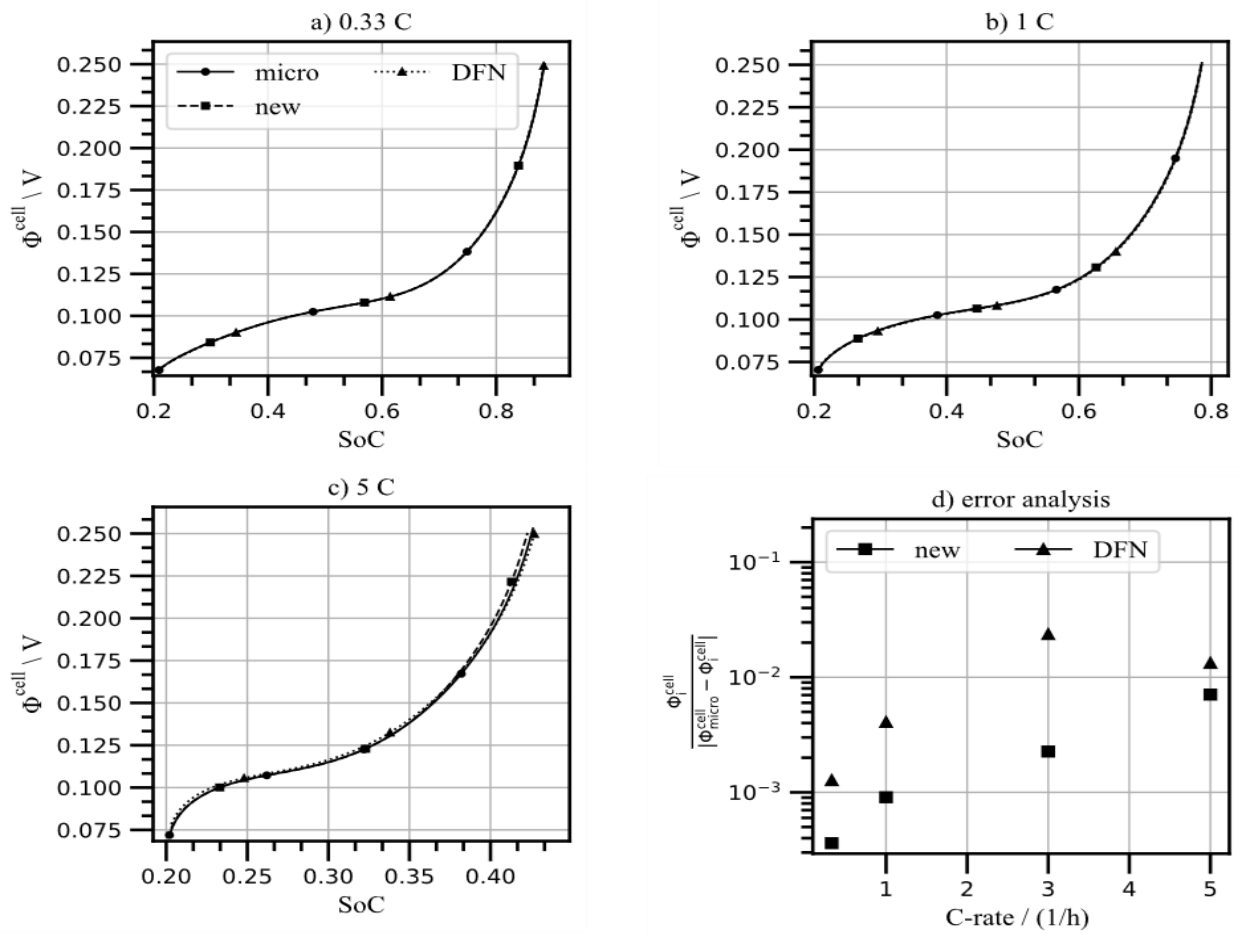


Figure 68. Comparison between the microscopic simulation, DFN model and the newly developed model after choosing an electrode geometry that takes the impact of the carbon binder phase into account in the new model. (a)-(c) Comparison of the predicted cell voltages over State of Charge (SoC) at different C-rates 0.33C, 1C and 5C. The results of the microscopic model are displayed as a solid line with round markers, the new approximation model as a dashed line with square markers and the DFN model as a dotted line with triangular markers. (d) Error at C-rates of 0.33 C, 1 C, 3 C and 5 C.

Study 3: Considering the overlap of non-spherical active material with different particle sizes

To generate an electrode geometry that takes the overlap of non-spherical active material into consideration, we placed 11 ellipsoids of different sizes and orientation at random positions within a cubic volume. The mirroring of the cube orthogonal to the current collector (depicted in **Figures 69a** and **69b**) ensures the periodicity of the generated unit cell and the half-cell.

