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## Materials design principles of amorphous cathode coatings for lithium-ion battery applications†

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Cathode surface coatings present one of the most popular and effective solutions to suppress cathode degradation and improve cycling performance of lithium-ion batteries (LIBs). In this work, we carry out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for LIBs. Our high-throughput screening includes descriptors to evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, and ionic diffusion of the cathode coatings. In the ionic diffusion analysis, we mainly focus on Li-containing compounds. From the 20 selected materials, we highlight the formidable challenge of mitigating oxygen diffusion when selecting an ideal cathode coating, and suggest 7 promising coating candidates:  $\text{Li}_3\text{B}_{11}\text{O}_{18}$ ,  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{LiB}_3\text{O}_5$ ,  $\text{LiPO}_3$ ,  $\text{LiSb}_3\text{O}_8$ ,  $\text{LiAlSiO}_4$  and  $\text{LiTaSiO}_5$ . Combining the screening results and detailed ionic diffusion analysis of the selected cathode coatings, we summarize the general selection guidelines of amorphous cathode coatings for LIBs.

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## Introduction

Lithium-ion batteries (LIBs) are ubiquitous in portable electronic devices and have enabled the development of cleaner energy storage and electric vehicles (EVs). For the past decade, LIB-powered EVs have gradually penetrated the automotive market. With an increasing demand of reducing greenhouse gas emissions, the global fleet of EVs will continue to rise for the coming decade.<sup>1</sup> Future improvements in LIBs include high energy density cathode materials to enable longer driving range; however these materials frequently operate at high potential and experience surface degradation with associated performance degradation under extended cycling. The current commercialized cathode materials of LIBs are classified as layered ( $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ , NMC), spinel ( $\text{LiMn}_2\text{O}_4$ ) and olivine ( $\text{LiFePO}_4$ ). Regardless of their crystal structure, these cathode materials all exhibit surface degradation and detrimental surface phase transformations, which compromise the cycle life and thermal stability of LIBs. For example, upon a higher voltage operation ( $>4.3$  V), surface oxygen evolution triggers an irreversible transformation in NMC cathodes from layered phase into a mixture of spinel and rock salt phases that deteriorates capacity retention.<sup>2</sup> Similarly, in  $\text{LiMn}_2\text{O}_4$ , surface

oxygen loss causes considerable compressive lattice strain, which densifies the cathode surface and blocks the Li-migration pathways.<sup>3</sup> The  $\text{LiFePO}_4$  cathode exhibits an excellent capacity retention, however, its eventual failure is associated with the surface amorphization and oxygen loss after the prolonged cycling.<sup>4</sup> In addition, side reactions between the electrolyte and cathode lead to transition metals dissolution and surface impedance build-up, which further accelerate the capacity/voltage fade.<sup>5</sup> Therefore, it is of high interest to engineer the cathode surface to achieve high energy density LIBs with a stable, safe, and long-term cycling performance.<sup>56</sup>

A common strategy to stabilize the cathode surface is to apply a multifunctional protective layer to mitigate surface degradation and simultaneously maintain facile  $\text{Li}^+$  transport.<sup>6</sup> Such cathode coatings typically exhibit an amorphous character, with a thickness between 1 to 10 nm.<sup>7,8</sup> A variety of coating materials have been explored and shown varying degrees of effectiveness in enhancing the cyclability of LIBs, such as metal oxides (e.g.,  $\text{Al}_2\text{O}_3$  (ref. 9)), nonmetal oxides (e.g.,  $\text{B}_2\text{O}_3$  (ref. 10)), polyanionic oxides (e.g.,  $\text{Li}_3\text{B}_{11}\text{O}_{18}$  (ref. 11)), and fluorides (e.g.,  $\text{AlF}_3$  (ref. 12)), etc. However, several reported cathode coatings have been found to exhibit chemical and/or electrochemical instability and large overpotential during cycling. For example,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  effectively mitigate the side reactions of the cathode surface with the electrolyte,<sup>9,13</sup> however, the metal oxide coating layer forms a metal oxyfluoride or a metal fluoride layer by scavenging  $\text{F}^-$  from HF in the electrolyte.<sup>13,14</sup> Furthermore, because of its inherent low  $\text{Li}^+$  ion diffusivity,  $\text{Al}_2\text{O}_3$  coatings can lead to large overpotentials and reduced capacity, even at a thickness as low as 2 nm.<sup>15,16</sup> On the other hand, Li-containing compounds have been found to exhibit better capacity retention than their non-

