

# Computationally Guided Synthesis of Battery Materials

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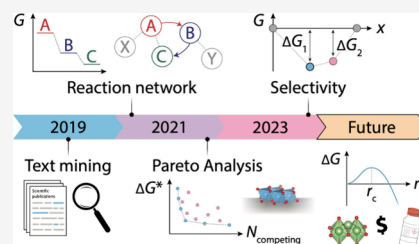
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**ABSTRACT:** Materials synthesis is a critical step in the development of energy storage technologies, from the first synthesis of newly predicted materials to the optimization of key properties for established materials. While the synthesis of solid-state materials has traditionally relied on intuition-driven trial-and-error, computational approaches are now emerging to accelerate the identification of improved synthesis recipes. In this Perspective, we explore these techniques and focus on their ability to guide precursor selection for solid-state synthesis. The applicability of each method is discussed in the context of materials for batteries, including Li-ion cathodes and solid electrolytes for all-solid-state batteries. Our analysis showcases the effectiveness of these computational methods while also highlighting their limitations. Based on these findings, we provide an outlook on future developments that can address existing limitations and make progress toward synthesis-by-design for battery materials.



The ongoing shift toward clean energy and electric transportation is largely driven by the increasing adoption of modern battery technologies. Since the commercialization of LiCoO<sub>2</sub> in the early 1990s, there has been substantial effort to develop Li-ion batteries with increased energy density, longer cycle life, and lower cost.<sup>1</sup> These efforts have resulted in LiNi<sub>1-y-z</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) and LiNi<sub>1-y-z</sub>Co<sub>y</sub>Al<sub>z</sub>O<sub>2</sub> (NCA) cathodes with high specific capacity, as well as LiFePO<sub>4</sub> (LFP) cathodes with low cost and good thermal stability. While these are usually combined with liquid electrolytes and graphite anodes, there has been progress in the development of all-solid-state batteries that use ceramic electrolytes and Li metal anodes, promising higher energy densities and improved safety.<sup>2</sup> The replacement of Li<sup>+</sup> as the intercalating ion with other monovalent (Na<sup>+</sup>) or multivalent (Mg<sup>2+</sup>) ions further expands the design space for battery materials and presents additional benefits in terms of Earth-abundance and energy density.<sup>3</sup>

Materials synthesis underpins the development of all battery technologies and contributes significantly to the costs, energy requirements, and environmental impact of manufacturing.<sup>4</sup> The synthesis process also influences cell performance by controlling the product composition and morphology.<sup>5</sup> Optimization of a synthesis recipe is typically performed through laborious experimental trials guided by domain expertise. While this approach can be effective, it often leads to high costs and prolonged time scales before an optimal solution can be reached. Further complicating matters is the prevalence of large design spaces (i.e., problems involving many variables), whose exploration becomes intractable when

using a brute-force experimental approach. Fortunately, computational techniques are emerging to assist in planning and optimizing synthesis procedures, promising to accelerate the timeline required to bring novel battery technologies to market.

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Computational methods based on Density Functional Theory (DFT) have long been used to identify promising new materials.<sup>6</sup> Nevertheless, realizing these compounds experimentally remains challenging. Even when a material is predicted to be stable, its synthesis often warrants careful experimental design.<sup>7,8</sup> There are techniques such as high-energy ball milling, long heating duration, and intermittent regrinding that can sometimes be used to increase the yield of

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stable materials; however, many technologically important materials are thermodynamically metastable, presenting additional challenges for efficient synthesis.<sup>9</sup> These methods are also generally undesirable as they can be difficult to scale, lead to increased manufacturing costs, and provide less control over product composition and morphology, which are key design handles when optimizing battery performance.

An important consideration for the synthesis of any target material is the choice of starting materials (i.e., precursors). For any given element, there is often a variety of commercially available precursors such as oxides, carbonates, hydroxides, nitrates, and oxalates. This selection can also be expanded by prereacting simple precursors together to form more complex materials like ternaries and quaternaries, which themselves can be used in synthesis experiments.<sup>10</sup> The choice of precursors influences which intermediates form during heating,<sup>11</sup> and these intermediates often dictate whether a target material forms,<sup>12</sup> under what conditions it forms,<sup>13,14</sup> and the final product morphology.<sup>15,16</sup> As such, choosing the right precursors is paramount to discovering new battery materials, reducing their manufacturing costs, and optimizing their performance. In this Perspective, we will focus primarily on guiding precursor selection for solid-state synthesis, one of the oldest and most prevalent techniques used to manufacture inorganic solids at an industrial scale. Following a brief overview of experimental studies that showcase the importance of precursor selection in solid-state synthesis, we will discuss how computational approaches can aid in the selection process and accelerate the realization of new materials for energy storage.

