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High-entropy and compositionally complex battery materials

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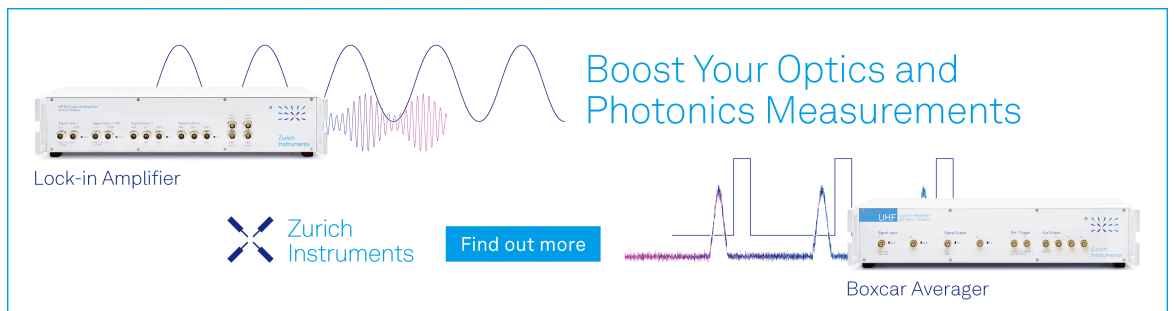
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F. Strauss  ; M. Botros  ; B. Breitung   ; T. Brezesinski 

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High-entropy and compositionally complex battery materials

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F. Strauss,^{a)}  M. Botros,^{b)}  B. Breitung,^{c)}  and T. Brezesinski^{d)} 

AFFILIATIONS

Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, Karlsruhe 76131, Germany

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^{a)}florian.strauss@kit.edu

^{b)}miriam.botros@kit.edu

^{c)} **Author to whom correspondence should be addressed:** ben.breitung@kit.edu

^{d)}torsten.brezesinski@kit.edu

ABSTRACT

The global demand for high energy density batteries, mostly for application in electric vehicles, offering increased durability, safety, and sustainability is growing rapidly. In the past, this demand has been met primarily by the development and/or improvement of new/established battery materials and technologies. The high-entropy design concept—aiming at increasing chemical complexity/occupational disorder—has recently been introduced into the field of electrochemical energy storage. Various high-entropy battery materials that are seemingly capable of outperforming low-entropy counterparts by offering desirable properties have been reported. However, future studies are required to explore if the concept is broadly applicable and can be extended to all types of battery materials, especially those that are of industrial relevance. Herein, we provide a brief overview of the existing high-entropy anodes, cathodes, and solid/liquid electrolytes for use in rechargeable Li- or Na-ion batteries and discuss potential research directions and opportunities.

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I. INTRODUCTION

The increasing demand for energy-dense (secondary) batteries is strongly pushing the development of new active and inactive electrode materials with improved physical and (electro)chemical properties. Over the last few decades, this development, which is at the heart of materials science, has led to continuous improvements in the cycling performance and stability of especially Li-ion batteries (LIBs), but the more sustainable and cost-effective Na-ion batteries (NIBs or SIBs) are also slowly gaining ground on the market. However, driven by the automotive and portable electronics sectors, commercial applications call for more advanced battery materials/technologies.¹ This can be realized either by modifying existing materials or by introducing new design concepts and principles. Regarding the latter, the high-entropy concept, initially demonstrated for multicomponent alloys (high-entropy alloys, referred to as HEAs), has recently been successfully applied to various

classes of materials, including ceramic and ionic materials. In general, high-entropy materials (referred to as HEMs) contain five or more constituents (elements) on a specific crystallographic site in a given crystal structure. According to definition, they are characterized by having a configurational entropy of $\Delta S_{\text{conf}} > 1.5R$, with R being the ideal gas constant. The introduction of multiple elements into different host structures opens the possibility of achieving unprecedented properties due to unique interactions between the constituents (cocktail effect), large lattice distortions, and/or stabilization of metastable phases (via the entropy contribution to the Gibbs free energy of formation).^{2,3} Originally, only HEAs (i.e., multicomponent metallic solid solutions) were studied, but in recent years, oxide, sulfide, carbide, and other HEMs have been demonstrated to be synthetically accessible. This suggests that a variety of crystal structures are in principle capable of accommodating compositional/occupational disorder. Interestingly, the concept has been quickly adopted by the battery community, and

