Quantifying the Search for Solid Li-Ion Electrolyte Materials by Anion: A Data-Driven Perspective

Austin D. Sendek, Gowoon Cheon, Mauro Pasta, and Evan J. Reed*

ABSTRACT: We compile data and machine-learned models of solid Li-ion electrolyte performance to assess the state of materials discovery efforts and build new insights for future efforts. Candidate electrolyte materials must satisfy several requirements—chief among them fast ionic conductivity and robust electrochemical stability. Considering these two requirements, we find new evidence to suggest that Cl-, Br-, and I-based solid ion conductors are generally more likely to satisfy fast ionic conductivity and electrochemical stability requirements than materials from other common families, e.g., the sulfides and oxides. Furthermore, we find that sulfide- and oxide-based materials are generally poor electrolyte candidates, but optimization of the sulfides for fast ionic conductivity and wide electrochemical stability may be more likely than optimization of the oxides. We also find that the nitrides and phosphides appear to be the most promising material families for electrolytes stable against Li-metal anodes. Furthermore, the spread of the existing data in performance space suggests that fast conducting materials that are stable against both Li metal and a >4 V cathode are exceedingly rare and that a multiple-electrolyte architecture is a more likely path to successfully realizing a solid-state Li metal battery by approximately an order of magnitude or more. Our model is validated by its reproduction of well-known trends that have emerged from the limited existing data in recent years, namely that the electronegativity of the lattice anion correlates with ionic conductivity and electrochemical stability. In this work, we leverage the existing data to provide the first data-driven quantification of trends and correlations among ionic conductivity, stability, and anion electronegativity, building a roadmap to complement material discovery efforts around the desired material performance.

I. INTRODUCTION

As the world continues to strive toward a carbon-neutral economy to mitigate the effects of global climate change,1 the need has never been greater for high-performance battery technology that can reliably supply clean electricity to everything from electronic devices to automobiles to the grid. The realization of an all-solid-state lithium metal battery would be a tremendous development toward improving the energy density, power density, long-term stability, and safety of energy storage devices. Janek and Zeir recently identified challenges that must be addressed to successfully develop solid-state batteries (SSBs), and we refer to their paper for a comprehensive analysis.2

The sole replacement of liquid electrolyte with a solid leaves energy density unchanged and actually results in a decreased specific energy, as solids are denser than liquids. However, using high-voltage cathodes (≥5 V) would result in an energy density increase of 20% over today’s most common cathode chemistries (~4 V).3,4 while replacing graphite with Li metal could potentially increase it up to 70% due to the high specific capacity of Li metal.5

The principal technological bottleneck toward the goal of high energy density SSBs is identifying suitable solid electrolyte (SE) materials. SEs can be divided in two groups: inorganic solids (crystalline, glass, or glass ceramics) and organic solid polymers. The latter have the great engineering advantage of accommodating volume changes of the electrodes by plastic and elastic deformation and are more easily processable. Nonetheless, at room temperature their Li-ion conductivity is too low, and their mechanical strength cannot prevent lithium dendrite growth, though improvements are being made on these fronts.6,7 Among the inorganic SEs, crystalline materials offer the highest Li-ion conductivities, are generally considered the most promising candidates, and are therefore the focus of this work.

The search for crystalline solids with liquid-scale lithium conduction goes back into at least the 1970s8–11 but has accelerated considerably in recent years.12–16 The major focus of this scientific undertaking has historically been on ionic conductivity, although with time it has become apparent that...
the search must involve more than simply looking for superionic behavior. For example, this realization tempered initial excitement surrounding reported superionic Li-ion conductivity in Li₃P in the late 1980s, once it was discovered to have an unacceptably small electrochemical stability window. Recently, it has begun to appear that simultaneous optimization of ionic conductivity and electrochemical stability is a persistent difficulty. Today, the question remains: how does one design materials with fast Li-ion conductivity that are stable against both Li metal and high voltage (>4 V) cathodes? Many materials have been studied for both single- and multiple-electrolyte architectures, and this question continues to drive significant research efforts in both academia and industry. The optimization of select known materials (e.g., LiPON and LLZO) is a major part of this effort, as is the search for new materials. In this work we focus on materials discovery.

Enabling a rapid pace of materials discovery for solid-state batteries is imperative in light of the urgency of addressing the impending impacts of climate change and the considerable amount of time required to explore and characterize new electrolyte materials. It is critical to extract all information from the limited existing data to optimally inform future efforts. In this light, even a small amount of data has the potential to go a long way.

Over the past several years, an important trend has emerged: oxide-based Li-ion conductors generally tend to have good electrochemical stability but poor ionic conductivity, while sulfide-based Li-ion conductors have good ionic conductivity but poor electrochemical stability, although there are some important high performance outliers to the trend. The electronegativity of the anion plays a direct role in setting the oxidation and reduction potentials and likely plays an important role in determining the energetic landscape in the material for ion conduction as well. This trend appears to extend to alternative anions, e.g., the fluorides, which have even higher stability and lower Li-ion conductivity than the oxides. While the anion has some predictive power for electrolyte performance, design principles beyond the anion identity have been reported recently, suggesting additional contributing factors may be important. Recently it has also been proposed that fast conductivity and poor stability (and vice versa) may be directly linked via lattice dynamics, although these properties do not always appear to be correlated.

Although the trends found in the existing data provide valuable guidance to searches for promising materials, these trends are based off of a small number of observations, and they cannot yet quantitatively answer important broad questions: For example, how common are the high performance outliers? How much more (or less) likely are we to discover a fast conducting, highly stable oxide material than a sulfide material? Chlorine (3.16), bromine (2.96), and iodine (2.66) possess Pauling electronegativities between oxygen (3.44) and sulfur (2.58), are they more likely to simultaneously satisfy both the conduction and stability criteria? Is the multiple-electrolyte architecture more likely to succeed than the single-electrolyte architecture? Answering these questions quantitatively requires a bird’s-eye view of the field informed by performance data. Here we seek answers to these questions and more by aggregating and analyzing the limited existing performance data in the literature and employing state-of-the-art predictive tools. We leverage the public materials database of the Materials Project and its associated toolkit, and we incorporate our previous work in data-driven property prediction. The goal of this work is not necessarily to probe the physics of SE materials but rather to quantitatively assess the state of the field through the lens of the existing data. This data sums up “what we know” thus far, serving as a Bayesian prior on our knowledge of materials space that enables us to quantitatively answer where the existing data suggest we should we look for promising new materials. We probe the likelihood of discovering superionic conducting materials with an electrochemical stability window width wider than 4 V; superionic conducting materials with anodic stability beyond 4 V vs Li⁺/Li, superionic conducting materials that are stable against lithium metal, and crystalline materials with a raw materials cost below the cost target of $10/m². We also discuss the impact of mechanical properties and layered structure on ionic conductivity.