## ■ THE ROLE OF PRECURSOR SELECTION IN THE SYNTHESIS OF BATTERY MATERIALS

There are many cases where precursor selection influences the temperature and hold time required to synthesize a desired compound with high purity. As one example, in the synthesis of NMC cathodes, the desired Ni concentration dictates the precursor choice due to the influence of temperature on defect formation. While  $\text{Li}_2\text{CO}_3$  is cheaper and less corrosive than  $\text{LiOH}$ ,<sup>17</sup> the synthesis of high Ni-cathodes such as NMC811 ( $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ) mandates the use of  $\text{LiOH}$  to avoid Ni substitution on Li sites.<sup>18,19</sup> Bianchini et al. showed that lithiation of rocksalt  $\text{NiO}$  begins at 300–350 °C when combined with  $\text{LiOH}$ .<sup>20</sup> Formation of a layered  $\text{Li}_{1-x}\text{NiO}_2$  ( $x < 1$ ) phase occurs at temperatures exceeding 436 °C, with further heating required to complete its lithiation. Several related studies have reported similar findings, in which  $\text{LiOH}$  begins to react with and lithiate  $\text{NiO}$  at temperatures ranging from 210 to 450 °C.<sup>17,21,22</sup> In contrast,  $\text{Li}_2\text{CO}_3$  does not react with the Ni precursor in appreciable amounts until the synthesis temperature exceeds 600 °C, likely due to the higher melting point of  $\text{Li}_2\text{CO}_3$  (723 °C) in comparison to  $\text{LiOH}$  (462 °C).<sup>23</sup> Increased reactivity at low temperature has also been reported when using  $\text{LiOH}$  to synthesize other cathode compositions.<sup>24,25</sup> These low temperatures not only diminish  $\text{Ni}_{\text{Li}}$  antisite defects, but also provide improved control over product morphology<sup>26</sup> at the expense of higher material costs and more processing challenges.

The choice of transition metal precursor is also important when synthesizing Li-ion cathodes. It is common to first prepare a mixed transition metal hydroxide—e.g.,  $\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}(\text{OH})_2$ —using a coprecipitation route followed by sintering this material with  $\text{LiOH}$  or  $\text{Li}_2\text{CO}_3$  at temper-

atures between 500 and 800 °C. This leads to fast reactions that are usually completed in <2 h, whereas simply mixing the binary metal oxides or carbonates together requires much longer hold times (>24 h) or higher synthesis temperatures.<sup>27</sup> A second benefit of the coprecipitation route is that it provides good control over product morphology, which is retained after sintering at sufficiently low temperatures. While mixed transition metal hydroxide precursors are currently predominant, recent studies have investigated the alternative use of transition metal carbonates and oxalates.<sup>26</sup> These require lower reaction temperatures and provide better control over particle morphology. However, they also have drawbacks including poor transition metal mixing and the need for longer coprecipitation times.

Depending on which precursors and synthesis temperature are used, melting and volatility can sometimes complicate the synthesis of battery materials. This is the case for several NASICON-type solid Li-ion electrolytes including  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) and  $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  (LAGP). Both compounds are typically synthesized using a melt quench approach, but precursor choice has a strong effect on the product composition and purity.<sup>28</sup> Previous work tested three different P sources ( $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{P}_2\text{O}_5$ ) and found that only one of them ( $\text{H}_3\text{PO}_4$ ) led to high purity.<sup>29</sup> The other two precursors resulted in  $\text{GeO}_2$  and  $\text{AlPO}_4$  impurities, whose formation can be attributed to the high-temperature volatility of P. Similarly, recent work showed that volatility affects the synthesis of  $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$  (LLTO) electrolytes, wherein off-stoichiometry can arise from Li loss at high temperature when traditional binary precursors ( $\text{Li}_2\text{O}$ ,  $\text{La}_2\text{O}_3$ , and  $\text{TiO}_2$ ) are used.<sup>30</sup> In contrast, selectively reacting these precursors before heating avoids Li loss by “trapping” it in solid intermediates. Similar ideas have also been used to prevent the loss of F from K- and Na-ion cathode materials.<sup>31,32</sup>

Ion exchange reactions are an alternative approach to control the synthesis pathway. In this approach, the starting material and target composition differ by one ion that is exchanged during synthesis. These reactions are often performed in the liquid phase (using molten salts<sup>33</sup> or dissolved alkali ions<sup>34</sup>) but can also be accessed via solid-state synthesis. For example, Kang et al. heated  $\text{Na}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$  with  $\text{LiNO}_3$  and  $\text{LiCl}$  to yield  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$  while mitigating the deleterious effect of Li/Ni disorder within the layered structure by keeping the synthesis temperature low.<sup>35</sup> Ion exchange reactions can also produce materials that are otherwise difficult to make using traditional methods. For example,  $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$  was uniquely obtained by first synthesizing  $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$  before performing Na/Li ion exchange with this compound through a solid-state reaction with  $\text{LiBr}$ .<sup>36,37</sup> Double-ion exchange “metathesis” reactions can also be used to control the synthesis pathway and bolster the thermodynamic driving force to form a desired target.<sup>13,38</sup> For example,  $\text{MgCr}_2\text{S}_4$  (a proposed Mg-ion cathode) was first synthesized by using  $\text{MgS}$  and  $\text{Cr}_2\text{S}_3$  as precursors, but this required weeks of annealing at 800 °C plus intermittent regrinding to achieve high target purity.<sup>7</sup> In contrast, recent work showed that  $\text{MgCr}_2\text{S}_4$  can be obtained in <30 min through a metathesis reaction between  $\text{MgCl}_2$  and  $\text{NaCrS}_2$ . The  $\text{NaCl}$  byproduct formed in this reaction can then be removed by washing the sample with water and isolating the solid, which results in high-purity  $\text{MgCr}_2\text{S}_4$ .<sup>8</sup>