17 April 2024 12:36:42

indeed some high-entropy anodes, cathodes, and electrolytes have already been explored.⁴ As examples of the beneficial effects that the high-entropy concept can bring to the realm of electrode materials,⁵ among others, increased capacity retention (due to stabilized crystal structures, complex interactions of elements during the redox reactions, etc.),^{6,7} reduced stress/strain accumulation (lowering the susceptibility for particle fracture, rendering more robust interfaces and interphase, etc.),⁸ and mitigated Jahn–Teller distortion⁹ have been reported. However, clear association between the improvements and the level of disorder (configurational entropy) is lacking.

In the following, we provide insights into the state of the art and perspectives on future research into HEMs for electrochemical energy storage.

II. DISCUSSION

A. Anode

The first report on high-entropy oxides (referred to as HEOs) as anodes for LIBs dates back to 2018, where the authors demonstrated that rock salt $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ can reversibly react with lithium through a conversion reaction forming Li_2O and the respective metals (except for Mg).¹⁰ Compared to related medium-entropy ($1.0R < \Delta S_{\text{conf}} < 1.5R$) and low-entropy materials ($\Delta S_{\text{conf}} < 1.0R$), the reversible electrochemical reaction of $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ with lithium allowed for long-term cycling, probably due in part to the formation of a stabilizing matrix during battery operation (Fig. 1). Shortly thereafter, various studies have reported on the Li-storage properties of similar HEO-based negative electrodes. Aside from rock salt materials, HEOs with other structure types have also been tested electrochemically, including transition-metal oxide spinels, such as $(\text{Fe},\text{Co},\text{Ni},\text{Cr},\text{Mn})_3\text{O}_4$ and $(\text{Cr},\text{Mn},\text{Fe},\text{Ni},\text{Cu})_3\text{O}_4$.^{11,12} In general, the relatively stable cycling performance of these conversion anodes is assigned

to the fact that the parent lattice is retained to some degree during cycling.⁶ Since few HEOs have been tested specifically for anode applications up until now, the impact of the initial structure and composition on redox activity and cyclability is still largely unclear.

A similar stabilizing effect on performance has been reported for non-oxide HEMs, namely, metal fluorides serving as LIB conversion cathodes.¹³ Yet, whether or not a high ΔS_{conf} helps overcome some of the major problems and limitations of conventional conversion anodes (large voltage hysteresis, low first-cycle Coulomb efficiency, etc.) remains to be seen.

B. Cathode

Layered metal oxides are extensively studied as high-capacity cathode active materials for both LIBs and SIBs. In the case of LIBs, much focus has been placed on alternative oxides to LiCoO_2 , especially for application in the automotive industry, the reason being that the production of batteries using LiCoO_2 comes at high environmental, ethical, and economic costs. This has led to the development of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (referred to as NCM or NMC) cathode active materials, with Ni-rich versions recognized as being state of the art in the field of high-density electrochemical energy storage.¹⁴ Surprisingly, only few examples have been reported for high-entropy NCM-type materials, such as $\text{Li}_{0.8}\text{Na}_{0.2}(\text{Ni},\text{Co},\text{Mn},\text{Al},\text{Fe})\text{O}_2$,¹⁵ the reason for which is unclear but may simply be due to limited stability. This is in contrast to layered metal oxide SIB cathodes, which have been produced with various compositions of different elements,^{16–18} indicating that they can more readily accommodate occupational disorder/compositional complexity. It has been hypothesized that this relates to the fact that layered sodium compounds can be synthesized from a wide variety of 3d transition metals, whereas the corresponding lithium-based cathode active materials are more or less limited to combinations of cobalt, nickel, and manganese.^{19,20} Regardless, introducing a high configurational entropy into layered metal oxides has been