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lithiated counterparts, due to their improved ability to transport  $\text{Li}^+$ .<sup>17</sup> However, a recent study found that an NMC cathode surface still transforms from a layered structure into an oxygen loss-induced rock-salt structure after cycling, even when conformally coated with a  $\text{Li}_3\text{B}_{11}\text{O}_{18}$  layer.<sup>11</sup> Similar surface reconstruction phenomenon has been observed in  $\text{Al}_2\text{O}_3$ - and  $\text{AlF}_3$ -coated cathodes,<sup>12,18</sup> regardless of liquid-electrolyte or solid-electrolyte battery implementations. As different coating materials may enhance one aspect of performance while hindering or falling short of another, ultimately, the question is what are the optimal coating design choices given the battery application, and can we provide a systematic guidance to identify them?

Given the complex reactions between the cathode, coating and electrolyte and the difficulty in deconvoluting experimentally measured solid state ionic diffusion, first-principles modeling provides robust guidelines for new cathode coatings. Aykol *et al.* reported a high-throughput screening of crystalline oxides materials that can stabilize the cathodes in a liquid-electrolyte battery system.<sup>19</sup> However, ionic diffusivity in the coatings was not considered. Liu *et al.* screened Li-containing crystalline fluoride materials and identified 10 promising coating materials along with their calculated  $\text{Li}^+$  migration barriers.<sup>20</sup> Xiao *et al.* screened crystalline Li-containing cathode coatings for solid-state batteries and proposed three polyanionic compounds as the most appealing candidates.<sup>21</sup> We note that the ionic diffusion analyses in all previous computational screening work have addressed exclusively the crystalline coating materials, whereas cathode coatings are often amorphous or polycrystalline. In addition, due to their isotropic non-periodic structures, amorphous films tend to be more conformal than polycrystalline films, with reduced grain boundaries, dislocations, or other defect regions.<sup>22</sup> Therefore, amorphous coatings provide a better cathode surface protection against surface oxygen loss and side reactions with electrolytes than polycrystalline coatings. Their unique processability also enables high degrees of interfacial contact with electrodes.<sup>22</sup> Moreover, many amorphous solids, such as  $\text{Li}_3\text{PO}_4$  and  $\text{Al}_2\text{O}_3$ , have been found to exhibit higher  $\text{Li}^+$  conductivity than their crystalline phases.<sup>23,24</sup> However, to our best knowledge, no study has considered  $\text{O}^{2-}$  diffusion in amorphous films, which is directly related to the oxygen-loss-induced cathode surface densification. In addition,  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion corresponds to the kinetics of the coatings but has never been applied broadly or systematically enough to derive design rules. In this work, we carry out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for LIBs. We evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, as well as the  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion in amorphous cathode coatings. Based on the trends in the screening results and ionic transport, we summarize general guidelines for selecting amorphous cathode coatings.

## Computational details

### First-principles calculation

All density functional theory (DFT) calculations are performed using the Vienna *Ab initio* Simulation Package (VASP),<sup>25,26</sup> with

Projector Augmented Wave (PAW) potentials.<sup>27</sup> The generalized gradient approximation (GGA) as parameterized by the Perdew–Burke–Ernzerhof (PBE)<sup>28</sup> is used for the exchange–correlation functional. For AIMD simulations, we employ  $\Gamma$ -point only Brillouin zone integration at a plane-wave cutoff energy of 400 eV and a time step of 2 fs.

We utilize a “liquid-quench” process to generate the amorphous structures, in which heating, equilibration, and quenching are performed through an AIMD workflow, which can be found as part of the open-source mpmorph package at <https://github.com/materialsproject/mpmorph>. We use the Packmol package<sup>29</sup> to generate all initial amorphous structures. To generate the “liquid” phase of the amorphous structures, we equilibrate the structures at 3000 K using a sequence of 4 ps AIMD simulations in the NVT ensemble until the external pressure and energy are converged. Next, the structures are simulated for an additional 10 ps, from which three independent configurations are selected and quenched to 0 K to obtain the ground-state amorphous structures. To perform ion diffusion analysis, we equilibrate the ground-state structure at  $T = 1800, 2000, 2200, 2400, 2600,$  and  $2800$  K, and then simulate an 80 ps diffusion trajectory at each corresponding temperature. The equilibration procedure follows the same steps used to equilibrate the “liquid” amorphous structure. In the end, there are three independent diffusion trajectories at each temperature. Further details about the entire AIMD and DFT workflows can be found in ref. 30.