Precursors from outside the chemical space of the target material can also be added as dopants, either to stabilize

product formation during synthesis or to alter its performance after synthesis. For example,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) garnet-based materials are promising Li-ion conductors whose conductivity is highly polymorph-dependent. Dopants such as Al, Nb, and Ta are often incorporated during LLZO synthesis to stabilize the preferred cubic polymorph with high ionic conductivity.<sup>39</sup> These dopants can also enhance the stability of LLZO in contact with Li metal, a feature that is crucial for the operation of all-solid-state batteries over a wide range of electrochemical potentials.<sup>40</sup> The synthesis of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS), another promising Li-ion conductor, also benefits from doping. Experiments targeting this compound are often complicated by the formation of impurities such as  $\text{Li}_3\text{PS}_4$  and  $\text{Li}_4\text{GeS}_4$ . Doping strategies, including through partial substitution of Ge with Sn and O with Cl, have been shown to avoid these impurities and enhance ionic conductivity.<sup>41</sup>

While these examples make it clear that precursor selection has an important effect on the synthesis and properties of battery materials, optimal precursors for a given target have typically been identified through years of iterative experiments. The advent of *in situ* characterization has facilitated more rapid determination of synthesis pathways,<sup>42</sup> providing crucial insight for improved precursor selection, but it remains a resource-intensive process that can be difficult to justify during exploratory synthesis. Computational approaches that can anticipate challenges in experimental synthesis and propose solutions *a priori* would enable the rational design of procedures that successfully result in the formation of a targeted material with desired composition, morphology, and performance.

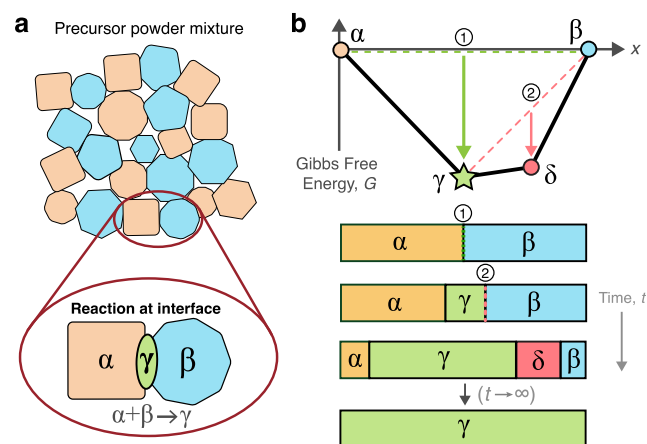
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## GUIDING PRECURSOR SELECTION WITH COMPUTATION

High-throughput DFT calculations have been used for several years to compute the thermodynamic stability of solid-state materials,<sup>43</sup> and open databases such as the Materials Project<sup>44</sup> have made this data available for thousands of materials. With the appropriate corrections and approximations, DFT can be used to compute the thermodynamic driving forces ( $\Delta G$ ) for chemical reactions at conditions relevant to solid-state synthesis.<sup>43,45,46</sup> Experimental data for common gaseous byproducts/reactants ( $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc.) can also be used in concert with DFT calculations of solid materials to quantify the influence of synthesis atmosphere on the relevant thermodynamics. Although solid-state synthesis is not always a thermodynamically driven process, the complexity of solid phase transformations (involving diffusion, amorphization, nucleation, crystallization, etc.) makes it difficult to

directly calculate reaction rates using atomistic simulations. Therefore, most existing approaches to computational synthesis science rely upon thermodynamic calculations.

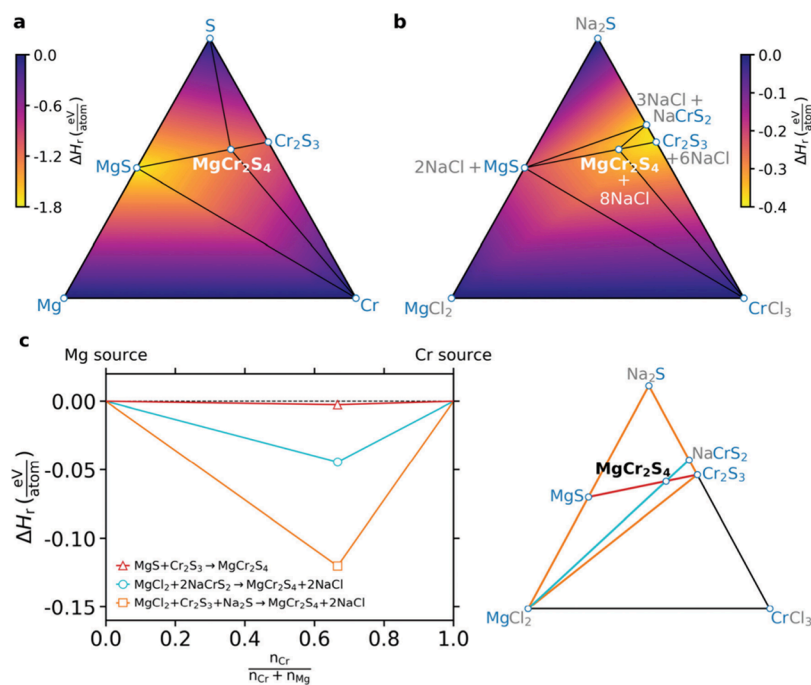
Solid-state reactions are generally thought to proceed locally at interfaces between pairs of reactants, leading to a sequence of intermediates preceding the formation of a multicomponent ceramic material.<sup>11,14,47</sup> This understanding, which is schematically illustrated in Figure 1a,<sup>48</sup> allows a synthesis pathway to be