Data-driven approaches have recently been applied to predict solid electrolyte material properties individually, including ionic conductivity, and mechanical properties, but have not been used to understand correlations among properties or to quantify the likelihood of finding new materials that meet engineering requirements, to our knowledge. Meanwhile, physics-based methods have been used recently to understand correlations among ionic conductivity and electrochemical stability, however, the computational expense of applying physics-based approaches makes it difficult to evaluate enough materials to build a broad data set to observe performance distributions or extract broad correlations. Existing reviews that discuss the effect of anion identity on solid electrolyte performance tend to qualitatively generalize performance based on the few known examples. For example, although new reports of high-performance halide-based solid electrolytes are emerging such as Asano et al. reporting promising performance in Li₃YBr₆ and Li₃YCl₆ it remains very difficult to make claims about the general performance of the entire space of halide-based compounds based on these two data points. This work seeks to leverage the whole of the existing data to predict and then quantify ionic conductivity and electrochemical stability across all known materials to understand the effect of anion identity on performance.

This effort to gain quantitative perspective from the whole of the available data might be interpreted as “the best we can do with the limited data we have” answering questions about the statistically expected performance of materials in a manner that is difficult with experimental or first-principles methods. Importantly, we note that these trends are subject to change as more data on solid electrolytes is gathered, perhaps significantly so. We emphasize that this roadmap is only the first iteration of such a framework, and we welcome such efforts to gain quantitative perspective from the whole of the existing data to predict and then quantify ionic conductivity and electrochemical stability across all known materials to understand the effect of anion identity on performance.

II. DISCUSSION

Ionic Conductivity and Electrochemical Stability. A SE material must exhibit high ionic conductivity and a wide electrochemical stability window, among additional require-
ments. To drive improvements beyond existing lithium-ion battery technology, this SE material must enable a battery voltage larger than 4 V and ideally is stable against a Li metal anode. In considering the physical picture behind this simultaneous optimization, a difficult design challenge emerges. High ionic conductivity means that cation diffusion occurs easily, while the sublattice remains rigid. High thermodynamic electrochemical stability requires that the structure is stable against the application of positive or negative lithium chemical potentials. One can envision a structure where both these criteria are simultaneously satisfied: the mobile cations are loosely bound and migrate easily through a rigid sublattice that is stable with respect to the addition or removal of lithium. Although such an ideal structure may be conceptually simple, achieving a structure where lithium is loosely bound to the sublattice but the sublattice is strongly bound to itself is difficult in reality. It is likely that these sharply differing electronic interactions may not decouple completely from one another, resulting in higher electrostatic diffusion barriers for lithium and/or weaker sublattice bonds.

These potentially conflicting demands of solid electrolyte materials beg the question: given what has been discovered to date, can we quantify the likelihood of discovering a structure with both liquid-scale ionic conductivity and robust electrochemical stability? We probe this question of likelihoods for the first time with a data-driven approach. This approach seeks to provide quantitative answers on the degree of correlation among these properties, but we note that this does not identify causal relationships.

Examining the interplay between ionic conductivity and electrochemical stability requires data on these properties for an overlapping set of materials. This overlapping data set currently does not exist and therefore requires construction. For data on the electrochemical stability window, we leverage the density functional theory (DFT)-computed formation energies and band gaps of 6600 materials as provided by the Materials Project. In general, the band gap (in electronvolts) provides an upper bound on the (thermodynamic) electrochemical stability window width (in volts). Because DFT tends to underestimate the true band gap, we examined the DFT-computed band gaps against computed electrochemical stability window data when available (see section II-i) and confirmed that the DFT-computed band gaps are in most cases effective upper bounds on the window widths. In this work, we use the DFT-computed band gap to predict an upper bound on the thermodynamic stability window width.

To compute the (thermodynamic) oxidation and reduction potentials of each candidate, we draw upon the methods developed by Ceder et al. that leverage the DFT-computed grand potentials of various phases in the Materials Project database. The oxidation and reduction potentials used in this work are those provided in the Materials Project. These potentials are only computed for materials that are thermodynamically stable (i.e., on the convex hull), limiting the number of candidate materials with predicted oxidation and reduction potentials to 723. All of these materials are predicted to be (meta)stable by density functional theory, and some materials may have been experimentally synthesized. It is possible that a small subset of these materials has reported ionic conductivity values in the literature, but the ionic conductivity of the vast majority has not been reported.

We compile electrochemical stability information for lithium-containing materials in the Materials Project database with the general formula Li−(X)−Y, where Y is one of the anions F, O, S, Cl, Br, P, I, N, Ge, or Si, and X is any combination of other elements. In other words, we consider only lithium-containing materials with monatomic anions; materials like Li2PS4 and Li2OCl are excluded due to the superionic likelihood model being ill-defined for materials with polyatomic anions. For the oxidation and reduction potential calculations there is no information about the germanides or silicides. For the band gap calculations we only include those materials that have a formation energy less than 0.1 eV/atom above the convex hull and are therefore predicted to be metastable and potentially synthesizable. The formation energy values compiled in the Materials Project database are calculated with DFT at 0 K and 0 atm, taking the pure elemental phases as the reference. These methods neglect potentially important kinetic factors for interfacial chemistry; the accuracy of the oxidation/reduction potential calculations is dependent upon the completeness of the phase diagrams in the Materials Project, but we consider them to be the most accurate methods currently available. All structural data are downloaded from the Materials Project database through the REST API and processed with the pymatgen Python library.

Evaluating ionic conductivity in candidate materials requires either time-consuming experimental synthesis efforts or computationally expensive methods like molecular dynamics simulations or diffusion barrier calculations for single crystals. It is likely that either approach requires at least several days to weeks per material, and computational approaches are unable to study the polycrystalline forms employed in devices. Instead of computing ionic conductivity in these many hundreds of materials, we employ a structure matching algorithm developed in our previous work. This model compares essential structural features of candidate materials to those observed in 40 well-known, diverse Li-ion conductors and returns a percentage match between the candidate material and the fast conducting reference materials (the “superionic likelihood”). These features include the lithium–lithium bond number (LLB), the anion framework coordination (AFC), the sublattice bond ionicity (SBI), the Li–anion separation distance (LASD), and the Li–Li separation distance (LLSD). The model is a logistic regression classifier, trained by optimizing the leave-one-out cross-validation error across combinatorial feature selection; we refer the reader to ref 20 for full details, including lists of promising candidate stable Li-ion conductor materials.

