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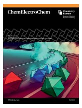
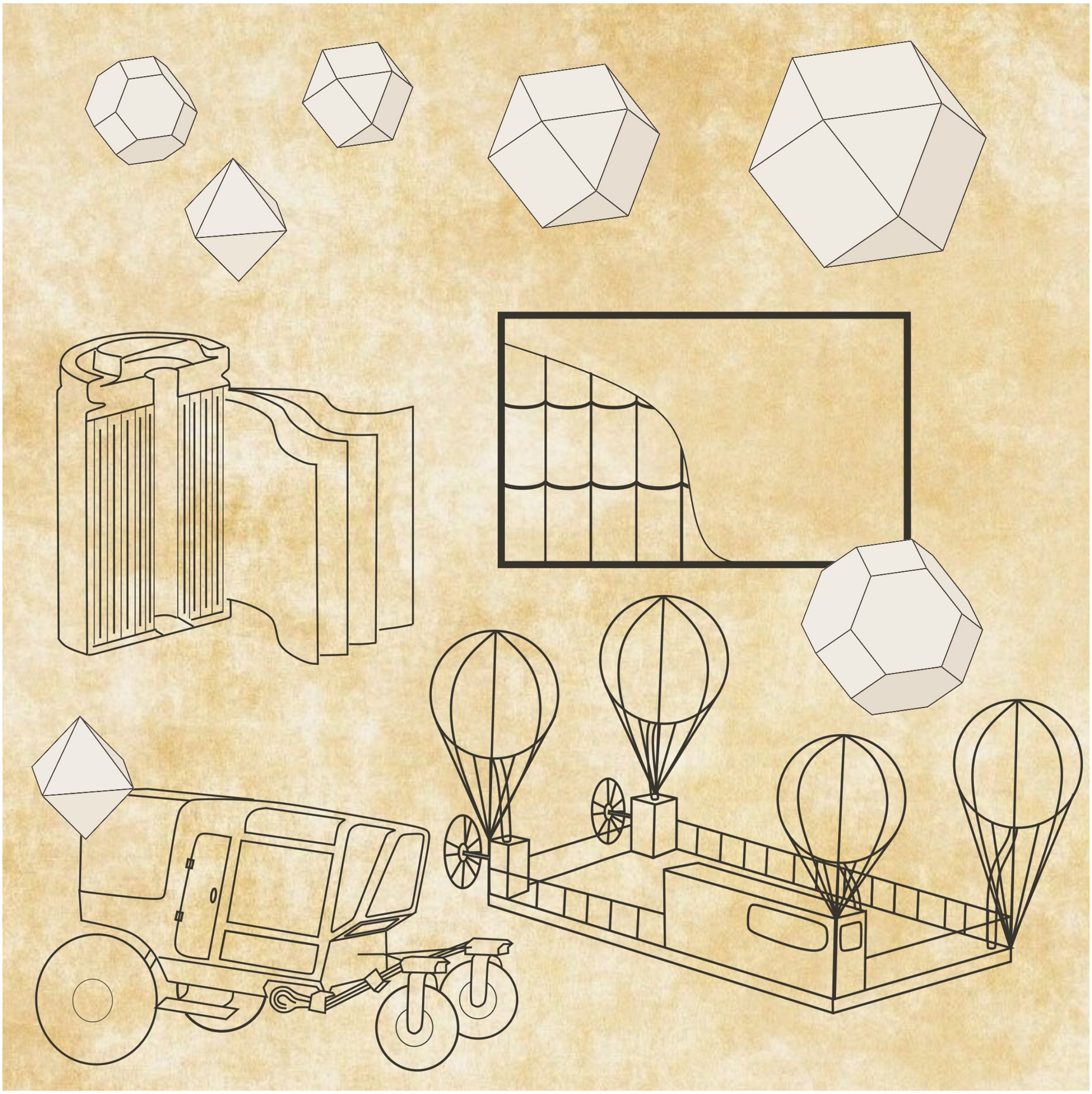


Single Crystal Layered Oxide Cathodes: The Relationship between Particle Size, Rate Capability, and Stability