**Figure 1.** (a) A schematic illustrating the concept of pairwise reactions. In a mixture of solids, reactions proceed locally at the interfaces between individual particles, without any knowledge of the overall sample composition. (b) The binary convex hull shows possible pairwise reaction products. A favorable pair of reactants ( $\alpha$  and  $\beta$ ) is anticipated to have a large driving force to form the desired product ( $\gamma$ ). To retain this product, it should also have little driving force to react with remaining precursors to form any secondary phases ( $\delta$ ). (Reproduced with permission from ref 48. Copyright 2023 American Chemical Society).

decomposed into a step-by-step sequence of pairwise reactions that iteratively lower the Gibbs free energy of a system. McDermott et al. introduced a graph-based approach that analyzes computed reaction energies to explore possible intermediate phases and products that can emerge from a set of precursors.<sup>49</sup> To assess which synthesis pathways are likely, they proposed a cost function based on the (stoichiometrically weighted) average change in  $\Delta G$  over all steps from precursors to final product.

In cases where the synthesis pathway consists of a single step, the reaction network developed by McDermott et al. favors the selection of precursors with the most negative  $\Delta G$  to form the desired product. For instance, the cost to form  $\text{LiNiO}_2$  at 500 °C is about 52% lower when using  $\text{LiOH}$  instead of  $\text{Li}_2\text{CO}_3$ , since the former compound has a larger driving force ( $\Delta G = -194$  meV/atom) than the latter ( $\Delta G = -103$  meV/atom) to react with  $\text{Ni}(\text{OH})_2$  at 500 °C. This supports the observation that  $\text{LiOH}$  tends to be more effective in synthesizing  $\text{LiNiO}_2$  (and related cathodes) at low temperature. Importantly, this fails to account for the fact that  $\text{Ni}(\text{OH})_2$  decomposes to form  $\text{NiO}$  well below 500 °C, which is then partially lithiated before it completely reacts to form  $\text{LiNiO}_2$ .<sup>20</sup> This example highlights the challenges in predicting reaction mechanisms, even for the relatively “simple” synthesis of ternary materials from two precursors. Purely thermodynamic arguments also fail to describe the kinetic factors (e.g., fast ion diffusion) that likely play a role as  $\text{LiOH}$  approaches its melting point of 462 °C. Nonetheless, the



**Figure 2.** (a) The ternary Mg–Cr–S phase diagram shows the traditional route to synthesize MgCr<sub>2</sub>S<sub>4</sub> from MgS and Cr<sub>2</sub>S<sub>3</sub>. (b) The pseudoternary MgCl<sub>2</sub>–CrCl<sub>3</sub>–Na<sub>2</sub>S phase diagram shows the improved metathesis route to synthesize MgCr<sub>2</sub>S<sub>4</sub> from NaCrS<sub>2</sub> and MgCl<sub>2</sub>. The color bar next to each phase diagram indicates the enthalpy at each point in the convex hull, computed relative to the corners. (c) The driving force to form MgCr<sub>2</sub>S<sub>4</sub> from three different combinations of precursors is shown. The position of each pair of precursors on the phase diagram is shown to the right. (Reproduced with permission from ref 8. Copyright 2020 Royal Society of Chemistry).

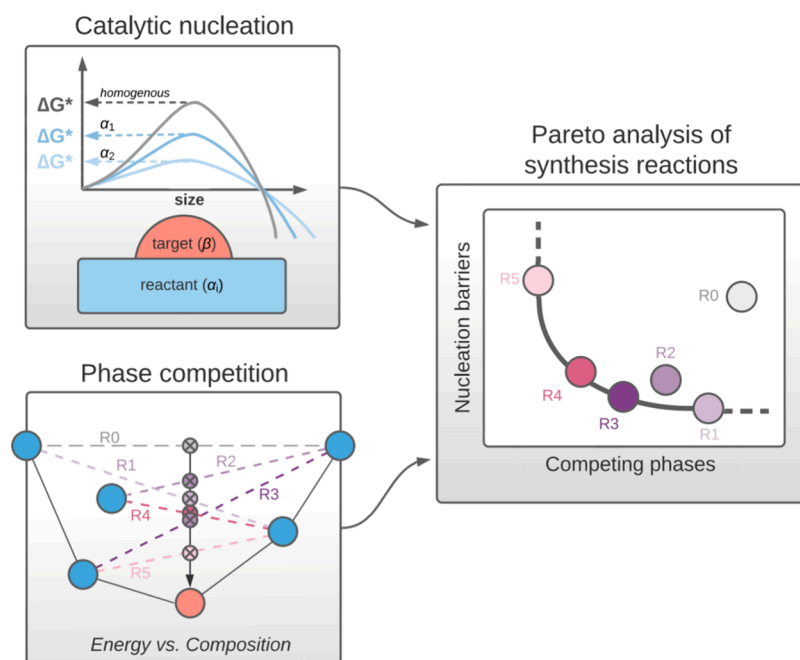
network-based approach of McDermott et al. can be useful to estimate which precursors may be most effective. This can be especially beneficial when more than two precursors are involved, and as a result, more than one reaction is likely to occur. For example, the reaction network predicts that (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> can form Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3–2y</sub>O<sub>2y</sub> (NVPF-O) with 23% lower cost than VOPO<sub>4</sub>, consistent with the work of Akhtar et al.<sup>31</sup> However, the proposed reaction pathway differs from the experimentally observed pathway, highlighting the challenges of accurately predicting the intermediate phases that form in multistep synthesis reactions.