Over 300000 GPU-hours of DFT simulation have been performed to benchmark the accuracy of this structure-matching model against DFT predictions of ionic conductivity, and this work reported the model to identify room temperature superionic Li conductors ~3 times more effectively than completely random guesswork. In this previous benchmarking study, the F1 score for correct superionic identification of the model is reported to be 0.5, where the F1 score is defined as the harmonic mean of the model precision, i.e., the fraction of positive model predictions that are true positives, and the model recall, i.e., the fraction of true positives that are positive model predictions. The F1 score for correct superionic identification via completely random guesswork is reported to be 0.14. This suggests the model possesses a useful degree of predictive power. Furthermore, the DFT evidence suggests the materials identified by this model
possess a log-average conductivity more than 44 times greater than that of randomly chosen materials. Importantly, this model is at least 5 orders of magnitude faster to evaluate than density functional theory simulations. Additionally, the model is trained on experimental conductivity measurements where microstructure may play a role; DFT simulations are limited to the range of hundreds of atoms, and so such predictions are beyond the capability of DFT and a data-driven approach is required. Although we do not expect 100% accuracy from the current form of this model, it does capture general structural trends based on the existing data used for training. For the purposes of this analysis, we assume the model represents the “ground truth” of conductivity. We expect this model to improve as the amount of data and collective wisdom surrounding Li ion conductors grows.

The form of the structure-matching model is the following:

\[ P_{\text{superionic}} = \frac{1}{1 + \exp(-\theta_T x)} \]

where

\[ \theta_T x = 0.184 \times \text{LLB} - 4.009 \times \text{SBI} - 0.467 \times \text{AFC} + 8.699 \times \text{LASD} - 2.170 \times \text{LLSD} - 6.564 \]

We refer the reader to section 3.3 and the Supporting Information of ref 20 for further discussion of these structural features and their implication for design thinking in superionic conductors.

Figure 1. Property spectrum of solid Li-ion conductor candidates by anion family. We plot predicted metrics of electrochemical stability against predicted likelihood of superionic conduction for stable Li-containing crystalline solid materials from the Materials Project database. These materials have the general composition \( \text{Li}(\text{X})\text{Y} \), where \( \text{X} \) is any combination of elements and \( \text{Y} \) is an anion from the following group: F, O, S, Cl, Br, I, N, P, F, Si, or Ge. In (a) we plot the predicted electrochemical window width (based on the DFT-calculated band gap in the Materials Project) against the superionic likelihood for the stable Li-containing materials. Materials in the upper right quadrant of the plot (>50% chance of fast ion conduction and >4 V stability window width) are considered promising candidates. In (b) we plot the centroid of each family and the ellipse that captures one standard deviation of the data as a rough guide to the eye. The chlorides, bromides, and iodides appear to be promising candidates for wide stability window, fast ion conducting structures. In (c) and (d) we plot the predicted thermodynamic oxidation potential (based on the DFT-calculated formation energies and the phase diagram tools in the Materials Project) against the superionic likelihood and see that the fluorides are particularly robust against oxidation while the nitrides and phosphides are not. The anion electronegativity appears to be positively correlated to the oxidation potential and negatively correlated to superionic likelihood; the electronegativities of the anions are provided as reference. In (e) and (f) we plot the predicted reduction potential (from the Materials Project) against the superionic likelihood and note that the nitrides and phosphides are particularly stable against lithium.
Table 1. Likelihood of New High Performance Outlier Discovery by Anion Family

| Anion Family | Likely Fast Li-ion Conductor, >4 V Window | Likely Fast Li-ion Conductor, Stable Above 4 V | Likely Fast Li-ion Conductor, Stable at 0 V and Above 4 V | Any Li-ion Conductivity, >4 V Window | Any Li-ion Conductivity, Stable Above 4 V | Any Li-ion Conductivity, Stable at 0 V and Above 4 V | Mean Likelihood of Fast Li-ion Conduction, Any Stability |
|--------------|------------------------------------------|-----------------------------------------------|--------------------------------------------------------|---------------------------------------|-------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| F            | <0.1% (<0.1%)                            | <0.1% (<0.1%)                                 | <0.1% (<0.1%)                                           | 9.1% (17%)                           | 91% (84%)                                 | 1.0% (4.4%)                                             | 0.9% (3.7%)                                             |
| O            | <0.1% (<0.1%)                            | <0.1% (<0.1%)                                 | <0.1% (<0.1%)                                           | 3.6% (2.7%)                           | 18% (22%)                                 | 2.8% (2.3%)                                             | 0.5% (0.5%)                                             |
| Cl           | 15% (4.1%)                               | 16% (6.3%)                                    | 4.0% (1.2%)                                            | 35% (24%)                             | 68% (42%)                                 | 12% (4.9%)                                             | 8.2% (2.1%)                                             |
| N            | <0.1% (0.4%)                             | <0.1% (<0.1%)                                 | 9.6% (8.5%)                                            | <0.1% (<0.1%)                          | <0.1% (<0.1%)                                 | 51% (28%)                                             | <0.1% (<0.1%)                                             |
| Br           | 14% (9.1%)                               | <0.1% (4.0%)                                   | <0.1% (0.2%)                                            | 52% (27%)                             | 14% (27%)                                 | 14% (6.7%)                                             | 2.0% (1.8%)                                             |
| I            | 9.1% (1.3%)                              | <0.1% (<0.1%)                                 | <0.1% (<0.1%)                                           | 55% (26%)                             | <0.1% (<0.1%)                                 | 17% (2.7%)                                             | <0.1% (<0.1%)                                             |
| S            | <0.1% (0.5%)                             | <0.1% (<0.1%)                                 | <0.1% (0.2%)                                            | <0.1% (0.3%)                          | <0.1% (<0.1%)                                 | 1.8% (0.3%)                                             | <0.1% (<0.1%)                                             |
| P            | <0.1% (<0.1%)                            | <0.1% (0.1%)                                   | 9.4% (8.0%)                                            | <0.1% (<0.1%)                          | <0.1% (<0.1%)                                 | 16% (9.3%)                                             | <0.1% (<0.1%)                                             |
| Ge           | <0.1% (<0.1%)                            | <0.1% (<0.1%)                                 | <0.1% (<0.1%)                                           | 0.1% (<0.1%)                          | <0.1% (0.1%)                                 | 91%                                                   | 91%                                                   |
| Si           | <0.1% (<0.1%)                            | <0.1% (<0.1%)                                 | <0.1% (<0.1%)                                           | 0.1% (<0.1%)                          | <0.1% (<0.1%)                                 | 91%                                                   | 91%                                                   |