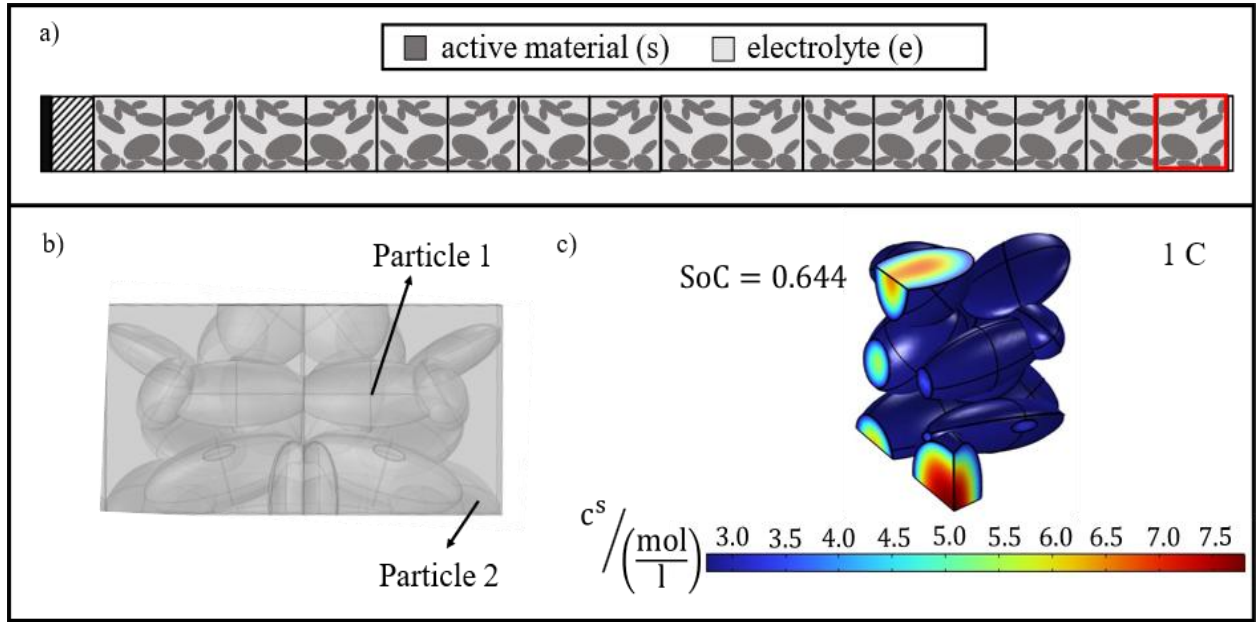


Figure 69. Simulation of active material with overlap in the new modeling approach. (a) Simplified set-up of a Li half-cell with active material covered by carbon-binder. (b) Unit cell of the electrode with ellipsoidal active material covered by cylindrical carbon-binder phase. (c) Microscopic concentration distribution within the active material at 1 C was SoC=0.644.

Microscopic simulations serve as reference for different charging scenarios. Since the ellipsoids have different overlaps and sizes, the concentration distribution c^s of each active material particle exhibits its own quasi-stationary deviation between the inner concentration and the surface concentration (see **Figure 69c**). The diffusion layer is checked on each particle. **Table 12** shows the $l^{\text{diff},\infty}$ and time constant.

Table 12. Stationary diffusion layer thickness, volume share and specific surface of each active material particle k within the unit cell when simulating active material overlap with the new model.

Particle Index k	$l_k^{\text{diff},\infty}/_1$	$\eta_k^s/_1$	$a_k^s/(\frac{1}{\text{m}})$
1	0.0514	0.0380	66718.0
2	0.0316	0.0291	95475.7
3	0.0306	0.0311	108085.3
4	0.0333	0.0453	134283.1
5	0.0363	0.0244	64776.2
6	0.0380	0.0436	119476.7
7	0.0469	0.0315	68786.4
8	0.0319	0.0272	83870.4
9	0.0466	0.0264	46962.6
10	0.0428	0.0464	108121.0
11	0.0492	0.0177	25653.9

Figure 70 presents the time functions of all eleven particles. As already mentioned in study 2, there is a clear trend: the higher the thickness of the stationary diffusion layer, the slower the decay rate of $\delta(\tau)$. Since particle 1 has the greatest diffusion layer thickness, the decay rate of its time function is significantly slower than for particle 2, which is smaller (see **Figure 70b**). Also, same as in study 1 and study 2, the diffusion layer time constant and the decay rate for single particles is independent of charging rates (**Figure 70b**). This means that the diffusion layer does not depend on battery operation and is purely structural information.

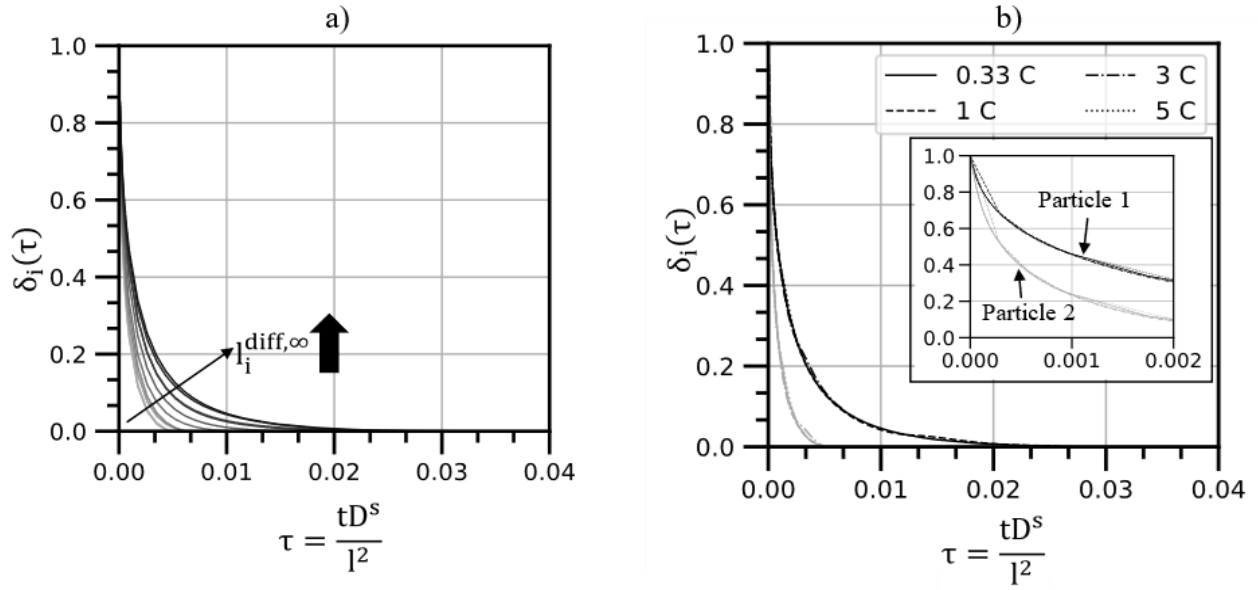


Figure 70. Calculation of the decaying time function in an electrode that takes overlap in the active material into consideration: (a) Decaying time function $\delta(\tau)$ of all eleven particles when charging with 0.33 C. (b) Decaying time function $\delta(\tau)$ of the diffusion layer at different C-rates. The deviation of the time function of 0.33 C at the beginning is caused by larger time steps.