Wessel van den Bergh,*[a] Leonhard Karger,[a] Saravanakumar Murugan,[a] Jürgen Janek,[a, c] Aleksandr Kondrakov,[a, b] and Torsten Brezesinski*[a]



With the increasing demand for safer, more stable, and energy dense batteries, investigations into single crystal layered oxide cathodes have gained momentum. However, translating considerations from polycrystalline to single-crystalline particles and their ensembles is not one-to-one. Lithium diffusion path length, surface, dopants and coatings, as well as the synthetic methods used take on different dimensions for single-crystalline particles. In this concept article, we review key considerations that must be made when developing well-performing single crystal layered oxide cathodes. We discuss how diffusion limitations can affect material stability in addition to how improvements to diffusivity can act as a method to simultaneously improve rate capability and surface stability. In addition, we briefly discuss how the unique feature of faceting and the synthetic design space for single-crystalline particles should be conceptualized.

1. Introduction

With the combined demands of climate change mitigation[1,2] and reduced cost in commercial applications,[3,4] Li-ion batteries are predicted to become ever more common in the future.[5] Yet, there remains a gap in regards to energy density and rate capability (charge time) that necessitates further improvement.[6] At the time of writing, the positive electrode remains as the most costly component of the battery, thus any improvements to cathodes will likely yield the greatest net improvement to battery application.[7,8] Layered metal oxide cathode materials have transitioned away from the original $LiCoO_2$ (LCO) composition first used in 1991[9] to greater fractions of Mn and Ni ($LiNi_xCo_yMn_zO_2$, referred to as NCM or NMC) for the sake of greater capacity and reduced cost. $LiNiO_2$ (LNO) represents one end of this progression with experimental observations approaching the theoretical specific capacity of 274 mAh/g.[10] However, there exists an inverse relationship between Ni content and the material's electrochemical,[11,12] mechanical[13,14] and thermal stability.[15] Each of these issues are barriers to application. Introduction of coatings and dopants to Ni-rich cathodes have mitigated these issues,[10,16] yet the mainstream battery, which pairs polycrystalline (PC) NCMs with liquid electrolyte, comes with degradation issues[17] and fire hazards[18] that require new battery designs to be adopted.

Single crystal (SC) layered metal oxides and their natural implementation into solid-state batteries present a way to mitigate the aforementioned concerns.[19–21] By one proposed definition,[22] SC morphology refers to the maximum agglomeration of 3–5 crystallites as opposed to the common PC microstructure, which has several dozen to hundreds primary particles (crystallites) agglomerated to form a large secondary particle. There exists an intermediate between these two descriptions, that of quasi single-crystalline materials. Whether quasi single-crystalline is a definition that contains its own unique benefits or an object of "definition creep" is to be determined by future work. Regardless, the SC morphology delivers a few unique benefits. Firstly, the intergranular cracking from repeated anisotropic volume change during cycling seen in especially Ni-rich PC designs is effectively eliminated and thus significantly reduces the rate of degradation from accelerated surface reactions and loss of electrical contact.[17,23,24] Secondly, SC materials have minimal porosity, which yields greater volumetric energy density and is better suited for solid electrolytes[19] that avoid the aforementioned fire hazard and could allow for Li metal anodes to be used.[25,26] However, SC cathode materials still are a relatively new concept. This is partially due to the on-going limitations of solid-state batteries as well as polycrystals being synthetically less complex, as will be discussed herein. Additionally, SC materials are limited to lower (dis)charge rates due to greater diffusion lengths, since they cannot undergo intergranular cracking during cycling as observed in PC materials.[27] Despite these challenges, the growing interest in SC's potential has led to an attempt to translate the knowledge gained from PC research.