While the reaction network approach can indicate which precursors yield low-cost pathways to form a given target, it does little to probe the selectivity of forming one target over another given a set of precursors and synthesis conditions. To address this, McDermott et al. developed a quantitative approach to rank precursor sets based on two metrics:  $C_1$ , the difference between  $\Delta G$  to form the desired product and  $\Delta G$  to form the next most favorable competing phase; and  $C_2$ , an average of  $\Delta G$  to form each possible secondary phase after the desired product is present.<sup>48</sup> These two metrics are graphically described in Figure 1b, where  $\gamma$  is used to denote the targeted phase and  $\delta$  represents a competing phase. By analyzing a large set of synthesis data mined from the literature, it was found that successful synthesis routes tend to have low values of  $C_1$ ,  $C_2$ , and  $\Delta G$ . However, it is still an open question how these metrics should be combined or separated for an arbitrary target material.

In the context of battery materials, the synthesis of KVPO<sub>4</sub>F from KF and VPO<sub>4</sub> is an example of a reaction with high selectivity (that is, low  $C_1$  and  $C_2$ ). The binary convex hull formed by these two precursors contains only the desired product, and this phase has a moderately large driving force to

form ( $\Delta G = -91$  meV/atom). Previous experimental studies have demonstrated that these precursors do indeed produce KVPO<sub>4</sub>F with high yield.<sup>32</sup> Nevertheless, favorable selectivity can in some cases be insufficient when the desired product has low driving force to form. For instance, MgCr<sub>2</sub>S<sub>4</sub> is the only product on the binary convex hull between MgS and Cr<sub>2</sub>S<sub>3</sub> (Figure 2a, c). However, because the driving force to form MgCr<sub>2</sub>S<sub>4</sub> from these precursors is so weak ( $\Delta G = -3$  meV/atom), several weeks of annealing are required to complete the reaction.<sup>7</sup> In contrast, the metathesis reaction between MgCl<sub>2</sub> and NaCrS<sub>2</sub> has much more favorable selectivity (Figure 2b, c) while also exhibiting a larger driving force ( $\Delta G = -45$  meV/atom), leading to high-purity MgCr<sub>2</sub>S<sub>4</sub> after only 30 min of annealing.<sup>8</sup>

In related work, Chen et al. proposed that the most effective synthesis routes should use precursors that have large  $\Delta G$  to form the desired product while also having much smaller  $\Delta G$  to form any competing phases.<sup>10</sup> The authors tested this hypothesis on a set of 35 quaternary oxide targets and found that precursor combinations satisfying the proposed constraints generally led to higher yield than those that do not. For example, attempting to synthesize LiBaBO<sub>3</sub> from traditional binary precursors (Li<sub>2</sub>O, BaO, and B<sub>2</sub>O<sub>3</sub>) did not result in any detectable yield of the target after heating the sample at 1000 °C for 8 h. The authors attributed this failure to the formation of highly stable intermediates, Li<sub>3</sub>BO<sub>3</sub> and Ba<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, which have relatively small thermodynamic driving force ( $\Delta G = -45$  meV/atom) to react and form the target. In contrast, high-purity LiBaBO<sub>3</sub> was successfully obtained using the same heating profile but with different precursors: LiBO<sub>2</sub> and BaO. These compounds exhibit improved selectivity toward the desired target as they have a large driving force ( $\Delta G = -153$  meV/atom) to form LiBaBO<sub>3</sub> and a much smaller driving force



**Figure 3.** A schematic illustrating the framework developed by Aykol et al. to identify promising reactions. In their approach, the nucleation barrier to form a desired product is approximated by computing its structural similarity and epitaxial matching with the available precursors. It also evaluates how many phases compete with the desired product when starting from each set of precursors. These two metrics are plotted as shown to the right, from which a Pareto front of optimal reactions is outlined. (Adapted with permission from ref 50. Copyright 2021 American Chemical Society).

to form any competing phases. The results presented by Chen et al. demonstrate that purely thermodynamic quantities, such as  $\Delta G$ , are useful to identify fast and effective synthesis routes.

While the direct calculation of reaction rates is extremely challenging, there have been some efforts to include kinetically inspired metrics in synthesis planning. Aykol et al. proposed that the most effective precursors should have a high degree of structural similarity and epitaxial matching with the desired target (associated with preferential nucleation) and few competing reactions that could result in phases other than the target.<sup>50</sup> The task of precursor selection then becomes a multiobjective optimization problem based on these two criteria, where the top candidate precursor sets are those that achieve an optimal or near-optimal trade-off of these two metrics. This can be considered a Pareto optimality problem, where these “optimal” precursor sets are those for which any modification to the set increases the anticipated nucleation barrier or increases the number of competing reactions. This concept is schematically illustrated in Figure 3, where promising reactions with low (approximated) nucleation barriers ( $\Delta G^*$ ) and few competing reactions are plotted in comparison to a line that represents the Pareto front. The authors validated their method with several case studies, including the synthesis of  $\text{LiCoO}_2$ , and recovered the conventional precursors (along the Pareto front) that are successfully used to synthesize this material.