We verify the performance of the proposed approximation by comparing it with the microscopic reference and the DFN model. The radius of the DFN model is fitted to the microscopic data at 0.33 C. The deviation between the microscopic and the macroscopic models increases with the C-rate. **Figure 71** shows the cell voltage calculation. High agreement is confirmed by the comparison of cell voltage predictions for different charging scenarios. The error of the DFN model increases to 2 % with higher C-rates, whereas the proposed approximation model continuously deviates by less than 1 %.

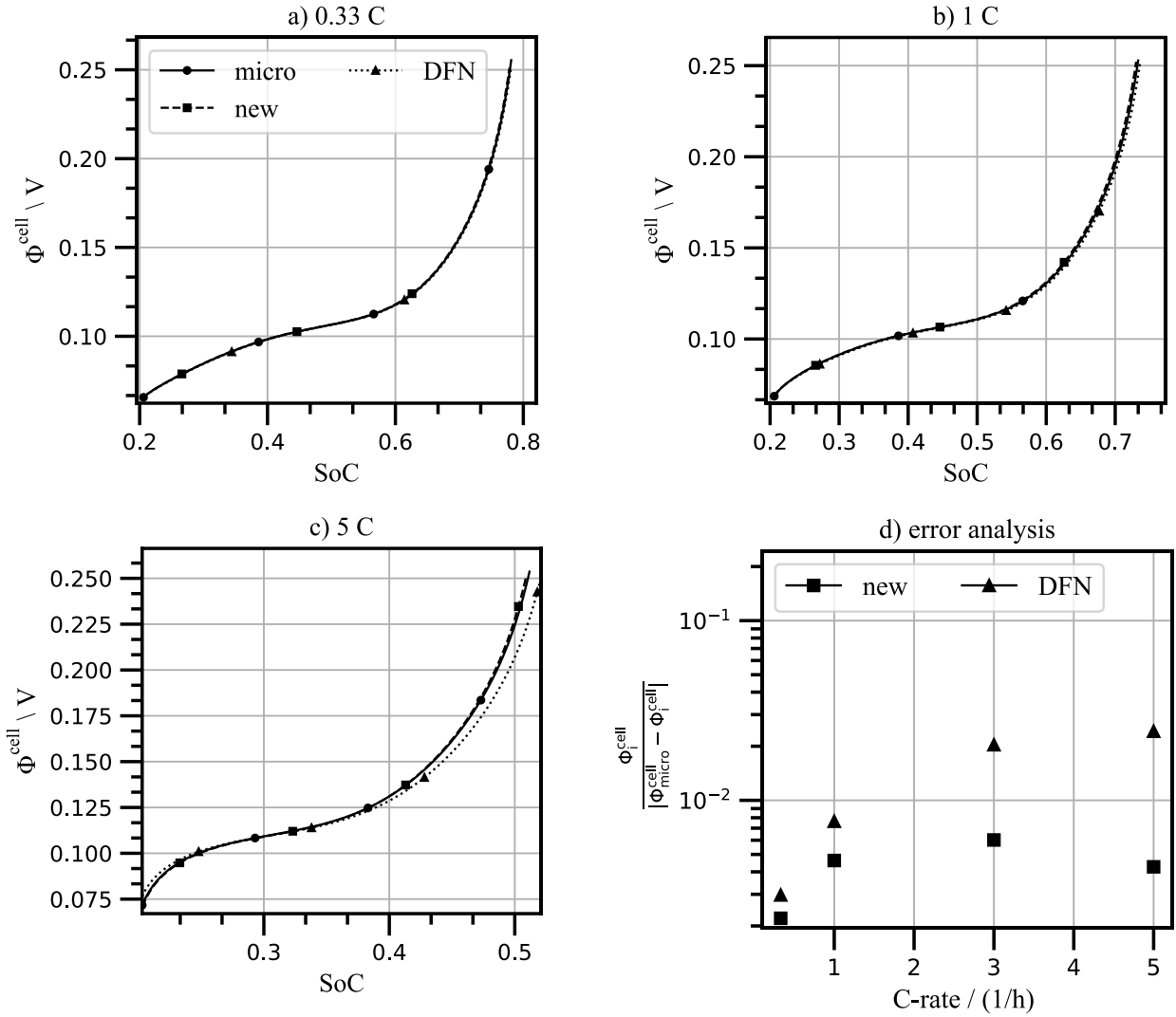


Figure 71. Comparison of the new approximation approach to the microscopic model and the DFN model after considering the overlap in the active material in the new approach. (a)-(c) Comparison of the predicted cell voltages over State of Charge (SoC) at C-rates of 0.33C, 1C and 5C. The results of the microscopic model are displayed as a solid line with round markers, the new approximation model as dashed lines with square markers, and the DFN model dotted lines with triangular markers. (d) Error at C-rates of 0.33 C, 1 C, 3 C, and 5 C.

Model parametrization

The 3 studies mentioned above show that the novel macroscopic model derived by FHM combined with diffusion layer theory is able to generate predictions with greater accuracy than the DFN model, since the active particle shape, particle size and conductive binder phase are considered.