The SC design is however distinct from PC and must be considered as such. We discuss how the transition from crystallites of a few hundred nanometers to multiple microns must contend with a square relationship between lithium diffusion path length and time for (de)lithiation. Furthermore, complex kinetics have a significant impact on material performance such as a loss of capacity due to poor/sluggish access to the crystallite core. The relationship between path length and relative surface area of crystallite grains is often neglected in PC cathode discussion, however, will become important for SC cathode design. The value of coatings and dopants and what they intend to modify must be reconsidered with these kinetics in consideration. With respect to particle morphology, SC can embody different crystal habits with facets whose stability/reactivity and Li-insertion capabilities vary and which can be controlled with proper synthetic conditions. Lastly, SC preparation is still in its infancy with varying methods that become much more dependent upon material composition and synthetic conditions to produce satisfactory cathode materials.

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[a] *Dr. W. van den Bergh, L. Karger, Dr. S. Murugan, Prof. J. Janek,*
Dr. A. Kondrakov, Dr. T. Brezesinski
Battery and Electrochemistry Laboratory (BELLA)
Institute of Nanotechnology
Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)
E-mail: wessel.saarberg@kit.edu
torsten.brezesinski@kit.edu
[b] *Dr. A. Kondrakov*
BASF SE
Carl-Bosch-Str. 38, 67056 Ludwigshafen (Germany)
[c] *Prof. J. Janek*
Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa)
Justus-Liebig-University Giessen
Heinrich-Buff-Ring 17, 35392 Giessen (Germany)

2. Discussion

While the simple relationship of grain size (path length) and lithium diffusion is commonly understood, discussion on the underlying implications of temporal limitations and material behavior is uncommon. The relation between path length and time required to diffuse this distance can be described in simple cases of homogeneous systems by the proportionality in Eqn. 1 based on a generalization of Fick's second law:[28–30]

$$x \propto \sqrt{Dt}, \tag{1}$$

where x is the diffusion length travelled, D is the diffusion coefficient and t is the time required to diffuse. With consideration of SC NCMs, outside of the nanoscale and into the microscale, the diffusion length will begin to significantly limit capacity at a given (dis)charge rate with respect to their PC counterparts.[31–33] While expanded forms of Eqn. 1 do include other factors such as concentration (lithium in bulk) and gradients, these are either difficult to tailor synthetically, are dynamic during operation, or both. Additionally, degree of lithiation does complicate the diffusion equations by varying diffusivity coefficients by orders of magnitude,[27] solubility limits should not vary significantly between SC and PC primary particle sizes[34] and for the sake of a simple model, D may be treated as an "average" D that is equal for both systems. This diffusion length issue is fortunately alleviated by the direct relationship of lithium diffusivity and Ni content in NCM stoichiometry.[35]

Aside from reduced rate capability, other issues can arise when diffusion length becomes sufficiently large and D is insufficient. For example, large (~2.4 μm) NCM particles have been observed to suffer from significant differences in lithium stoichiometry between the core and near-surface region during operation, causing first-cycle capacity loss.[36,37] This behavior has also been observed in $NaNiO_2$ (NNO), where local inhomogeneities lead to the (irreversible) formation of adverse phases and capacity fading.[38] Similar to this phenomenon is the possibility of intense concentration gradients within the particle that have been found to lead to elevated stress on and deviations in the interlayer spacing of single crystal $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111). These deviations act as a source of intragranular cracks to alleviate that imposed stress.[39] While not an issue that arises from path length, the distribution of path lengths that is experimentally observed to broaden with increased particle size[33,40] can be a cause of issues in relation to autocatalytic delithiation (see Figure 1).[41] For example, should the C-rate be sufficiently high, smaller particles could experience self-accelerated delithiation from increasing lithium diffusivity well before larger particles in the size distribution yet are exposed to coulometric conditions, which drives undesired states of charge and accelerated degradation;[42] however the nature of this phenomenon is subject to active study.[30,43]

Wessel van den Bergh is a post-doctoral researcher at the Battery and Electrochemistry Laboratory (BELLA) at the Karlsruhe Institute of Technology (KIT). His research interests are focused on the use of controlled design methodologies to study the relationship between material features and electrochemical behavior for energy-storage applications.