For each of the anion families, we calculate the percentage of the underlying data distribution that exists in the high performance region of performance space. This percentage represents the likelihood that a new stable material from this family will satisfy these requirements if sampled at random from the existing data distribution. This calculation is done by binning the most promising materials. In parentheses we provide the results from modeling the data distributions as Gaussian and integrating to find the cumulative probability; we see alignment generally within a factor of 2 in these numbers. Significant likelihoods are in bold. The bromides, chlorides, and iodides are the best candidates for a fast conducting, >4 V window width structure. The chlorides and bromides are also particularly likely to exhibit fast ion conduction and possess an oxidation potential above 4 V. If ionic conductivity is unimportant and only high anodic stability is desired, the fluorides are the most promising candidates. The nitrides and phosphides are the most promising class of materials for fast ion conductors that are stable against lithium metal. If ionic conductivity is not a requirement, the bromides are promising as well. No families have significant likelihoods of yielding materials that are fast conducting, stable against lithium metal, and have a >4 V oxidation potential. This suggests that it is much more likely to realize a >4 V solid-state Li metal battery with two electrolytes rather than one ideal material; the Gaussian integration method suggests the likelihood of success of a double-electrolyte architecture is ~2 magnitudes greater.
i. Optimizing for a Wide Stability Window. Using the band gap as an upper bound on the electrochemical window width, we plot this value against the superionic likelihood for all 6600 materials in Figure 1a. We note that DFT formation energy calculations predict only 11% (723) of these 6600 candidates to be on the convex hull, i.e., are thermodynamically stable. The remaining 89% of these materials are predicted to be metastable. Training a model on as large a data set as possible is crucial for any data-driven effort, and we justify using the band gap instead of the DFT-computed thermodynamic electrochemical stability window width because it allows us to train on over 8 times more data points. We leverage the DFT-based grand potential methods in the following subsections ii, iii, and iv where specific potential values are desired rather than window widths.

In total, we compute performance prediction data for 5350 oxides, 790 fluorides, 172 sulﬁdes, 21 bromides, 46 chlorides, 11 iodides, 75 nitrides, 33 phosphides, 62 germanides, and 40 silicides. Although there is signiﬁcant variance among the data in each family, Figure 1a reproduces the performance trends known among the community: the sulﬁdes generally conduct well but have poor stability; the oxides have poor conductivity and high stability. The sulﬁdes have low conductivity and high stability as well. The alignment of these trends with the conventional wisdom builds conﬁdence in our modeling approach. Relatively few materials are in the promising upper-right quadrant of Figure 1a, reinforcing the difﬁculty of simultaneous optimization.

We replace the data for each family with its centroid (mean value) in the two-dimensional performance space in Figure 1b to clarify the performance distribution of each family. An ellipse that delineates one standard deviation of the two-dimensional data is plotted to guide to the eye. Although the data are fairly noisy, there are clear cases where the distance between means of families is smaller than the standard deviations (e.g., the oxides versus the sulﬁdes). This plot also shows the approximate trend that the average structural similarity to known ion conductors (predicted superionic likelihood) decreases and the electrochemical stability increases as the electronegativity of the anion increases. The strongly electronegative anion families are more likely to form strong ionic bonds, apparently improving stability but decreasing conductivity. Pure lithium metal represents the limit of zero electronegativity difference between Li atoms and the anion lattice, yielding a notoriously reactive but superb lithium conductor.

We have also extended this analysis to the polyaniionic oxide compounds, where the anion Y may be one of P2O5, B2O3, Si2O5, F2O7, C2O4, Sb2O5, SnO2, TeO4, S2O7, Ge2O7, N2O7, or ClO7. We ﬁnd the general performance trends tend to mirror that of the oxides, and because of this similarity we exclude these data from Figure 1.

To quantify these trends, we interpret the two-dimensional data distributions for each family plotted in Figure 1a as a Bayesian prior on electrolyte performance as a function of anion. If future research in each family were to blindly sample from the same probability distribution as these currently known materials, these distributions represent the expected performance of the new materials as a function of anion choice. To calculate the likelihood of encountering a “high performance outlier” as a function of the anion family via sampling new materials in the same way as materials have been sampled historically, we find the fraction of the underlying data distributions that lie beyond the minimum required metrics of 50% likelihood of superionic conduction and a minimum window width of 4 V. We consider these materials to be the most promising candidates. This analysis allows for direct and quantitative comparison of “promise” between diﬀerent anion families as interpreted by these models.

Because PBE DFT-computed band gaps give an upper bound for the electrochemical stability window width, using DFT-computed band gaps as a proxy for electrochemical stability window widths will correspondingly place an upper bound on the likelihood of finding highly electrochemically stable materials. Materials will generally appear to have wider stability windows than in reality, and the model constructed on this data will therefore predict an artiﬁcially higher likelihood of ﬁnding highly stable materials.

We note that the current state of research does not necessarily follow these conditions; i.e., materials are not chosen by choosing an anion and sampling exactly from that anion’s existing performance distribution. In practice, researchers may only study a subset of a given anion family and may employ design principles with signiﬁcant predictive power. Indeed, some materials discovery eﬀorts are more likely to succeed than others depending on the strategy employed. We emphasize that does not strictly quantify the likelihood of a breakthrough discovery coming from any given research eﬀort but rather quantiﬁes the broad performance of entire material families based only on the anion. Rather than classifying the families by anion, one could classify materials by structural motifs, e.g., garnets, which could give different values of .

The underlying distributions are not well-known and are diﬃcult to infer with small amounts of data. We note in some cases the data approximately follow Gaussian behavior, e.g., the oxides in Figure 1c, while sometimes the data are less Gaussian, e.g., the bromides in Figure 1a. To see the underlying distributions more clearly, we plot the histograms of each performance metric for each anion family in the Supporting Information (Figure S1).

Without clear knowledge of the underlying distributions, we compute the probability of discovering promising new materials from each family by counting the fraction of materials from each family above the minimum required performance metrics (“binning”). It is unavoidable that not every promising candidate material will demonstrate superior performance experimentally (i.e., the models have some error), but we expect the overall performance distribution of each family to possess a degree of statistical accuracy.

The performance of material is deﬁned by its superionic likelihood and predicted electrochemical stability window width . The binning approach counts the fraction of materials in each family with or .

Here the I(X) symbol denotes the indicator function, which evaluates to 1 if the argument X is true and 0 otherwise. The numerator represents the number of materials in the upper-right quadrant of the graph for a given family, and the denominator represents the total number of materials in that family. The likelihoods for each family are provided in the second-to-left column of Table 1.
In addition to this binning method, we also compute the likelihood of high performance outliers in each family by fitting the data to a two-dimensional Gaussian distribution and then finding the cumulative probability of the distribution beyond the minimum required performance metrics via integration. This method relies on the data being approximately normally distributed. This method is detailed in the Supporting Information, section S1, along with an assessment of the Gaussian character of the data via the Shapiro–Wilk test for normality in Figure S1. Although some of the distributions are approximately normal, most of the distributions fail the Shapiro–Wilk test. Noting our low confidence in the normality of the data, we provide the results of this alternative test in parentheses in Table 1. We take the binning method to be more precise as it does not assume an underlying distribution. Interestingly, in most cases the results from the two methods align within approximately a factor of 2. This suggests that despite the question of normality of the data, the results are not overly sensitive to whether the binning or Gaussian method is used.