Nucleation barriers have been studied extensively in the context of solution-based synthesis, but their role in governing the selectivity of competing products in solid-state synthesis is less well understood. Recent work suggests that nucleation becomes important when two phases have a comparable driving force to form, in which case the first product to form may be decided by their interfacial energies.<sup>51</sup> Metrics for structural similarity and epitaxial matching can help rationalize

observed synthesis outcomes in such cases. For instance, multiple studies have reported that the formation and growth of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO), a common Li-ion anode, is sensitive to the presence of different  $\text{TiO}_2$  polymorphs (rutile vs anatase).<sup>52,53</sup> Through *in situ* characterization, these studies showed that LTO growth tends to be more rapid when preceded by anatase. Although neither polymorph of  $\text{TiO}_2$  is structurally similar to LTO, it is the anatase polymorph that has more favorable epitaxial matching. The measure used by Aykol et al. suggests that LTO is 41% more epitaxially commensurate with anatase than rutile  $\text{TiO}_2$ , consistent with experimental observations that anatase facilitates LTO growth.

The previously outlined methods rely on atomistic calculations and theory-driven hypotheses to describe how solid phases transform during heating. An alternative data-driven approach relies on natural language processing (NLP) to extract synthesis data from the scientific literature. For example, Kononova et al. extracted  $\sim 50,000$  solid-state synthesis recipes from the literature, where each recipe contains information regarding the precursors, heating profile, and atmospheric conditions used to synthesize a reported compound.<sup>54</sup> Machine learning (ML) algorithms have since been trained on this data to predict optimal precursors for targeted synthesis, showing some degree of success.<sup>55,56</sup> Similar methods have been developed to predict effective reaction temperatures based on a set of precursors and a target.<sup>56–58</sup> However, the reliability of these methods is limited by the lack of negative data (i.e., failed syntheses) that are reported in the literature, and it has been demonstrated that such data is needed to train accurate ML models.<sup>59,60</sup> Furthermore, these methods fail to account for individual precursor properties such as particle size and purity, which can affect reaction temperatures and outcomes.<sup>61</sup> Indeed, experiments performed in a recently introduced autonomous synthesis lab had a

moderate success rate of 53% when using the highest ranked synthesis recipes proposed by ML,<sup>65</sup> underscoring the opportunities that remain to further improve these literature-based models.

Because initial synthesis attempts often fail, adaptive optimization techniques can be useful to leverage insight from experimental outcomes and propose new synthesis procedures. Bayesian optimization (BO) is most often used for this purpose in the context of solution-based synthesis,<sup>64</sup> which involves tuning continuous quantities like reactant concentrations, flow rates, and temperature. Similar techniques have also been extended to thin film deposition,<sup>65</sup> where product composition and yield can be highly sensitive to the atmospheric conditions used during synthesis. BO is less prevalent in solid-state synthesis, where precursor selection plays an important role. Optimizing the choice of precursors is complicated by the fact that it involves orthogonal and categorical variables to represent whether a given precursor is included. In place of black box optimization algorithms, rule-based and physics-informed methods can be used to find optimal precursors for targeted materials synthesis. ARROWS is one such algorithm that has demonstrated improvement over black box optimization methods by decomposing failed synthesis reactions into associated pairwise reactions that must be avoided to form the desired target.<sup>12</sup> This method was recently applied in-line with autonomous experiments, leading to the successful synthesis of six materials that could not be made using ML-proposed recipes.<sup>62</sup> However, there were still 17/58 materials targeted that could not be obtained, even after attempting to optimize their synthesis procedures with ARROWS. These failures were attributed to practical issues like melting and volatility, as well as the formation of highly stable intermediates that had low driving force to react and form the target. These findings highlight the ample room left to improve upon existing approaches for precursor selection and synthesis optimization.

## ■ REMAINING CHALLENGES AND OPPORTUNITIES

For the design and optimization of materials synthesis procedures, computations are most often used to model reaction energies. However, the studies outlined in this Perspective have shown that there is much more to synthesis than (bulk) thermodynamics as interfacial effects and reaction kinetics—the rate at which diffusion, nucleation, and growth occur—can also play an important role. It remains unclear how large a thermodynamic driving force must be to ensure that a product will form without explicitly modeling these kinetic factors. The regime of kinetically limited processes is also likely to depend on chemistry and structure, as diffusion rates can vary substantial for different ionic species and environments. Predicting these rates in a rigorous and quantitative fashion warrants the modeling of atomic-scale processes that are difficult to handle computationally. Simulating long-range diffusion and nucleation using *ab initio* molecular dynamics, for example, requires long time scales that are often prohibitively resource intensive. There are some methods available to quickly estimate relative nucleation rates, such as the structural similarity analysis used by Aykol et al.,<sup>50</sup> but their reduced computational workload comes with less detailed insight into the synthesis pathway.