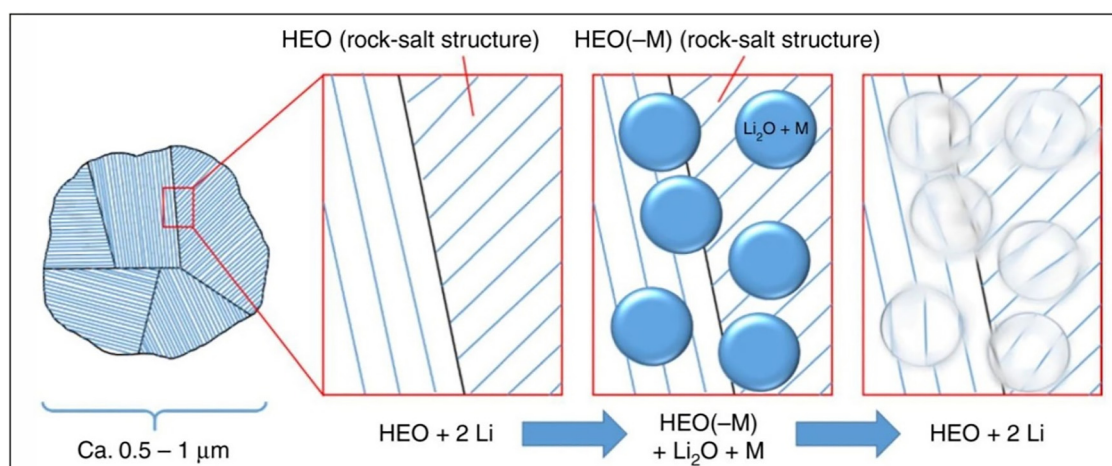


FIG. 1. Schematic of the proposed de-lithiation mechanism for the conversion reaction of rock salt $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$. Reproduced with permission from Sarkar *et al.*, Nat. Commun. **9**, 3400 (2018). Copyright 2018 Author(s), licensed under a Creative Commons Attribution (CC BY) license.

17 April 2024 12:36:42

shown to increase structural stability during battery operation, and apparently, it also helps mitigate transition-metal dissolution from the cathode. In addition to layered HEOs, some redox-active rock salt and cation-disordered rock salt (DRX) cathode active materials have been reported [Fig. 2(a)].^{21,22} In one of these studies, high electrochemical activity (improved capacity and rate performance) was found for $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Cr}_{0.1}\text{Ti}_{0.1}\text{Nb}_{0.2}\text{O}_{1.7}\text{F}_{0.3}$, which the authors attributed to facilitated lithium transport due to reduction in short-range order. High-entropy polyanionic phosphates [e.g., $\text{Na}_{3.4}\text{Fe}_{0.4}\text{Mn}_{0.4}\text{V}_{0.4}\text{Cr}_{0.4}\text{Ti}_{0.4}(\text{PO}_4)_3$] crystallizing in the so-called NASICON (NA SuperIonic CONductor) structure type have also been reported lately [Fig. 2(b)].^{23,24}

With regard to layered HEO cathodes, enhanced cyclability was explained by entropy-mediated increased structural integrity during sodium insertion and extraction (less severe volume change, etc.). Structural stabilization has also been demonstrated for metal-organic frameworks (MOFs) or, more specifically, for Prussian blue analog (PBA) and Prussian white cathodes.^{25,26} Comparing high-, medium-, and low-entropy manganese-based hexacyanoferrates, both studies confirmed that there is a correlation between configurational entropy and cycling performance.

Though various high-entropy and compositionally complex cathode active materials have been reported over the last five years or so, for the more mature ones, no major improvements in energy and/or power density, compared to batteries using the respective base materials, could be achieved. Nevertheless, compositional disorder may help suppress detrimental phase transitions during cycling, which ultimately positively affects stability and improves kinetics (ion mobility). Yet, similar effects can likely also be achieved by “simple” iso- and/or aliovalent doping.