Leonhard Karger studied Chemistry at Heidelberg University (graduated in 2020). He is currently working at BELLA (KIT) as a PhD student under the supervision of Prof. Janek. His research focuses on the synthesis and characterization of cathode active materials with tailored substitutional defects.

Saravanakumar Murugan earned his PhD in Chemistry from the University of Stuttgart in 2022. As a post-doctoral researcher at BELLA (KIT), he currently concentrates on the synthesis and characterization of Co-free, Ni-rich cathode active materials for solid-state batteries. His research also delves into investigating the effect of particle morphology and analyzing the gassing behavior.

Jürgen Janek holds a chair for physical chemistry at Justus-Liebig-University Giessen and is a scientific director of BELLA (KIT). He received his doctoral degree in Physical Chemistry and was a visiting professor at Seoul National University, Tohoku University and Université d'Aix-Marseille. His research spans a wide range from transport studies in mixed conductors to in-situ studies in electrochemical cells. Current key interests include solid-state batteries, solid electrolytes and kinetics at interfaces.

Aleksandr Kondrakov obtained his diploma in Chemistry from Lomonosov Moscow State University (2010) and a PhD in Chemistry from KIT (2014). After postdoctoral years spent at BELLA (KIT), he joined BASF Battery Materials in 2017 working on the development of high-Ni cathode active materials. As the lab team leader of BELLA, he focuses on the research of next-generation battery materials.

Torsten Brezesinski is a chemist by training, earning his doctorate in Physical Chemistry from the MPI of Colloids and Interfaces/University of Potsdam in 2005. He is laboratory manager of BELLA and group leader at the Institute of Nanotechnology (KIT). His work encompasses the characterization of next-generation battery materials for electrochemical energy storage and the design of advanced mesoporous metal oxides.

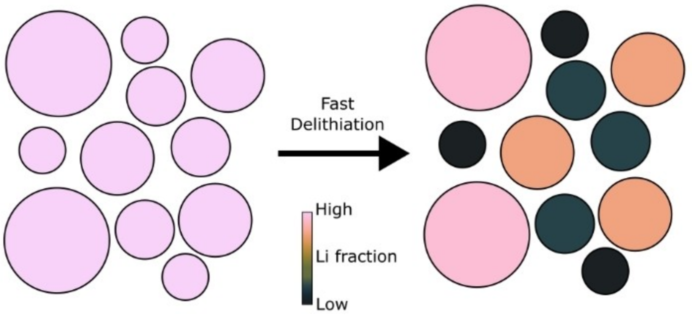

Figure 1. A representation of the deviation in x(Li) in NCM based on particle size for a fast delithiation (charge) process. This deviation can lead to loss of capacity and accelerate degradation of material.

Simple solutions do present themselves based on Eqn. 1: firstly, reducing grain size (path length) and, secondly, increasing diffusivity by including specific dopants. Reduction of path length is the most direct method of enhancing the rate capability of SC materials; however with a reduction in particle size comes an increased ratio of surface area to volume in the following relationship for spherical particles:[44,45]

$$\frac{A_s}{\rho V} \propto \frac{1}{\rho x} \propto a_s, \tag{2}$$

where A_s is the surface area of the particle of x radius (path length), V is the particle volume, ρ is the material density and a_s is the surface area per unit mass (specific surface area). This relationship between path length and surface area suggests reducing size past a critical threshold dramatically increases the relative surface area. While this does increase the number of surface insertion sites, this is not a valuable feature for a bulk-diffusion limited material. Rather increased surface area can lead to greater surface-based side reactions including consumption of electrolyte[11] and microcrack formation,[46] elevated oxygen release[47] and transition-metal (Ni, Co, Mn) dissolution,[48] thereby reducing material cycle lifetime and rate capability. With this in mind, one should prepare a SC material with the maximum size that still can achieve complete lithium exchange at the desired rates. To foster a greater maximum SC size, diffusivity must be increased, as it becomes an important two-pronged tool to combat the inverse relationship between particle size and surface area reduction.