To validate the results obtained by the modeling and assess how well it performs in a real-world scenario, an anode half-cell (film electrode) was used for a case study, an experimentally based parameterization was carried out (details see Chapter 3.2), structure information was obtained by 3D reconstruction, the electrolyte properties were characterized by PFG-NMR, OCV data and

solid-phase diffusivity of the AM particle was obtained by GITT, the electrical conductivity of the electrode was obtained by the Van der Pauw method, and the Butler-Volmer rate was calculated based on EIS. Specifically, a half-cell graphite anode with 70 μm AM thickness and 1.3 g/cm^3 AM density was utilized for a case study. Experimental data at various charging rates was then compared employing the microscopic model, the DFN model and our new model. **Table 13** shows the results of the model parametrization.

Table 13. Parametrization of the graphite half-cell based on experimental techniques.

Parameter	Unit	Value	Experimental technique
Electrode dimension	$(\mu\text{m})^3$	$70 \times 80 \times 80$	μ -CT
Volume fraction η^s	1	0.5452	μ -CT
Porosity η^e	1	0.3262	μ -CT
Theoretical capacity Q	Ah	$1.72769288 \cdot 10^{-7}$	GITT
Effective electronic conductivity $K^{s,\text{eff}}$	S/m	346	Van-der-Pauw method
Solid-phase diffusivity D^s	m^2/s	$5.62 \cdot 10^{-15}$	GITT
Electrolyte ionic conductivity K^e	S/m	1.29	PGSE-NMR
Electrolyte diffusivity D^e	m^2/s	$2.1 \cdot 10^{-10}$	PGSE-NMR
Electrolyte transference number t_+	1	0.4	PGSE-NMR
Electrochemical reaction rate k	$A \cdot \text{m}/\text{mol}$	$4.87 \cdot 10^{-4}$	EIS
Open-Circuit Potential of graphite vs Lithium U_0	V	Error! Reference source not found. a)	GITT
AM maximum Li concentration c_{max}^s	mol/m^3	26390	-
Electrolyte initial concentration c_{init}^e	mol/m^3	1000	-

The functional relationship between the OCV of graphite against Li and the State of Charge (SoC) is shown in **Appendix II**.

Model validation

The half-cell was cycled at 0.5C, 1C, and 2C charge rates for the case study. The microscopic model, the DFN model, and our new approximation approach were compared to experimental data. The error of the battery cell models against the experimental data was analyzed using the root mean square (RMSE) of the SoC for a given cell voltage.

$$\text{RMSE} = \sqrt{\sum_i \frac{(\text{SoC}_i - \text{SoC}_i^{\text{exp}})^2}{n}} \quad (36)$$

Figure 72 shows the result of the comparison. Here, exp refers to experimental data, 3D refers to the microscopic model, 1D+1D refers to the DFN model, and 1D refers to our model. With a maximum RMSE of about 5 %, we were able to observe a high agreement between the microscopic model and the experimental data. This is because of the high fidelity of the μ -CT reconstructed structure and the real parameters extracted from various experiments. The deviation at low SoC values can be attributed to the influence of the initial conditions. In the microscopic model c^e is a constant set at $\text{SoC} = 0.2$, whereas in the experiments there is already a stationary gradient.

One further reason for the deviation at both low and high SoC values is the electrochemical reaction rate k , which is a function of the SoC. In EIS measurements, the k value was quite low for low as well as high SoC values and optimal for moderate SoC values. In the microscopic model we used the measured value of k at $\text{SoC} = 0.5$, which is a relatively high value. Therefore, at lower and higher SoC values the measured interfacial overpotential was higher than the predicted overpotential. Another possible explanation is that the diffusivity and the ion conductivity of the electrolyte were concentration-dependent. During charging/discharging, a concentration gradient is established within the porous phase, which is why the local diffusivity and ionic conductivity deviate from the expected values.