C. Electrolyte

Due to the renaissance of solid-state batteries as potential next-generation energy-storage devices, the exploration of superionic solid electrolytes is gaining increasing momentum. Currently, configurational entropy is being examined as a means to tailor ion dynamics and (electro)chemical stability. Frankly speaking, increasing occupational disorder in the anion and/or cation sublattice(s) of the host structure can be seen as a transition from the common single or dual substitution to multielement substitution. However, only a few high-entropy solid electrolytes adopting different crystal structures, such rock salt [e.g., $(\text{Mg},\text{Co},\text{Ni},\text{Cu},\text{Zn})_{1-x}\text{Li}_x\text{O}$],²⁷ garnet [e.g., $\text{Li}_3(\text{La},\text{Pr},\text{Nd})_3(\text{Te},\text{W})_2\text{O}_{12}$], NASICON [e.g., $\text{Na}(\text{Ti},\text{Zr},\text{Sn},\text{Hf})_2(\text{PO}_4)_3$],²⁸ argyrodite [e.g., $\text{Li}_{6.5}\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}\text{S}_5\text{I}$ and $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_x\text{Br}_{1.5-x}$] [Figs. 3(a) and 3(b)]²⁹⁻³¹ or $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) type [e.g., $\text{Li}_{9.54}(\text{Si}_{0.6}\text{Ge}_{0.4})_{1.74}\text{P}_{1.44}\text{S}_{11.1}\text{Br}_{0.3}\text{O}_{0.6}$],³² have been reported in the literature. With regard to the oxide rock salt, garnet, and NASICON ion conductors, a high ΔS_{conf} has been achieved by the incorporation of various transition metals, while in sulfide-based solid electrolytes, compositional disorder can be increased both by cation and anion mixing. Despite the progress made in recent years, a solid understanding of the effect of configurational entropy on ion mobility is lacking. However, preliminary data point toward overlapping site energies due to local ion distortions [Fig. 3(c)]. In addition, very high ionic conductivities of σ_{ion} , $\tau_t > 25\text{ mS/cm}$ have only been realized in LGPS-type solid