Inclusion of coatings and dopants remains a subject of intense research that can be used to stabilize both surface reactivity and enhance observed diffusivity for SC materials. Bulk dopants are the more direct method of enhancing diffusivity, however there is an unavoidable energy density cost for stability with LNO standing as the natural apex of specific capacity for NCMs using mainstream operation conditions. Therefore, selecting for dopants that maximally increase diffusivity per species introduced is ideal. This is not a simple task. For example, dopants (Mg,[49,50] Ga[51]) that are known to rest in the lithium site can positively affect diffusivity by acting as a "pillar" to increase/stabilize interlayer spacing but will also act as a barrier in the lithium diffusion path. Coatings remain important to SC materials. Firstly, one must consider that coatings have been experimentally observed to increase apparent diffusion coefficients despite being a surface modification. This can be attributed to a decrease in fraction of disordered (NiO-type) rock salt and cathode electrode interphase (CEI) formation at the electrode/electrolyte interface,[52] which have orders of magnitude lower diffusivity than bulk active material.[53,54] Secondly, this contribution does not diminish with reduced relative surface area and rather requires less "inactive" coating to be used to achieve the same effect. In the case of solid-state batteries, where single crystals are best applied, coatings are common.[55–57] Regardless, increasing diffusivity so that longer path lengths are permitted to be used provides the additional benefit of reducing the relative surface area, thus reducing the rate of surface-based degradation. This represents an intersectional dynamic between Eqn. 1 and Eqn. 2 shown in Figure 2. Introduction of coatings can allow for a greater tolerance for surface side reactions and thus allow for

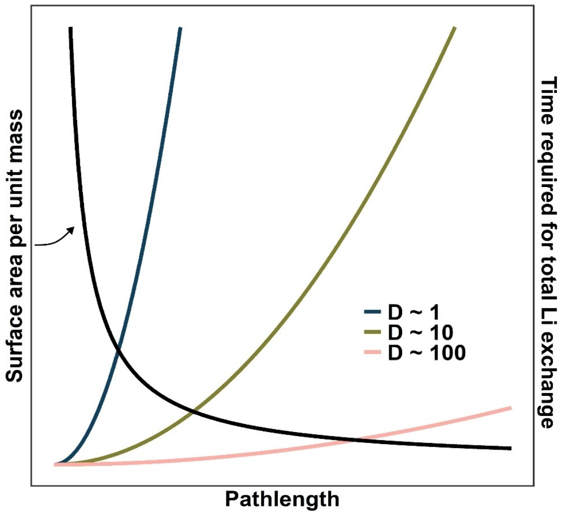

Figure 2. A representation of Eqn. 2, which is the dependence of specific surface area with respect to path length (particle size) shown by the black curve, as well as the representation of the relationship between x and t (time required for lithium exchange) in Eqn. 1 with differing D showing the quadratic time cost can be suppressed with greater diffusivity. Particles of greater diffusivity can meet the same time requirement with greater path lengths (size) and thus reduced specific surface area.

smaller particles with sufficient cycling stability, while enhancements to diffusivity allow for larger particles to be implemented and reduce surface side reactions. Designing a particle with sufficient diffusivity just past the "knee" of the surface area per unit mass curve represents a likely happy medium to target.

Synthesis of SC particles is still in its infancy, as simple adjustments without convolution of critical parameters have yet to be achieved. While discussed briefly here, modern SC synthesis and its theoretical considerations for NCMs is well described in a review by Langdon and Manthiram.[22] The ultimate ambition of SC synthesis is the ability to independently modify features such as size, faceting and additives. This will likely remain a significant challenge for the foreseeable future, as something simple such as targeting the same particle size with different dopants would require different synthetic conditions to compensate for changes in crystallization kinetics with inclusion of said dopants. In addition, something such as size distribution, which is observed to broaden with greater particle size,[33,40] can lead to aforementioned complications in material performance. In general, there exists three popular methods for SC preparation:

High-temperature synthesis accelerates solid-state reaction kinetics and drives SC formation.[58] We believe that this method, while simple, will not allow for the desired control, since only size is meaningfully changed with this approach. Additionally, high-temperature synthesis suffers from significant agglomeration issues, requiring milling and/or grinding to convert quasi single-crystalline material to a true SC character.[59] Such solutions compound the issues of $Ni_{Li}^{\bullet}$ defects (Li off-stoichiometry) that arise at high temperatures.[60,61]

Second is multistep synthesis and is the approach that is most sparse for study, likely due to the requirement of multiple calcination steps. However, it may provide a method with which size can be tailored independently of additives and facets, as SC motifs could be first formed before the other features can be targeted in subsequent steps.