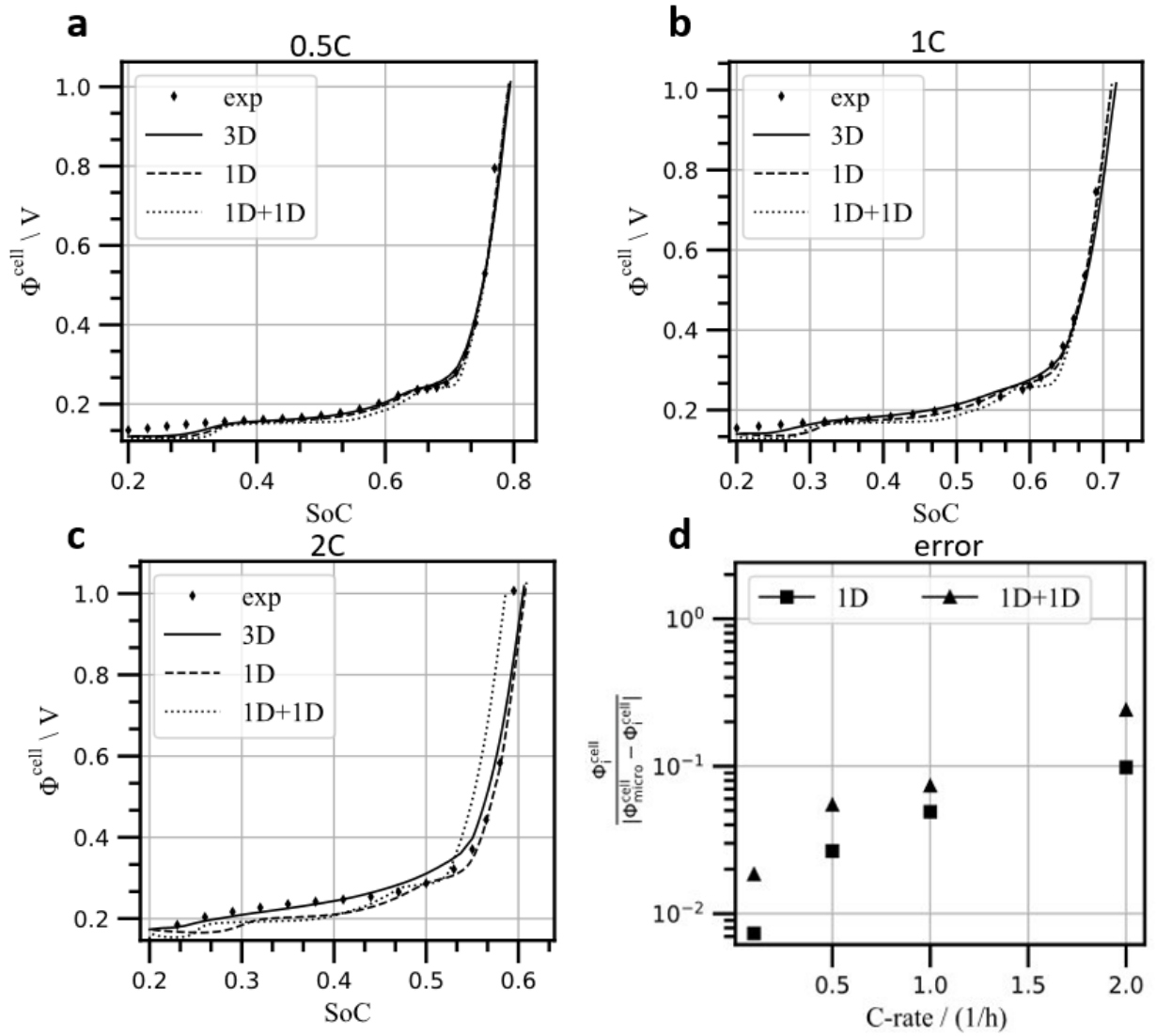


Figure 72. Comparison of microscopic simulation, DFN model simulation, and our model simulation to experimental data at different charging rates.

In the case of the DFN model the deviation between the measured voltage and the prediction grows with an increasing C-rate. As shown in **Figure 72**, this is due to the neglect of the conductive binder phase. At higher C rates a larger overpotential is needed to ‘push’ the ion through the porous electrode. However, DFN models underestimate the tortuosity because the conductive binder phase is not taken into consideration. In addition, the intercalation/deintercalation steps are ‘clearer’ in the DFN model. This is because in the DFN model all particles are identical, however, in a real-world scenario smaller particles will be charged first due to the smaller solid-phase diffusion resistance. Thus, every particle has a different SOC value and at the terminal voltage the intercalation steps will become ‘smoother’.

Our model takes the conductive binder phase, particle shape distribution, and size distribution into consideration. As shown in **Figure 72**, the voltage prediction is quite accurate, comparable to the

microscopic model, and really close to the experimental data. The deviation is less than 10 % regardless of the C rate, thus, making it more accurate than DFN modeling (**Figure 72d**). This can be attributed to two reasons: (i) our model offers an insight into the microstructure of the real electrode, which improves the fidelity of the simulation, especially for the graphite anode, and (ii) our model considers the solid-state diffusion in arbitrary particle geometry, which fills the missing piece of the DFN model.

Moreover, the spatially resolved parameters are also quite important when researchers try to design the electrode morphology assisted with a simulation model. As shown in **Figure 73**, our model is also good at predicting the in-situ ion concentration profile within the electrolyte and the lithiation/delithiation state at different points within the electrode. Here we choose the microscopic model as a reference (**Appendix II**) because of its high agreement with experiments.

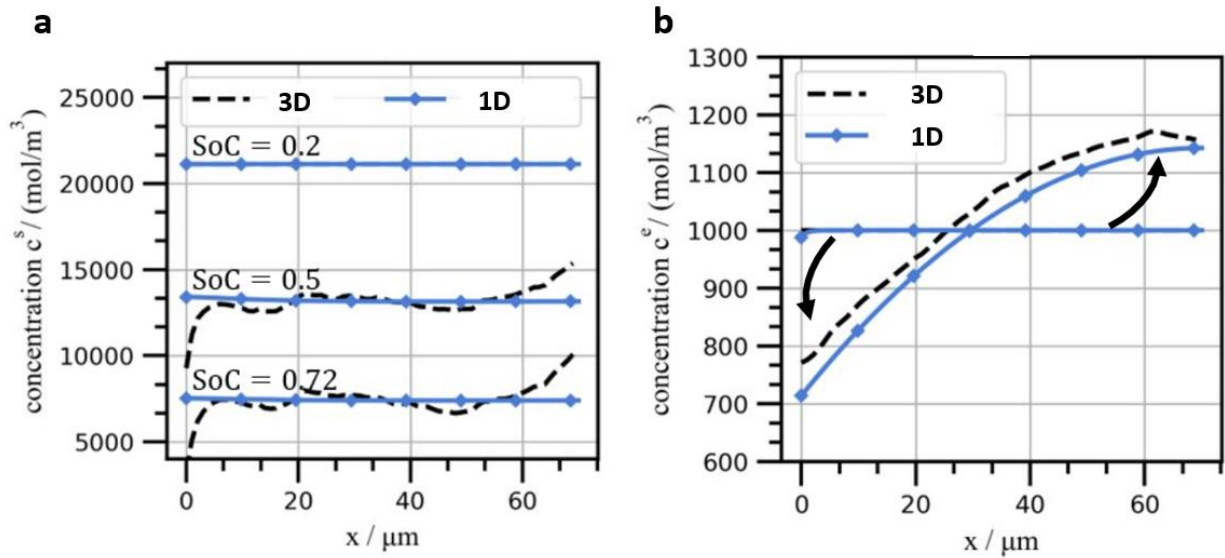


Figure 73. Spatially resolved concentration in the microscopic model (3D) compared to our model (1D). (a) Spatial distribution of c^s over different points in time. (b) Steady-state profile of c^e .