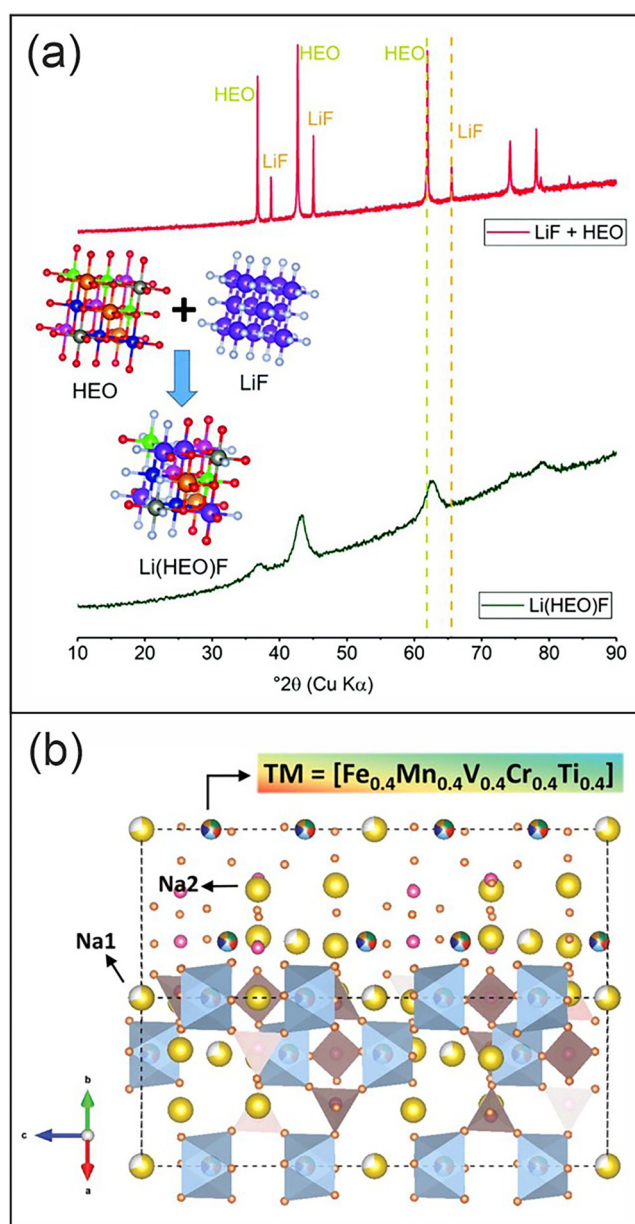


FIG. 2. (a) XRD patterns of a physical mixture of LiF and $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ and as-prepared $\text{Li}_x(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{OF}_x$. Reproduced with permission from Wang *et al.*, *Energy Environ. Sci.* **12**, 2433 (2019). Copyright 2019 Author(s), licensed under a Creative Commons Attribution (CC BY) license. (b) Schematic illustration of the crystal structure of $\text{Na}_{3.4}\text{Fe}_{0.4}\text{Mn}_{0.4}\text{V}_{0.4}\text{Cr}_{0.4}\text{Ti}_{0.4}(\text{PO}_4)_3$. Reproduced with permission from Li *et al.*, *Adv. Sci.* **9**, 2202082 (2022). Copyright 2022 Author(s), licensed under a Creative Commons Attribution (CC BY) license.

electrolytes. Similar to site disorder in lithium argyrodites, increasing compositional complexity has been suggested to lead to some kind of energy landscape flattening and to help activate otherwise immobile charge carriers. Apart from that, the high-entropy design

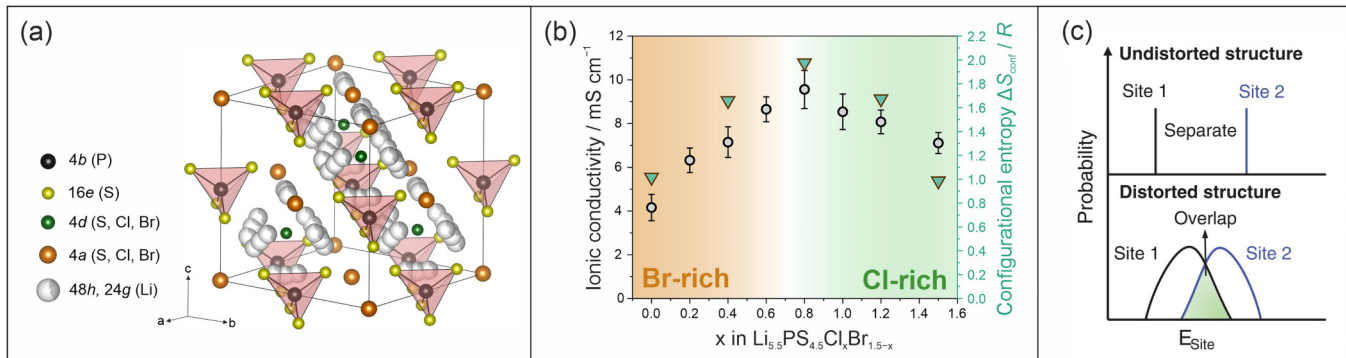


FIG. 3. (a) Schematic illustration of the crystal structure of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_x\text{Br}_{1.5-x}$ argyrodite solid electrolytes with the Wyckoff positions and constituents indicated in the legend and (b) correlation between configurational entropy and ionic conductivity. Reproduced with permission from Li *et al.*, *Angew. Chem. Int. Ed.* **62**, e202314155 (2023). Copyright 2023 Author(s), licensed under a Creative Commons Attribution (CC BY) license. (c) Schematic showing that local distortions affect the site-energy distribution. Reproduced with permission from Zeng *et al.*, *Science* **378**, 1320 (2022). Copyright 2022 The American Association for the Advancement of Science.

concept can be used to improve upon the anodic and/or cathodic stability, as demonstrated for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)-based solid electrolytes for example.³³