These data predict that the likelihood of discovery of a fast Li conducting material with a stability window width beyond 4 V from all known oxides, given the existing data, is quantitatively much smaller than other anion families. This might suggest that continued efforts in searching the oxides generally for SEs in single-electrolyte architectures are better invested in other families, although there has been interest in oxides for other applications including resistive electronic memories. The fluorides are also a poor prospect for this battery architecture. The Gaussian integration method suggests the likelihood of high performance outliers coming from the sulfides is relatively low yet higher than for the oxides and fluorides. From this data, we derive the following insight: given what has been discovered so far, one is more likely to find a fast conducting, >4 V window sulfide high performance outlier than an oxide. Essentially, this suggests one is marginally more likely to overcome stability issues with sulfides than conductivity issues with oxides.

Uneven sampling of these distributions has the potential to impact uncertainty in the computed $P_{\text{outlier}}$. The poor performance of the oxides generally is unaffected by the fact that a large number of Li-containing oxides are known, having been synthesized and characterized in much greater number than any other family. This might suggest that continued efforts in searching the oxides for SEs in single-electrolyte architectures are better invested in other families, although there has been interest in oxides for other applications including resistive electronic memories. The fluorides are also a poor prospect for this battery architecture. The Gaussian integration method suggests the likelihood of high performance outliers coming from the sulfides is relatively low yet higher than for the oxides and fluorides. From this data, we derive the following insight: given what has been discovered so far, one is more likely to find a fast conducting, >4 V window sulfide high performance outlier than an oxide. Essentially, this suggests one is marginally more likely to overcome stability issues with sulfides than conductivity issues with oxides.

Uneven sampling of these distributions has the potential to impact uncertainty in the computed $P_{\text{outlier}}$. The poor performance of the oxides generally is unaffected by the fact that a large number of Li-containing oxides are known, having been synthesized and characterized in much higher volume many years before the other families, and may be overrepresented in materials databases such as the Materials Project. By contrast, Li-containing sulfides have only been the focus of major research efforts within the past decade, making the average known Li-containing sulfide a much better conductor than the average known Li-containing oxide. The conclusions claimed here pertain to random selection from the anion family as a whole based strictly on the distribution of known materials which may be biased. Additionally, this analysis should not be interpreted as commenting on the promise of specific structure types within each family, e.g., the garnet oxides.

Both methods reveal that the most promising classes appear to be the often overlooked halides (excluding fluorine): the chlorides, bromides, and iodides show the highest likelihoods. These materials have been less exhaustively investigated than the oxides and sulfides, so a much smaller pool of data is available for both model training and for screening (for screening, there are only 46 chlorides, 21 bromides, and 11 iodides, versus 5350 oxides), but the existing data suggest new efforts in this area may be worth the investment. The phosphides, silicides, and germanides appear to have major stability issues and thus may not be appropriate for battery applications, although their average conduction properties are much better than other families. These results are line with recently published work by Muy et al., in which the authors performed the first high-throughput screening of all known Li-containing solids for candidates with simultaneously fast ion conduction and wide electrochemical stability windows using predictive descriptors rooted in lattice dynamics; of the 18 most promising materials identified from the 14000+ screened, 11 were halide-based (9 chlorides and 2 bromides), two were oxides, and none were sulfides. Our model’s independent reproduction of this trend provides confidence in the modeling approach.

For comparison, we also calculate the likelihood of discovery of materials only with window width above 4 V and not considering our superionic structure matching model. These results are provided in Table 1. With this selection criteria, the non-fluoride halides remain promising and the promise of the (poorly conducting) fluorides increases, as we might expect.

We note that the chlorides, bromides, and iodides are the families with the smallest amount of structural data in this study. Given that small data sets are more likely to deviate from their true underlying distributions, the results for these particular families are the least likely to be converged; the addition of new data may change these predictions in perhaps significant ways. The $p$ values in section S1 of the Supporting Information attest to the degree of convergence in each case. Regardless, one may safely make the following claims: statistically representative or not, the current set of existing data suggest significant promise among these families, and that more data should be gathered on the performance of these promising classes of ion conductors.

It should also be reiterated that there is significant variation within each family, and the likelihood data in Table 1 are a statistical average over the performance data of all known materials in each family. Taking additional design principles into consideration during the materials search beyond just anion choice may result in better observed material performance on average. Furthermore, we note that, in practice, such strong constraints on electrochemical stability may not be necessary, as the solid–electrolyte interphase (SEI) may stabilize the electrolyte against interfacial reactions. However, without a priori knowledge of the interfacial chemistry arising from a given electrolyte/electrode combination, we assume these strict demands must be met in candidate materials to minimize false positives.

**ii. Stability against High-Voltage Cathodes.** An alternative strategy for enabling high energy density SSBs is to use a multiple-electrolyte architecture, where a high oxidation potential electrolyte/coating is placed on the cathode and a low reduction potential electrolyte/coating is placed on the anode as proposed by Richards et al. In this approach, the objective of a materials search for cathode coatings is to discover a fast Li-ion conductor material with an oxidation potential beyond 4 V vs Li+/Li. Ideally, the cathode voltages in candidate SSB chemistry should be 5 V vs Li+/Li or higher to drive significant improvement over existing LIB technology.

We compute the superionic likelihood and predicted oxidation potential for as many candidates as possible and quantify the likelihood of discovering high performance outliers in each family. Here we consider the oxidation...
Li metal batteries than single-electrolyte architectures. More likely than fast Li-ion conducting materials, one of which that is stable against reduction at 0 V and one of which is stable against oxidation at 4 V, is much predicted superionic likelihood for all 723 entries, and in inverse correlation (Pearson correlation coefficient -0.5) between ionic conductivity and oxidation potential. In this case the trend of ionic conductivity with oxidation potential is more pronounced than it was with ionic conductivity and stability potential listed in the Materials Project database for 723 materials based on DFT grand potential methods. In all, we consider 427 oxides, 56 sulfides, 97 fluorides, 25 chlorides, 7 bromides, 6 iodides, 73 nitrides, and 32 phosphides. With this smaller pool of materials under consideration, there is no data available for the silicides or germanides.

In Figure 1c we plot the predicted oxidation potential versus predicted superionic likelihood for all 723 entries, and in Figure 1d we replace the data with the centroids and standard deviations to guide the eye. In Figure 1d, we see a moderate inverse correlation (Pearson correlation coefficient of -0.5) between ionic conductivity and oxidation potential. In this case the trend of ionic conductivity with oxidation potential is more pronounced than it was with ionic conductivity and stability window width in Figure 1b (which had only a Pearson correlation coefficient of -0.1). The electronegativities of the anions are provided in Figure 1d for reference. The oxides and sulfides appear to be too ionically insulating and too unstable, respectively. We note again that the non-fluoride halides, with their electronegativities somewhere between the too-stable oxides and the too-unstable sulfides, appear to be particularly promising candidates for this purpose.