Figure 73a shows the spatial distribution of c^s over different points in time. Starting at the initial condition SOC=0.2, the lithium intercalates into the electrolyte during charging, causing the concentration c^s to decrease. The curves of the microscopic model (3D) deviate from the predictions of our model (1D) due to the heterogeneity of the electrode structure. The unit cell only considers the homogenized geometric properties and cannot cover the spatial variation of the geometry. Thus, on average, our model represents the microscopic model's spatially resolved data sufficiently well.

Maintaining a constant half-cell charge requires a certain mass flow from the cathode to the anode. Starting from the initial condition of SOC=0.2, the steady-state profile of c^e resulting from the

required mass flow is displayed in **Figure 73b**. Our model approximates the electrolyte concentration of the microscopic model data with sufficient accuracy. The deviation between the steady-state profiles of the two models is, again, due to the heterogeneity across the thickness of the electrode. This heterogeneity can only be represented by the unit cell. In conclusion, our model enables insight into the real morphology of electrodes and, thus, offers as accurate a prediction as the microscopic model but with far less computation power and effort.

The computation times of both models are compared in **Figure 74**. The computation time of the microscopic model is in the range of hours and is the lowest at 1C. The higher computation time at 0.5C is due to the higher integration time. At 2C the system is stiffer and the solver integrates with smaller time steps. For the newly derived model, the calculation time is in second-range, which is another main advantage of the 1D model.

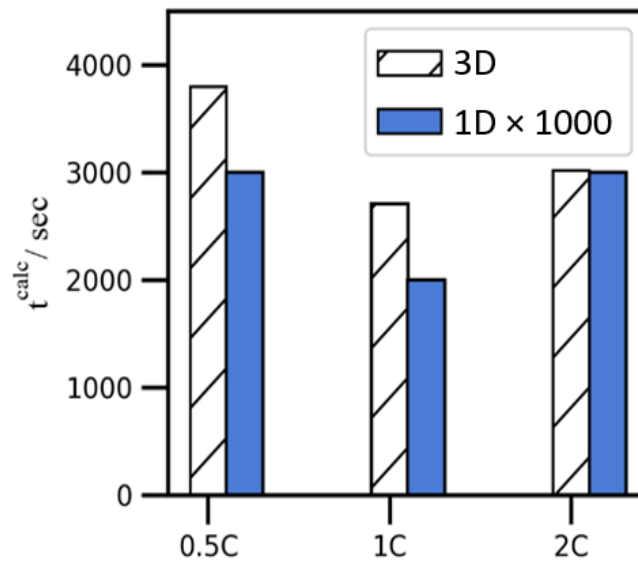


Figure 74. Comparison of the computation time between the microscopic model (3D) and the proposed new approach (1D).

The results show that the newly developed model is able to accurately and efficiently predict real foil electrode performance. Most importantly, the model has high flexibility compared to the DFN model, as it can take phases other than the AM and the electrolyte into consideration. This means that the model can also be validated for the fleece battery and integrate fiber conductivity and surface diffusion into the calculation. In future, the next step will be to focus on characterizing fleece electrode parameters and validating the model for fleece batteries.

V CONCLUSION AND OUTLOOK

The diffusivity of Li^+ ions in ultra-thick anodes with 3-dimensional copper fleeces is radically increased by the formation of an electrical double layer on the charged copper surface. The approximately 80-fold increase in diffusivity calculated for the bulk electrolyte compared to the charged copper surfaces only considers the increased mobility of the Li^+ ions due to the loss of the solvation shells. However, an even higher increase in mobility can be expected due to possible Li^+ ion gradients across the metallic fleece. A slight increase in the Li^+ ion concentration at one location within the metal fleece, e.g., at the separator, leads to an immediate equalization of Li^+ ion concentration gradients throughout the fleece. This is due to (i) the above-mentioned increased mobility of the bare Li^+ ions, (ii) the minimal interaction of the Li^+ ions with the copper, and (iii) the ultrafast relaxation of any polarization on charged metal surfaces. The latter is due to the high conductivity of the electrons at a constant Fermi level throughout the fleece, i.e., at an identical electric potential. Any gradient in the Fermi level of metals generates an equilibrium force that counteracts heterogeneously distributed Li^+ ion concentrations. Such effects are not to be expected with carbon-based fibers, because of the expected interaction of Li^+ ions with the carbon and the non-metallic electrical properties, resulting in the trapping of Li^+ ions along the carbon surface.

Moreover, this metal/electrolyte combination can be characterized as a super ionic conductor as well as a powerful electronic conductor. These features can be adapted to a wide range of applications, such as batteries, super capacitors, electrocatalysis systems, permeation membranes, and in this case lithium-ion batteries that show great potential in electrochemical tests and break previous limits of electrode thickness. We believe this study will spark a systematic study of the electrical double layer on metallic surfaces, especially the ultrafast migration of the electrical double layer along the charging surface. The EDL, one of the oldest and most fundamental concepts in electrochemistry, still lacks detailed understanding at the molecular level as it is spatially concealed between two bulk phases – the solid and the liquid phase. The existence of the liquid phase hinders the development of methods & techniques to study the dynamics of EDL formation, its microscopic structure, and its expansion along the interface. Here we implement an exquisite experimental set-up combining Raman spectroscopy with a microfluidic system to allow diffusion measurements with laminar co-flow for the study of interfacial diffusion mechanisms at liquid/solid interfaces.