Moreover, the concept has recently been extended to liquid electrolytes, mostly for the application in conventional LIBs. A quasi-high-entropy state can be achieved either by dissolving various conducting salts into a single organic solvent³⁴ or by using different organic solvents and co-solvents (up to five in total, for increasing “molecular diversity”) in combination with a single conducting salt.³⁵ In contrast to solid (crystalline) HEMs, where the ΔS_{conf} is assumed to be the driving force for phase formation/stabilization and occupational disorder may affect ion mobility, in high-entropy liquid electrolytes, the entropy of mixing is decisive to achieve uniformity on the molecular level by avoiding ion clustering and altering solvation structures,³⁶ the latter leading to improved transport properties and formation of stabilized interphases. In this regard, it should be noted that battery technologies relying on aqueous electrolytes also appear to benefit from application of the high-entropy concept.³⁷

III. OUTLOOK AND FUTURE PERSPECTIVES

Though the field of high-entropy battery materials is still in its infancy, rapid progress has led to the development of a number of inorganic and hybrid inorganic/organic compounds showing promise for application as anode, cathode, or electrolyte. In all cases, additional complexity has been introduced into structurally predefined materials via cation and/or anion mixing. However, only for some of the materials reported, compositional/occupational disorder evidently resulted in improved performance and stability, thus lacking solid evidence that the advent of high-entropy and/or compositionally complex battery materials represents a significant advance in the field of electrochemical energy storage. Overall, it remains to be seen if they will be capable of outperforming those used in the current generation of rechargeable batteries. Nevertheless, the virtually infinite chemical space available for

exploration will likely hold many surprises in the future. In this regard, high-throughput experimentation in combination with computational materials science based on artificial intelligence (machine learning methods) is becoming increasingly important and will help make pivotal discoveries faster. Despite the significance of implementing automated experimentation in tandem with artificial intelligence, the vast chemical design space of HEMs poses severe challenges in identifying the most promising compounds. The enormous number of possible compositions and stoichiometries makes it impossible to first prepare and then test all potential materials. Therefore, accelerated synthesis and characterization methods are required to navigate efficiently through the labyrinth of compositions. High-throughput screening offers one approach to address this problem. Numerous elemental combinations can be realized through robot-assisted synthesis. In general, autonomous laboratories will be a major focus of future research in different fields³⁸ and will significantly accelerate scientific progress, particularly in the realm of compositionally complex materials. However, even with high-throughput methodologies, the sheer number of possible combinations cannot be fully covered. For this reason, an iterative combination of artificial intelligence-driven synthesis and characterization in combination with machine learning is beneficial, as it may allow for the identification of possible cross-connections between experimental results and material compositions that may elude human observers. These insights must inform the planning of the next series of experiments, thereby guiding the path toward optimized materials.

Apart from that, the high-entropy design concept has not yet, or only marginally, been applied to industrially relevant battery materials, such as olivine or layered cathodes, and alloy anodes. Moreover, it can contribute toward the development of more sustainable battery technologies and further show promise for other uses, such as bulk doping/substitution,⁷ defect engineering, or as a surface/gradient modification strategy to improve stability by mitigating side reactions and mechanical degradation during cycling. However, concerning industrially applicable materials, some

17 April 2024 12:36:42

prerequisites need to be considered, including scalability of the synthesis method (preferably with continuous precursor feed and product collection), precursor availability, and costs. The latter may be particularly challenging for HEMs. For example, pyrolysis is an industrially established technology, yet the powder morphology may not be suited for all applications. Moreover, synthesis temperatures are usually high, ranging from 600 to 1000 °C, leading to economic implications. Consequently, like for non-HEMs, low-temperature and, therefore, low-cost synthesis methods need to be developed. The choice of precursors is also crucial due to recent regulations, with the reuse, recyclability, and carbon footprint of battery materials gaining more and more importance. Nevertheless, aside from the performance aspect, HEMs may possess other advantages over state-of-the-art materials, such as reducing the concentration of critical elements and prioritizing certain precursor supply chains.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

F. Strauss: Writing – original draft (equal); Writing – review & editing (equal). **M. Botros:** Writing – original draft (equal); Writing – review & editing (equal). **B. Breitung:** Writing – original draft (equal); Writing – review & editing (equal). **T. Brezesinski:** Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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17 April 2024 12:36:42

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