We bin this data as before, now using the bounds of >50% superionic likelihood and oxidation potential \( V_{\text{ox}} \geq 4 \text{ V} \): 

\[
P_{\text{outlier}} = \frac{\sum_{i=1}^{N} \mathbb{I}(p^{(i)}_{\text{superionic}} > 50\%) \times \mathbb{I}(V^{(i)}_{\text{ox}} \geq 4 \text{ V})}{N}
\]

These likelihoods are provided in Table 1 along with the likelihoods from the Gaussian method.

Recent reports suggest that cathode coatings may be made thin enough that materials with poor ionic conductivity are acceptable.44,45 In this case, a materials search would only seek high anodic stability. We compute the likelihood of finding materials with high oxidation potential, regardless of predicted ionic conductivity, for each family and provide the results in Table 1. Perhaps unsurprisingly, the fluorides are the strongest candidates by far.

**iii. Stability against Lithium Metal.** The multiple-electrolyte architecture also requires the discovery of fast Li-ion conducting materials that are stable against Li metal as the anode-facing electrolyte. Using the same pool of candidate materials and the same methods as in the previous section, we analyze the reduction potential of all 723 candidate materials against the superionic likelihood. In Figure 1e we plot the results for all materials, and in Figure 1f we visualize the distributions. The likelihoods for discovery in this case are found by counting those materials with a reduction potential of \( V_{\text{red}} \leq 0 \text{ V} \):

\[
P_{\text{outlier}} = \frac{\sum_{i=1}^{N} \mathbb{I}(p^{(i)}_{\text{superionic}} > 50\%) \times \mathbb{I}(V^{(i)}_{\text{red}} \leq 0 \text{ V})}{N}
\]

These results are provided in Table 1. We observe particularly high stability against Li metal in the nitrides, a trend recently noted by Zhu et al.46 The phosphides also appear to be promising candidates. Li,P is a case in point: its electrochemical window is narrow (~1 V), but it is a fast ion conductor that is stable against Li metal.59 It has been experimentally observed to form at the Li-metal/LGPS interface, where its fast ion conduction properties are particularly beneficial.

As is the case with cathode coatings, anode coatings may be made thin enough that ionic conductivity becomes a less important constraint. In this case, we compute the likelihood of high performance outlier discovery of a material with high stability against Li metal in each family, regardless of predicted ionic conductivity, and provide them Table 1. This is the only category where all anion families considered have a nonzero likelihood, although the nitrides are much more likely than others.

**iv. Fast Ionic Conductivity, Stability against Li Metal, and High Oxidation Potential: Does the “Wonder Material”
Exist? The ideal electrolyte material is a fast ion conductor that is stable against lithium metal and simultaneously has a high oxidation potential. Leveraging the known likelihoods for zero reduction potential and oxidation potential given in Table 1, we compute the joint probability that a material from a given anion family is stable against lithium metal and has an oxidation potential $V_{\text{ox}}$ that is above a minimum $V_{\text{ox,min}}$. Treating the oxidation potential as independent of the reduction potential, the intersection of these two requirements requires a product of probabilities:

$$P_{\text{outlier}}(V_{\text{red}} \leq 0, V_{\text{ox}} \geq V_{\text{ox,min}}) = P_{\text{outlier}}(V_{\text{red}} \leq 0) \times P_{\text{outlier}}(V_{\text{ox}} \geq V_{\text{ox,min}})$$

The results of this calculation are provided for $V_{\text{ox,min}} = 4$ V in Table 1, and as a function of $V_{\text{ox,min}}$ in Figure 2, by using the Gaussian integration method. The Gaussian integration method is used over the binning method because a continuous probability distribution is required to evaluate the above expression and extrapolate likelihoods beyond the current spread of the data. The results from this approach will be most accurate in the cases where the underlying distributions are most normal (see the Supporting Information, section S1).

We compute the error bars in Figure 2 by computing the standard deviation in the Gaussian integration results upon systemically removing a unique set of 10% of the data from each anion family ten separate times and redoing the Gaussian integration on the remaining 90% of the anion family data each time. We note that the correlation among different realizations of the 90% remaining data set may result in an underestimate the true error. We compute this metric to assess how sensitive the results are to the size of the data set used in the analysis; the relatively small error bars ($\pm 1\%$) in Figure 2 suggests the results are largely stable under a 10% removal of the data.

When ionic conductivity is considered, the phosphides and nitrides are the only families with significant likelihoods, although they fall to zero near $V_{\text{ox,min}} = 2$ V. The chlorides are the only family with a nonzero likelihood (0.6%) at $V_{\text{ox,min}} = 4$ V. This means one is very unlikely to discover a high performance outlier material in any family with fast ion conduction, stability against lithium metal, and $>4$ V stability against oxidation. In fact, according to the Gaussian method, this data suggests that superionic materials with a $>4$ V stability window and stability against Li metal are $\sim 2$ orders of magnitude less common than superionic materials with only a $>4$ V stability window (and arbitrary reduction potential). The outlook is more promising when ionic conductivity is not considered; here the fluorides, oxides, chlorides, and bromides have nonzero likelihood at $V_{\text{ox,min}} = 4$ V. This has implications for the design of solid-state Li-ion batteries with Li metal anodes: it suggests a dual electrolyte architecture is much more likely to be able to meet necessary material performance requirements.

v. Discussion. The results in Figure 1 suggest some correlation exists between ionic conductivity and electrochemical stability. This negative trend is particularly apparent between oxidation potential and ionic conductivity, where the electronegativity of the anion in the lattice appears to play a significant role.

This negative correlation, and the relatively small discovery likelihood percentages in Table 1, quantitatively reinforce that simultaneously optimizing a material for both ionic conductivity and a wide electrochemical stability window is a difficult task indeed. It appears to be even more difficult when requiring stability against lithium metal. Judging by their relative positions in performance space, exploring oxide and sulfide materials appears to be more difficult than the chlorides, bromides, and iodides. The odds are not much higher for the multiple-electrolyte strategy either, although the data do offer a most likely way forward: a nitride-based SE on the anode and a chloride- or bromide-based SE on the cathode or a thin, nonsuperionic conductor fluoride-based cathode coating. We note the combination of a thin fluoride-based cathode coating that does not need to be a superionic conductor ($\sim 90\%$ likelihood) and a fast conducting nitride-based anode coating ($\sim 10\%$ likelihood) has similar predicted likelihood of success (90% x 10% = 9%) to the discovery of a fast conducting bromide with a window width beyond 4 V ($\sim 10\%$). However, the likelihood of discovering a chloride “wonder material” that is stable against Li metal ($\sim 4\%$) and has an oxidation potential of $>4$ V ($\sim 16\%$) is more than an order of magnitude less likely by using the binning method (4% x 16% = 0.6%) and 2 orders of magnitude less likely by using the Gaussian method (6% x 1% = 0.06%), suggesting that the successful realization of a SSBs with Li metal anode is more likely with a dual electrolyte architecture.