In addition, we also developed a new mathematical model to depict the electrochemical properties of lithium-ion batteries. The motivation for building this model was to achieve high-fidelity

electron-ion transduction, consider a greater range of electrode reactions, and also decrease the computation time and effort. A particular focus was laid on the particle shape and size as well as the impact of the CBP on battery performance. The results show that the model can offer high fidelity simulations of the electrode structure, which significantly increases the simulation accuracy and reduces the time and effort necessary for full-scale microscopic simulations. Furthermore, this model offers high flexibility in that it is possible to simulate different types of batteries that, for example, contain pure silicon anodes with high amounts of CBP, graphene anodes with flake-shaped AM particles, or an electrode embedded with 3D CC, like our fleece electrode.

To further optimize this promising prototype with regards to fiber size and orientation, fleece porosity, and tortuosity a large systematic study using a physical-based digital twin will be required. Towards this end, our mathematical model can support fast predictions of fleece electrode behavior under different operational conditions.

It should also be mentioned that in this study I used a very preliminary electrolyte (1 m LiPF_6 in EC: DMC at a ratio of 50:50). Obviously, the property and composition of the electrolyte can significantly impact the formation and characteristics of the EDL, and, thus, greatly impact the fast surface diffusion mechanism that the fleece introduces. Therefore, an optimization of the electrolyte is also vital for fully developing this technique. The developed microfluidic experiment combined with MD simulations is a great tool and can be used to optimize the electrolyte composition towards making full use of the full potential of fleece electrodes.

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APPENDIX I

Cycling protocol (anode half-cell)

1 st to 5 th cycle	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.1C CC charge to 1.5V
6 th to 10 th cycle	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.1C CC charge to 1.5V
11 th to 15 th cycle	Discharge	0.2C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.2C CC charge to 1.5V
16 st to 20 th cycle	Discharge	0.5C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.5C CC charge to 1.5V
21 st to 25 th cycle	Discharge	1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	1C CC charge to 1.5V
26 st to 30 th cycle	Discharge	0.2C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.2C CC charge to 1.5V

GITT protocol

Lithiation process

1 st to 5 th cycle	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.1C CC charge to 1.5V
1 st to 100 th step	Discharge	0.05C CC discharge for 12 mins
	Rest	Rest for 2 hours

Delithiation process

1 st to 5 th cycle	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.1C CC charge to 1.5V
discharge 1 x	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
1 st to 100 th step	Charge	0.05C CC charge for 12 mins
	Rest	Rest for 2 hours

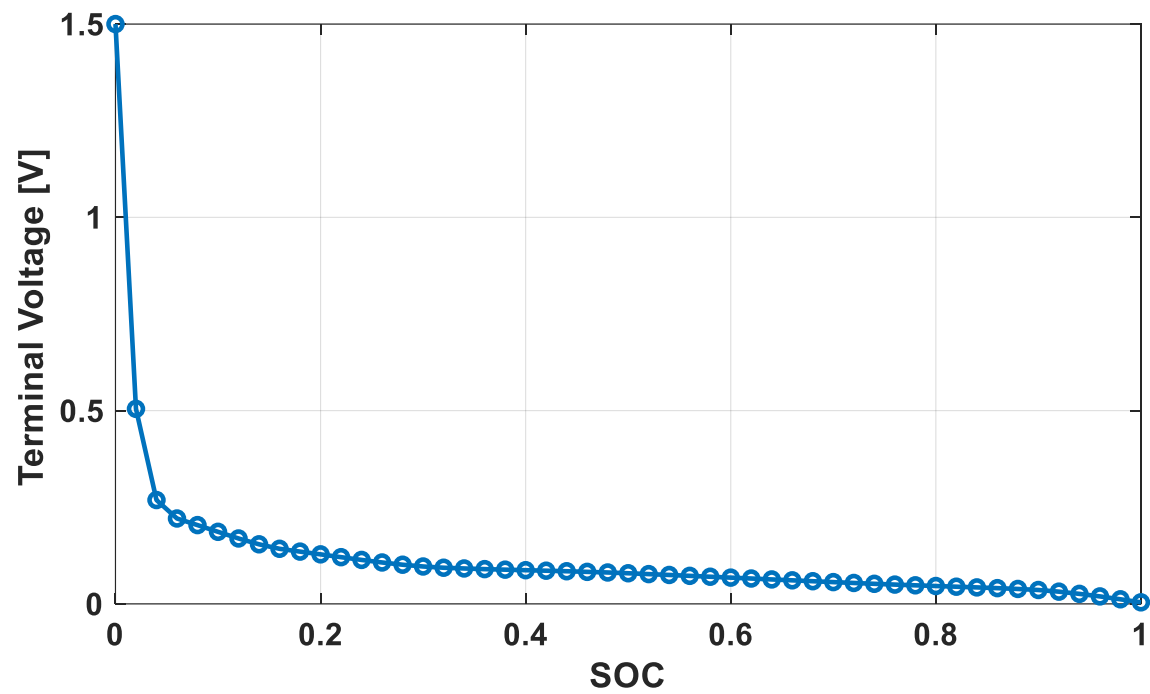
EIS protocol

1 st to 5 th cycle	Discharge	0.1C CC discharge to 12 mV; CV discharge until current reaches 0.05C
	Charge	0.1C CC charge to 1.5V
discharge 1 x	Discharge	0.1C CC discharge to 1.2V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.8V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.4V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.3V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.2V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.175V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.15V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.125V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.1V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.075V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	

discharge 1 x	Discharge	0.1C CC discharge to 0.05V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	
discharge 1 x	Discharge	0.1C CC discharge to 0.025V; CV discharge until current reaches 0.02C
Impedance measurement	5 mV amplitude, 1 MHz to 0.01 Hz 10 sampling points per decade	