The increasing use of universal ML potentials to drive molecular dynamics simulations with high fidelity and generalizability may soon enable the modeling of complex

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processes underlying solid-state synthesis.<sup>66–68</sup> Because ML techniques can be applied faster than DFT calculations, they can be used to perform molecular dynamics simulations at long time scales that are relevant for long-range diffusion.<sup>66</sup> ML potentials have also been shown to be effective for computing the thermodynamics of surfaces<sup>69</sup> and for probing the crystallization of phases from amorphous structures.<sup>70</sup> Nonetheless, these approaches are still a long way from providing a full description of the kinetics involved in solid-state transformations, which remains challenging to obtain even using *in situ* experimental characterization.<sup>53,71</sup>

The increasing use of universal ML potentials to drive molecular dynamics simulations with high fidelity and generalizability may soon enable the modeling of complex processes underlying solid-state synthesis.

In addition to reaction kinetics involving diffusion and nucleation, melting and volatility are difficult to model but can be highly influential in the synthesis of battery materials. Melting is often problematic when it leads to amorphization of the sample<sup>62</sup> or when it causes the sample to adhere to the walls of its container. These challenges are exacerbated by the fact that melting often leads to increased volatility of light elements.<sup>72</sup> Excess amounts of the Li precursor are typically used to compensate for volatility when Li-ion cathodes are synthesized at high temperature,<sup>73</sup> but it remains challenging to anticipate when and how much excess is needed. The use of excess precursor also raises production costs and can trigger unwanted reactions with the sample containers. On the other hand, the presence of a molten flux can often be beneficial as it leads to fast ion transport, short reaction times, and improved homogeneity in the synthesis products. For example, the melting of LiOH can lead to rapid formation of Li-ion cathodes such as LiNiO<sub>2</sub>.<sup>20</sup> Whether the goal of an experiment is to cause or avoid melting, the choice of precursors and synthesis temperature may be facilitated by ML algorithms that have been developed to predict the melting points of inorganic materials.<sup>74–76</sup> Although even the best-performing models exhibit a root-mean-square error of ~110 K relative to experimental data, they at least permit a computationally trivial estimate of the melting points of possible starting materials.<sup>74</sup> Predictions from these algorithms could be combined with known (experimentally determined) melting

points and used to refine the suggestions of computational methods for synthesis planning subject to constraints—e.g., to propose synthesis temperatures or precursors that avoid undesired phase changes.

Precursor melting points can also be useful to predict the temperatures at which reactions will proceed, e.g., by using heuristics based on Tamman's rule.<sup>56</sup> However, we suspect that such predictions will become less accurate in situations where eutectic melting is prevalent (and the melting point of an isolated solid is less relevant), as is the case for many of the oxide chemistries used in batteries. This problem has not yet been addressed using ML, though some level of predictive capability may be achieved from the incorporation of CALPHAD-based approaches.<sup>77</sup> Because melting and volatility are not always correlated, it would also be useful to develop standalone methods for predicting volatility. In addition to the knowledge that lighter elements are generally more volatile than heavy ones, future algorithms could account for experimentally determined vapor pressures when predicting whether volatility will occur. If it is anticipated to be an issue, then excess precursor amounts should be used, or an alternative synthesis route should be designed.

Expanding the design criteria for synthesis can lead to complications in precursor safety, air stability, cost, and process scalability. Because many of the existing algorithms for synthesis planning prioritize reactions with large thermodynamic driving force, they tend to favor highly reactive precursors. These precursors are typically more expensive and less air-stable than more conventional precursors, which can make them impractical for industrial use. The use of certain precursors can also be complicated by reactivity with the sample container, depending on the material from which it is made.<sup>61</sup> For instance, attempting to synthesize  $\text{Na}_3\text{PS}_4$  in a gold crucible leads to the formation of a persistent  $\text{Na}_3\text{AuS}_2$  impurity phase.<sup>78</sup> Similarly, preparing LLZO in an  $\text{Al}_2\text{O}_3$  crucible results in a product with as much as 0.63 Al per formula unit.<sup>79</sup> To address this challenge, we propose that future algorithms can frame synthesis planning as a multi-objective optimization problem that aims to balance anticipated success (target yield) with the choice of precursors that are amenable to manufacturing and stable with respect to commonly available reaction vessels. Information on safety and air stability is available in safety data sheets (SDSs), with more detailed insight provided by scientific publications, and both sources could be analyzed in high throughput using established text-mining workflows<sup>54</sup> or large language models with appropriate tuning.<sup>80</sup> Measures of precursor cost could also be extracted from common vendors (e.g., Sigma-Aldrich and Alfa Aesar) through web scraping, enabling optimization based on chemical prices in real time. Thermodynamic stability of the precursors (and products) with the proposed reaction vessels can be evaluated using DFT-computed reaction energies.