In Figure S2 we provide the high performance outlier discovery likelihoods computed with the Gaussian integration method for arbitrary window widths, minimum oxidation potentials, and maximum reduction potentials, with and without requiring fast ionic conductivity. The small magnitude of the high performance outlier discovery likelihood values computed in this section also highlight the importance of considering kinetic electrochemical stability in candidate materials. Although some material families have significant discovery likelihoods for certain applications, the data suggest the outlook for simultaneous conductivity/stability optimization is generally poor when requiring thermodynamic stability. However, kinetic stabilization may enable the use of fast Li-ion conductors with limited thermodynamic stability. To our knowledge, no data-driven or first-principles tools exist for rapidly assessing the kinetic stability of materials exposed to a chemical potential, although such tools would clearly be of high value to the community’s ability to perform efficient searches of materials’ space.

Additional Correlations with Ionic Conductivity: Mechanical Properties, Layered Structure. Mechanical properties are an important contributor to overall solid electrolyte performance. There are several complex and potentially conflicting mechanical demands put on candidate SE materials; e.g., a material should be “soft” enough to maintain contact with rough electrode surfaces while simultaneously being “hard” enough to block dendritic growth and withstand abuse without cracking. The development of fast, machine-learned models for predicting elastic properties is an ongoing area of research, and large amounts of elastic property data on Li-containing materials do not yet exist. This makes extrapolating from the small amount of existing materials data difficult.

Recent work from the Ong group reported computed elastic properties for 23 well-known inorganic crystalline SE materials. Their report suggests the shear modulus (which was used as a metric for stability against dendritic growth) is correlated to the electronegativity of the anion in the lattice and is inversely correlated to ionic conductivity. If high ionic conductivity, high shear modulus SE materials are desired, an
additional difficult optimization process may lie beyond the electrochemical stability/ionic conductivity optimization.

Additionally, we predict that materials with Li intercalated into two-dimensional layered structures (i.e., layers held together by van der Waals forces) are significantly less likely to exhibit fast Li-ion conductivity than nonlayered materials. Today’s lithium-ion batteries utilize layered materials to achieve lithium intercalation on both cathode and anode; superionic layered materials could feasibly function as solid-state electrolytes as well. Having identified the subset of layered structures that exhibit weak interlayer bonding and strong intralayer bonding in the Materials Project database in our previous work,\textsuperscript{50} we compute the probability that a stable material is predicted to contain the necessary structural characteristics to be a fast ion conductor, given that it is a layered structure with intercalated lithium, is only 5%. This is a factor of 2 lower than the predicted 10% background probability that a stable lithium containing solid is a superionic conductor. The posterior distribution is similar: the likelihood of being layered, given that a material is predicted to be a superionic conductor, is 10% and also a factor of 2 lower than the 21% background probability that any stable Li-containing compound is layered. This analysis is based on the set of currently known layered structures; we refer the reader to ref 50 for more details on these materials.

The existing data suggest that layeredness decreases the likelihood of fast ion conduction in a candidate material by half. Although undiscovered layered superionic conductors may exist, we predict layeredness itself is a poor indicator of fast ion conduction. This suggests that optimizing layered cathode materials for fast rate capability is likely to be more difficult than optimizing nonlayered cathode materials, although bulk materials generally introduce an additional difficulty with electrochemical expansion upon lithiation.

Costs and Manufacturing. The cost of solid electrolyte materials is a metric of critical importance. The U.S. Department of Energy’s Advanced Research Projects Agency—Energy (ARPA-E) has adopted an aggressive cost target of $10 (USD)/m² for electrolyte materials, as originally proposed by McCloskey.\textsuperscript{51} The overall cost is broken down into materials cost and processing cost.

In Figure 3 we plot the median raw materials cost per area per 10 μm thickness for the materials in each family, following the values provided in the Supporting Information of ref 20. Overlaid on this graph is the materials cost per mole of the anion. Raw materials costs change in time, and several of these reference values are already significantly different from current prices; in most cases the current prices are lower than utilized in Figure 3. Even when recognizing these values are likely upper bounds on material costs, the median cost for all families except the fluorides and germanides is below the $10/m² threshold. The standard deviation in the cost data is very large. However, with these cost values we find that 70% of all 6600 candidate materials considered here fall below this cost target before processing costs are considered. Because it is more likely than not that a candidate material will meet this cost target, we conclude materials cost is unlikely to be a significant barrier, and the larger amount of material required for multiple-electrolyte architectures may be acceptable.

Excluding compositions with particularly expensive elements (e.g., Sc, Ge, Rb, Ru, Rh, Cs, Yb, Os, etc.) from consideration will increase the likelihood of candidate materials being under the cost target. Making electrolytes thinner will also scale materials costs down linearly, but the manufacture of thin ceramic materials is difficult and manufacturing costs will likely begin to increase as the materials approach single micrometer thickness or thinner. In addition, many materials often become very brittle in this thickness regime; brittle electrolytes may crack or pulverize during use, decreasing ionic contact and enabling dendritic growth. In this respect, cost concerns would dictate that candidate SE materials should be made flexible or should have high fracture toughness.

The manufacturing processes and costs of materials are difficult to generalize, but the anion in the structure can have a significant effect on the methods and ease of synthesis at the laboratory scale. Oxides have perhaps the greatest ease of manufacture due to the natural oxidation that occurs when precursors are exposed to air. Most other compounds must be synthesized either in a dry room or under inert gas or vacuum to minimize unwanted reactions with atmospheric oxygen. Sulfides and phosphides, the two most electropositive anions considered here, have additional issues with water sensitivity and therefore must be carefully sealed to minimize unwanted hydrolysis. Fluorides are often synthesized from HF gas, which reacts with moisture in the air to form dangerous hydrofluoric acid. The chlorides, bromides, and iodides, highlighted in the previous section for their promise, can typically be synthesized in solution, a much easier process than the solid state synthesis required of sulfides. This may make the non-fluoride halides an even more attractive family for laboratory scale study.