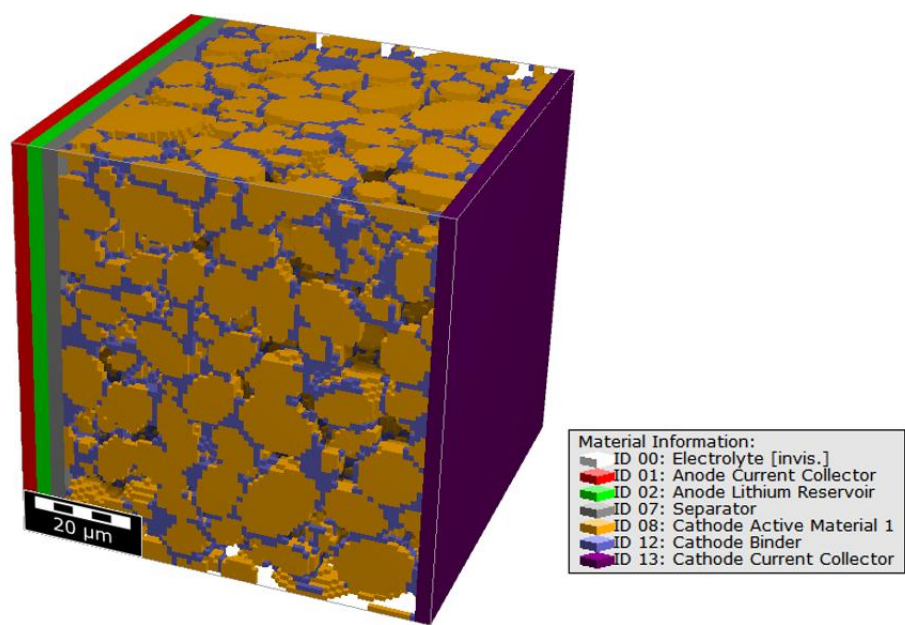
APPENDIX II

Graphite half-cell anode OCV curve



Spatially resolved concentration and potential data from microscopic simulation

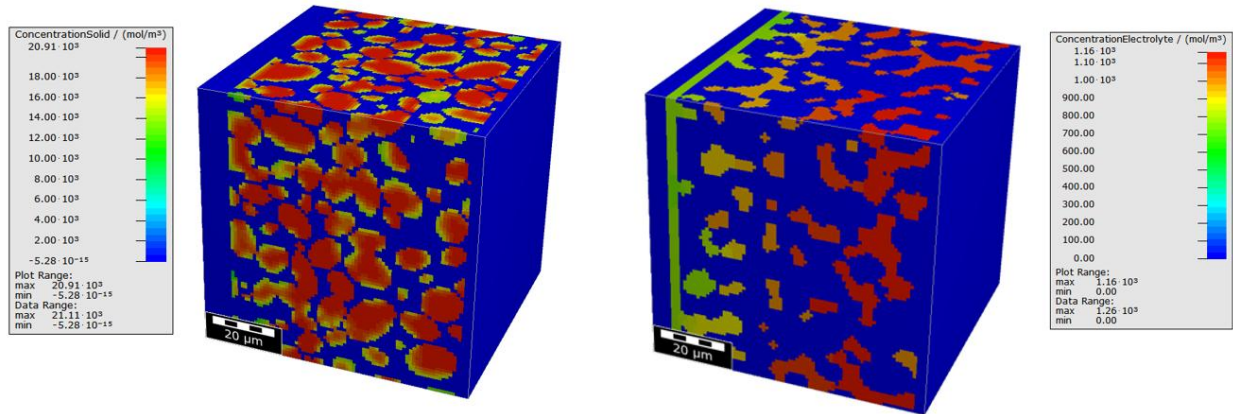
Structure Information



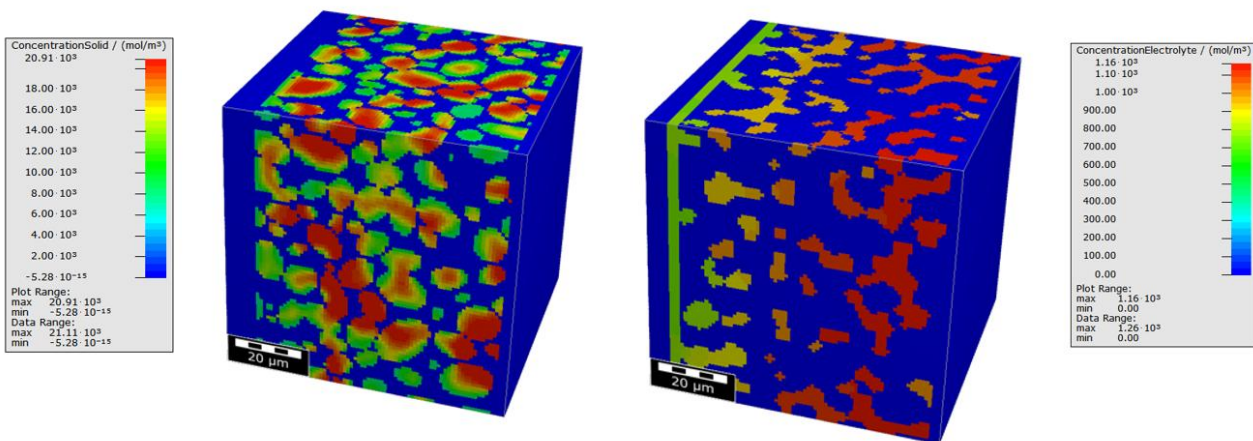
AM ion concentration

Electrolyte ion concentration

SOC = 0.3



SOC = 0.5



SOC = 0.7