Molten salt synthesis presents possibly the most compelling route with proper improvements to methodology.[40] In short, introduction of molten salts, either active lithium sources or inactive spectator ions, acts to accelerate crystallite growth through Ostwald ripening. This method has the potential to yield large SC particles at relatively low temperatures, thus forgoing the convolution of particle size and $Ni_{Li}^{\bullet}$ defects caused by high-temperature synthesis. Molten salt synthesis has allowed for tailored design of the crystal habit (faceting), which is a unique SC feature. Faceted single crystals can be prepared with the proper selection of salts, salt-to-metal ratios and calcination temperature.[62–65] Different facets represent different crystallographic indices, which in turn have different (electro)chemical stabilities/reactivities with respect to electrolyte (see Figure 3).[66,67] In addition, these facets can either be lithium permeable or blocking. Designing a particle must consider both, the effort to maximize the lithium permeable facets but select for those that have low reactivity. This subject should be explored further experimentally and theoretically. However, molten salt synthesis does come with its own issues, as washing/annealing post-processing must be done to attain well-performing NCM. Regardless, efforts should be focused on syntheses that can allow for independent tailoring of different features of the SC material; isolation and quantification of effects from specific features is the best methodology to improving SC NCMs as a whole.

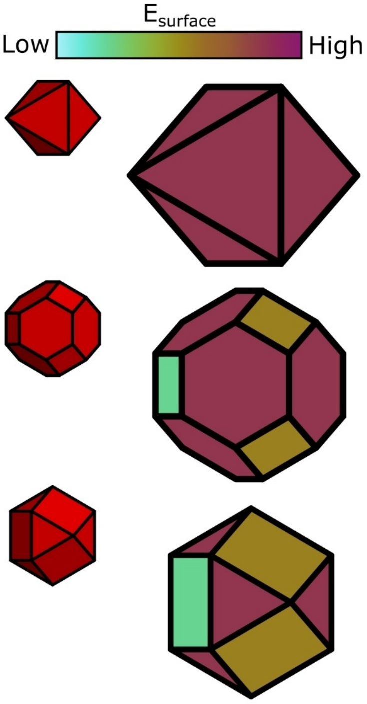

Figure 3. Shaded representations of different, common crystal habits for NCM cathode materials (shown in red). Each shaded representation has a conceptual representation of the relative reactivity with electrolyte of different crystallographic facets. Maximizing lithium permeable facets with the minimum reactivity should be the synthetic objective of SC faceting.

3. Conclusions

Increasing pressure for safer, longer-lasting batteries is driving the development of single crystal (SC) layered oxide cathodes. This development however must acknowledge SC materials as distinct from their polycrystalline (PC) counterparts, since SC grains are significantly larger in size than the primary particles of PC materials. This size difference introduces an inability for sufficient lithium diffusion and leads to capacity loss and unique degradation mechanisms. Therefore, there is a greater need to consider the relationship between size, diffusivity and rate capability for SC materials. This can be done by reducing particle size or with the implementation of dopants and coatings. However, one must acknowledge the cost of increasing rate of surface side reactions and reduction of particle size that cannot be modified. Rather the use of dopants to increase diffusivity allows for greater particle sizes and in turn a reduction in relative surface area. Furthermore, coatings can play a more powerful role in SC materials, especially when properly combined with faceting to maximize "insertion active" surface area. Lastly, SC synthesis is still underexplored and should use these considerations as a navigation aid for designing better materials.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Cathode morphology · Diffusivity · Faceting · Lithium-ion battery · Solid-state battery

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