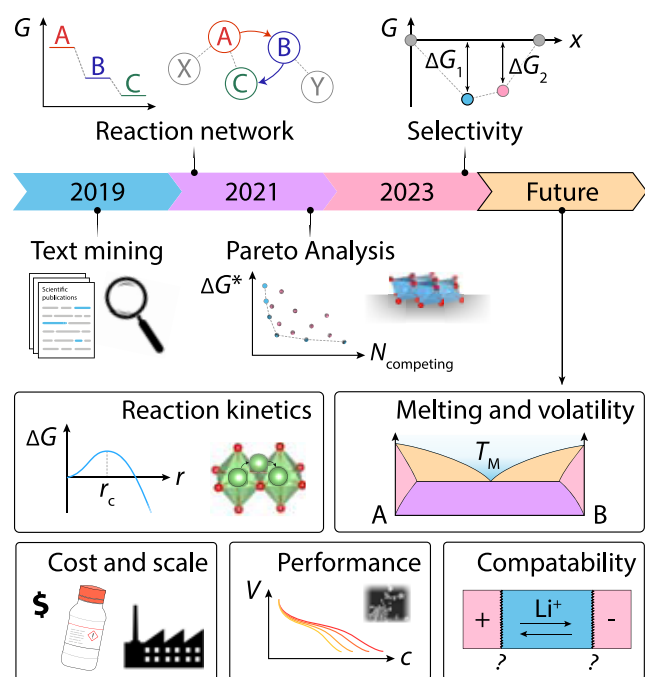
After optimizing a synthesis procedure to generate high target yield at low cost, there are many downstream tasks that warrant further consideration. Composition, site disorder, and morphology can all have a significant effect on the performance of battery materials.<sup>5</sup> While each of these properties can sometimes be modified with postprocessing (e.g., ball milling or heat treatment), it is beneficial to achieve the desired performance directly from synthesis. Factors including the reaction temperature and hold time, in addition to the particle size and purity of the precursors, often have a prominent effect on the properties of the final product.<sup>61</sup> It is difficult to model

these effects using computational techniques that fail to describe kinetics, though some understanding has been developed from experimental data—e.g., that reducing the precursors' particle size leads to faster reactions at lower temperatures.<sup>53,81</sup> In contrast, it is feasible to predict the range of compositions and site orderings that are accessible for a product at different temperatures. This can be done by fitting cluster expansion models for the system of interest, as demonstrated for a variety of Li-excess cathodes.<sup>82</sup> However, because battery materials are often compositionally complex, cluster expansion calculations become less tractable for high-throughput computations, and more work is needed to advance this area of modeling.

Composition changes in the form of defects are also known to influence battery performance—e.g., modifying the conductivity of solid-state electrolytes by several orders of magnitude.<sup>83</sup> DFT-calculated point defect thermodynamics are well established to predict equilibrium defect concentrations as a function of temperature and atmospheric conditions,<sup>84</sup> though doing so in high-throughput remains challenging. Beyond point defects, extended defects (e.g., dislocations and twin boundaries) commonly influence synthesis and processing but present additional challenges for atomistic simulations due to the larger system sizes required for modeling. Recent work utilized large simulation cells of 576 atoms to study the effects of stacking faults in layered  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  cathodes, which are suspected to initiate cell degradation through vacancy condensation along dislocation lines.<sup>85</sup> To study these processes in higher throughput, the integration of ML potentials in the computational design of synthesis pathways again seems like a promising area for future research. Beyond the atomic scale, morphological control of the synthesized particles is also important for manufacturing battery materials. Addressing this requires multiscale modeling or the integration of experimental characterization techniques, such as Scanning Electron Microscopy (SEM), into the pipeline for synthesis planning. Gathering morphological data in high throughput is increasingly possible as benchtop SEMs are becoming commonplace.

As batteries are multicomponent devices, it is necessary to ensure that all components are compatible with one another when designing their synthesis procedures. This is particularly important in all-solid-state batteries, where the electrolyte must be stable in contact with both electrodes over a wide range of electrochemical potentials. Doping is one strategy that is often used to expand this range of stability for promising electrolyte materials.<sup>35</sup> Combining this approach with computational methods that have been developed to evaluate the interfacial stability between arbitrary compositions,<sup>40</sup> it is now possible to screen for optimal dopants in high throughput. Following their identification, appropriate precursors and synthesis conditions may be designed by using many of the techniques outlined throughout this Perspective, facilitating the end-to-end development of solid-state batteries.

While current approaches to precursor selection have proven useful in optimizing the synthesis of many battery materials, there remains much work to be done before such computational methods can fully capture the intricacies of solid-state synthesis. A timeline of several existing algorithms for computational synthesis planning are summarized in the top panel of Figure 4, followed by an overview of additional features that may be included in the next generation of these algorithms. As we look to the future, *in situ* characterization



**Figure 4.** Top panel shows a timeline of recent efforts to automate the selection of precursors for solid-state synthesis using computational techniques based on *ab initio* computations, machine learning, and text mining. The bottom panels illustrate proposed features to be included in the next generation of computational techniques for synthesis planning.

will continue to play a critical role in validating synthesis pathway predictions based on atomistic simulations.<sup>86</sup> Self-driving laboratories also present an exciting playground for predictive synthesis by ensuring the systematic execution of synthesis experiments and aggregation of their results (which importantly include negative examples).<sup>87</sup>

In the nascent field of predictive solid-state synthesis, much of the focus has been placed on how to first synthesize a new material (i.e., speeding up discovery). While this remains an ongoing challenge,<sup>88</sup> there are also ample opportunities to accelerate the transition from initial synthesis to fully optimized synthesis-at-scale. Developments up until this point have largely been enabled by close collaboration between experimental and computational researchers, and it is essential that this collaboration continues in order to further improve upon existing methods and ensure that computational developments meet the requirements of those making materials and devices. Industrial-academic partnerships would also surely help drive the development of synthesis prediction approaches that consider important metrics for processing and manufacturing battery materials at scale. As computational predictions of synthesis outcomes increasingly align with experimental results, it may become possible to drastically reduce the need for trial-and-error experiments, in turn reducing the cost and accelerating the development timeline for next-generation battery technologies.

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