These various restrictions make laboratory scale synthesis of certain conductor families difficult, creating a barrier to studying candidates outside of the oxides. Moving outside the oxides, however, appears to be critical to driving the field forward. Exploring these alternative families will likely increase financial and time costs for research laboratories, but costs and other manufacturing barriers tend to scale away at the industrial level. The cost of synthesizing and studying Li conductors from unconventional families may be high in the short run, creating barriers to new materials discovery, but once these high performance materials are discovered the anion type will likely have limited to no impact on the ability for promising new chemistries to hit industrial cost targets.
Table 2. Maximal Information Coefficients and Pearson Correlation Coefficients for the Observed Correlations between Important Solid Electrolyte Properties

|                                 | superionic likelihood | electrochemical stability window width | oxidation potential | reduction potential | materials cost | anion electronegativity |
|---------------------------------|-----------------------|----------------------------------------|---------------------|--------------------|----------------|------------------------|
| superionic likelihood           | 1.0, 1.0              | 0.12, −0.10                            | 0.43, −0.49         | 0.25, −0.28        | 0.13, 0.08     | 0.22, −0.71            |
| electrochemical stability window | 0.12, −0.10           | 1.0, 1.0                               | 0.25, 0.41          | 0.23, −0.26        | 0.17, −0.02     | 0.12, 0.19             |
| oxidation potential             | 0.43, −0.49           | 0.25, 0.41                             | 1.0, 1.0            | 0.34, 0.50         | 0.27, 0.04     | 0.54, 0.72             |
| reduction potential             | 0.25, −0.28           | 0.23, −0.26                            | 0.34, 0.50          | 1.0, 1.0           | 0.23, 0.09     | 0.31, 0.49             |
| materials cost                  | 0.13, 0.08            | 0.17, −0.02                            | 0.27, 0.04          | 0.23, 0.09         | 1.0, 1.0       | 0.37, 0.03             |
| anion electronegativity         | 0.22, −0.71           | 0.12, 0.19                             | 0.54, 0.72          | 0.31, 0.49         | 0.37, 0.03     | 1.0, 1.0               |

*Correlations between predicted performance metrics in hundreds to thousands of candidate solid Li-ion electrolyte materials are quantified here, where the first number in each box is the maximal information coefficient (MIC) and the second number is the Pearson correlation coefficient. We note that the MIC quantifies nonlinear structure among the data and is always positive, while the Pearson correlation coefficient quantifies linear structure among the data and the sign represents the direction of the linear correlation. We note a negative correlation between superionic likelihood and the three different indicators of electrochemical stability. We also note that the electronegativity of the anion in the lattice exhibits substantive correlations with most properties except materials cost. Materials cost shows low correlations with all properties.

### III. CONCLUSIONS

By taking a data-driven approach, we uncover correlations between several fundamental performance metrics in SEs that would be difficult to observe from first-principles approaches. We emphasize that this data-driven approach can identify correlations among properties but cannot necessarily identify causal relationships. To summarize and quantify these correlations, we compute the Maximal information coefficients using the MinePy library and the Pearson correlation coefficients between ionic conductivity, electrochemical window width/band gap, oxidation potential, reduction potential, materials cost, and anion electronegativity for all candidate materials. These correlation coefficients are provided in Table 2. Although some metrics such as cost have low correlation with other metrics, we find the magnitude of the Pearson correlation coefficient is as high as 0.5 between ionic conductivity and oxidation potential.

We draw four central conclusions from this data: (1) Some material families are more likely to yield high performance outliers for certain applications, and this is quantified in Table 1. (2) The coating/multiple-electrolyte strategy appears to have a similar likelihood of success to finding a > 4 V stability window material for a one-electrolyte architecture, although the multiple-electrolyte architecture is over 10 times more likely to be successful when stability against lithium is required. (3) The low magnitudes of high performance outlier discovery likelihoods for thermodynamically electrochemically stable fast ion conductors in general highlight the importance of considering kinetic stabilization of fast ion conducting phases. (4) These low magnitudes also underscore the importance of implementing targeted searches of material space informed by data and design principles.

On conclusion 1, we recommend new searches of the chlorides and bromides for fast Li-ion conducting, electrochemically stable materials. Although the volume of data in this space is limited, the existing data points suggest strong overall performance in these families. Recent reports suggest some promising new materials may be emerging from these families. The nitrides appear to be an exciting class of materials for Li-ion conducting materials that are stable against Li metal. The distribution of performance data in the oxides and the sulfides suggest they are less likely to produce the high performance materials required for the SSBs of the future. On conclusion 2, we note a single-electrolyte battery with stability against Li metal appears to be much less likely than a multiple-electrolyte Li metal battery as proposed by Richards et al. This suggests that efforts to develop SSBs with Li metal anodes are more likely to succeed if a multiple-electrolyte architecture is employed. Most candidate materials are under the DOE cost target of $10/m2 when considering raw materials costs only, so thicker electrolytes with multiple layers may be acceptable. The manufacturing costs of these architectures is likely to be higher, however, and this may ultimately determine the cost competitiveness of this strategy.

On conclusion 3, we note that complete thermodynamic stability is a fairly strict requirement for candidate materials, significantly decreasing the likelihood of discovery in most cases. However, some of these thermodynamically unstable materials may be kinetically stable; requiring thermodynamic stability may introduce some false negatives. Future searches should consider kinetic stability, and the development of new tools for rapid prediction of kinetic stability from atomistic structure would be of great value to the community. Finally, on conclusion 4, the existing data warn against continuing to search materials space with the same approaches as have been employed historically, particularly in the oxides and sulfides. Emerging design principles and data-driven efforts provide a new route for beating the odds and identifying the promising high performance outliers. The addition of new data could change some of the conclusions presented here. However, it is clear that the continued development of data-driven predictive models is of utmost importance to seeing accelerated progress in the field, and we expect many exciting new advancements as these efforts expand.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10650.

Description and discussion of the Gaussian integration method; the results of the Shapiro–Wilks test for normality on the material family distributions; high performance outlier discovery likelihoods computed with the Gaussian integration method for the “wonder material”, i.e., the likelihood of high performance outliers that are stable against Li metal and exhibit arbitrary window widths, minimum oxidation potentials, and maximum reduction potentials, both with and without requiring fast ionic conductivity (PDF)
AUTHOR INFORMATION

Corresponding Author

Evan J. Reed — Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States; Phone: (650) 723-2971; Email: evanreed@stanford.edu

Authors

Austin D. Sendek — Department of Materials Science and Engineering, and Department of Applied Physics, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-3338-1615

Gowoon Cheon — Department of Applied Physics, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-3026-6796

Mauro Pasta — Department of Materials, Oxford University, Oxford OX2 6HT, U.K.; orcid.org/0000-0002-2613-4555

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.9b10650

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by a seed grant from the TomKat Center for Sustainable Energy at Stanford University and in part by Toyota Research Institute through the Accelerated Materials Design and Discovery program. The authors thank Prof. Nicole Adelstein, Gowoon Cheon, Dr. Ekin D. Cubuk, William E. Gent, Leonid Kahle, Ruby A. Lai, Prof. Nian Liu, Prof. Robert Sinclair, Dr. Brandon Wood, and Qian Yang for constructive conversations on these ideas.

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