### Self-diffusion coefficients and overpotentials

From the obtained diffusion trajectories, we calculate the self-diffusion coefficients ( $D$ ) of  $\text{Li}^+$  and  $\text{O}^{2-}$  ions in amorphous structures using the Einstein relation:  $D = \frac{1}{6} \frac{d\langle \Delta r^2 \rangle}{dt}$ , where  $t$  is the time,  $r$  is the ion position and  $\langle \Delta r^2 \rangle$  is the mean square displacement (MSD). Within the temperature window 1800–2800 K, there are three  $D$  values calculated from three independent diffusion trajectories at each temperature. The  $D$  values at room temperature are extrapolated from those at high temperatures using the Arrhenius relation of  $D$  as a function of  $T$ :  $D = D_0 \exp(-E_a/k_B T)$ , where  $k_B$  is the Boltzmann constant,  $D_0$  is the pre-exponential factor and  $E_a$  is the activation energy of ion diffusion. In addition, the trajectories at lower temperatures (*e.g.* 1800 K) frequently exhibit fewer ionic hops, which incurs higher statistical uncertainties of fitted  $D$  values than those at higher temperatures (*e.g.* 2800 K). Therefore, we consider the uncertainty of the  $D$  values at each temperature when linearly fitting  $\log D$  vs.  $1/T$  by assigning the standard deviation of  $\log D$  as the uncertainty for each averaged  $D$ .

From the calculated room temperature  $\text{Li}^+$  diffusivity  $D_{\text{Li}}^{\text{Li}}$ , we estimate the overpotential,  $\Delta V$ , across a cathode coating layer using a theoretical model which assumes a constant potential gradient, a uniform  $\text{Li}^+$  concentration and the Einstein relation to relate  $\text{Li}^+$  mobility and diffusion coefficient in the coating.<sup>31,32</sup> The model calculates  $\Delta V$  as a function of current density, coating thickness,  $\text{Li}^+$  concentration,  $\text{Li}^+$  diffusivity and temperature, providing a qualitative evaluation on coating's



ability to transport  $\text{Li}^+$  ions. The relation between  $\Delta V$  and  $D_{\text{rt}}^{\text{Li}}$  follows the methodology used in the earlier work,<sup>24,33</sup> namely:

$$\Delta V = \frac{J l_c k_B T}{D_{\text{rt}}^{\text{Li}} c^{\text{Li}} q^2} \quad (1)$$

where  $l_c$  is the coating thickness,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $c^{\text{Li}}$  is the  $\text{Li}^+$  concentration in the coating,  $q$  is the electron charge, *i.e.*,  $q = |e| = 1.602 \times 10^{-19}$  C, and  $J$  is the current density through the cathode coating, which results from a flux of  $\text{Li}^+$  ions and can be approximated as:<sup>24</sup>

$$J = \frac{\rho V_P C}{S_P t} = \frac{\rho r C}{3t} \quad (2)$$

where  $\rho$  is cathode density,  $V_P$  is the particle volume,  $S_P$  is the particle surface area,  $r$  is the particle radius,  $C$  is the cathode capacity, and  $t$  is the charging/discharging time. Combining eqn (1) and (2),  $\Delta V$  can be expressed as:

$$\Delta V = \frac{\rho r C}{3t} \frac{l_c k_B T}{D_{\text{rt}}^{\text{Li}} c^{\text{Li}} q^2} \quad (3)$$

In the ESI† we provide the full derivation and assumptions for eqn (1). According to eqn (2), the current density  $J$  is normalized by the cathode surface area, while experimentally,  $J$  is more commonly normalized by geometric area of the cathode disk. In addition, we assume that the entire spherical cathode particle surface area is available for  $\text{Li}^+$  intercalation.

### Oxygen flux and transport time

We use the Onsager transport equations to estimate the  $\text{O}^{2-}$  flux  $J^{\text{O}}$  under the driving force of the oxygen chemical potential gradient  $\nabla \mu^{\text{O}}$  across the coating layer, which can be expressed as:

$$J^{\text{O}} = -L^{\text{OO}} \nabla \mu^{\text{O}} \quad (4)$$

where  $L^{\text{OO}}$  is the Onsager transport coefficient for oxygen transport. It should be noted that in this study we ignore the contributions from cross-correlations between oxygen and other species, such as  $L^{\text{OLi}}$ , and between distinct oxygen sites, *i.e.*  $L_{\text{distinct}}^{\text{OO}}$ , to  $J^{\text{O}}$ . We approximate the  $\nabla \mu^{\text{O}}$  to be a constant across the thickness of the coating under steady-state conditions. Therefore, eqn (4) can be expressed as:

$$J^{\text{O}} = L^{\text{OO}} \frac{\mu_c^{\text{O}} - \mu_e^{\text{O}}}{l_c} \quad (5)$$

where  $\mu_c^{\text{O}}$  and  $\mu_e^{\text{O}}$  are the oxygen chemical potential at the cathode and electrolyte sides, respectively. Ignoring the  $L_{\text{distinct}}^{\text{OO}}$  term,  $L^{\text{OO}}$  can be directly related to the self-diffusion coefficient  $D^{\text{O}}$ :<sup>34</sup>

$$L^{\text{OO}} \approx L_{\text{self}}^{\text{OO}} = \frac{D^{\text{O}} c^{\text{O}}}{k_B T} = \frac{D_0^{\text{O}} e^{-\frac{E_a}{k_B T}} c^{\text{O}}}{k_B T} \quad (6)$$

where  $c^{\text{O}}$  is the  $\text{O}^{2-}$  concentration in the coating. The room-temperature  $L_{\text{rt}}^{\text{OO}}$  is extrapolated from  $L^{\text{OO}}$  values at high temperatures by fitting eqn (6). It should be noted that previous experiments have reported several active oxygen intermediates

during oxygen evolution reactions at cathode surface, such as covalent peroxide bonds, oxygen radicals and singlet oxygen ( $^1\text{O}_2$ ).<sup>35–37</sup> Because of their high reactivity, we assume these oxygen intermediates will react with the coating materials and become  $\text{O}^{2-}$ . Therefore, we use  $\text{O}^{2-}$  diffusion to represent oxygen diffusion in the coatings.

### Materials database and descriptors

The entire database used in this study contains 146 323 crystalline compounds, which are queried from the Materials Project (v2021.11.10).<sup>38</sup> The materials properties include DFT calculated total energies, formation energies, energies above convex hull ( $E_{\text{hull}}$ ), band gaps ( $E_g$ ), *etc.* It should be noted that at zero temperature, the Gibbs free energy of a crystalline polymorph is always lower than that of its amorphous state.<sup>39</sup> However, there is no universal description for the energetics of the amorphous materials, therefore we use the energies of the crystalline phases to approximate the stability of the amorphous phases. Indeed, the distribution of synthesizable crystalline polymorph energies tends to follow the trend of the amorphous energies.<sup>39</sup>

**Phase stability.** A compound's  $E_{\text{hull}}$  value is calculated by constructing the convex hull that includes the formation energies of all known crystalline phases in the same chemical space. The compounds that constitute the convex hull, *i.e.* have  $E_{\text{hull}} = 0$ , are deemed stable phases (at low temperature) or ground states for the system studied. The  $E_{\text{hull}}$  value for metastable phases therefore provides a measure of the driving force for decomposition and a descriptor for the phase stability of each compound.

**Electrochemical stability.** The calculations of the electrochemical stability window follow the methodology proposed by Aykol *et al.*,<sup>19</sup> which combines DFT formation energies in the Materials Project, experimental thermochemical data for gaseous species and experimental electrochemical data for solvated ions. First, we calculate the standard Gibbs free energy of a reaction ( $\Delta G^0$ ), which is obtained as:

$$\Delta G^0 = G_{\text{products}} - G_{\text{reactants}} \quad (7)$$

At room temperature, we assume the entropy contributions of solid phases are negligible while the entropy contributions of gaseous species ( $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2$  and  $\text{N}_2$ ) are much higher than that of solid phases. For the gaseous species, their entropy values  $S$  at room temperature are taken from the JANAF tables.<sup>40</sup> Thus,  $\Delta G^0$  can be approximated as:

$$\Delta G^0 \approx H_{\text{products}} - H_{\text{reactants}} - T(S_{\text{gaseous products}} - S_{\text{gaseous reactants}}) \quad (8)$$

where  $H$  represents enthalpy. For solid phases, we assume  $P\Delta V$  contributions are negligible and  $H$  can be approximated with the DFT calculated internal energy  $E$  at 0 K. For gaseous species, we add the anion corrections, which also includes the  $P\Delta V$  contribution to their enthalpy.<sup>41</sup> For a reaction involved with solvated ions, we assume a one-step single ion dissolution:  $\text{A} = \text{A}^{n+} + n\text{e}^-$  and we add the standard free energy of formation of



a solvated ion,  $\Delta G_{A^{n+}}^0$ , to  $\Delta G^0$  in eqn (8).  $\Delta G_{A^{n+}}^0$  can be calculated as:

$$\Delta G_{A^{n+}}^0 = -nFE_{A^{n+}}^0 \quad (9)$$

where  $n$  is the valence state of the ion,  $F$  is the Faraday's constant, and  $E_{A^{n+}}^0$  is the standard oxidation potential of the  $A^{n+}$  ion taken from the IUPAC publication.<sup>42</sup> Next, the free energy of a given reaction can be obtained as:

$$\Delta G = \Delta G^0 + RT \ln \frac{\prod_{\text{products},i} a_i}{\prod_{\text{reactants},i} a_i} \quad (10)$$

where  $a_i$  is the activity of species  $i$ . In Aykol's work, they assumed a small activity of  $a_{\text{ion} \neq \text{Li}} = 10^{-6}$  for non-Li solvated ions to approximate their dilute concentration in the electrolyte.<sup>19</sup> As this  $a_{\text{ion} \neq \text{Li}}$  is arbitrary and its effect on the calculated reaction potential is trivial, *i.e.*,  $-0.35/z$ , where  $z$  is the number of electrons transferred in the reaction, we assumed  $a_i$  values of unity for condensed phases and all solvated ions, thus  $\Delta G \approx \Delta G^0$ . Finally, the reaction potential (*versus* Li metal),  $V$ , can be obtained using the Nernst equation:

$$V = -\frac{\Delta G}{zF} \quad (11)$$

**Chemical stability.** The chemical stability of a cathode coating involves the reactivity of the coating with cathode and electrolyte as described by the reaction energy  $\Delta E_{\text{rxt}}$ .<sup>21,43</sup> For two reactants  $a$  and  $b$  in contact, the reaction can consume arbitrary amounts of either phase:  $xc_a + (1-x)c_b \rightarrow c_{\text{equil}}$ , where  $c_a$  and  $c_b$  are the compositions of  $a$  and  $b$  normalized by the numbers of atoms, respectively,  $c_{\text{equil}}$  is the composition of ground-state or phase equilibrium structure determined from the convex hull and  $x$  is the mixing parameter between 0 and 1.  $\Delta E_{\text{rxt}}$  is determined with an  $x$  that yields the largest reaction driving force:  $\Delta E_{\text{rxt}} = \min_{x \in [0,1]} [xE[c_{\text{equil}}] - xE[c_a] - (1-x)E[c_b]]$ .

## Results and discussion

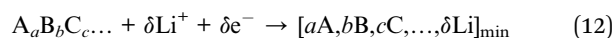
### Screening process

Fig. 1 illustrates the sequential high-throughput screening procedure for cathode coating materials with descriptors including radioactivity, energy above convex hull ( $E_{\text{hull}}$ ), band gap ( $E_g$ ), reduction limit ( $V_{\text{red}}$ ), oxidation limit ( $-V_{\text{ox}}$ ), and reaction energy ( $\Delta E_{\text{rxt}}$ ) with cathodes and electrolytes.

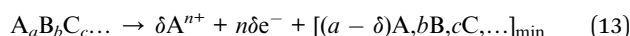
We exclude compounds containing radioactive elements and categorize the remaining compounds in 8 groups based on their anion chemistry: fluorides, chlorides, oxyfluorides, oxychlorides, metal oxides, nonmetal oxides, polyanionic oxides and others. We use  $E_{\text{hull}}$  values given in the Materials Project database<sup>38</sup> to screen for the thermodynamically stable compounds and select only the compounds that are on the convex-hull, *i.e.*,  $E_{\text{hull}} = 0$ . Furthermore, we are interested in electronically insulating coating materials that can block the electron transfer between the cathode and electrolyte and the subsequent electrolyte oxidation at high voltage.<sup>12</sup> Therefore, we exclude all metallic compounds and compounds that exhibit a bandgap,  $E_g$ , less than 0.5 eV. However, it should be noted that

there is a positive effect of a conductive surface coating on the performance of the cathode, as it provides an electron-conducting media that facilitates the charge transfer at the electrode surface.<sup>44</sup> For example, carbon-coating on  $\text{LiFePO}_4$  has proven to deliver a higher active material loading and energy density in a full-size battery.<sup>45</sup> The use of  $E_{\text{hull}}$  and  $E_g$  descriptors returns 13 498 compounds for further consideration.

In addition, a coating material that participates in the redox reaction during extensive cycling may cause degradation of the surface film, thus a loss of the surface protection.<sup>15</sup> Therefore, we retain only electrochemically stable compounds that can sustain the desirable voltage window. The electrochemical stability window of a cathode coating represents the voltage range (*versus* Li metal) in which the material is thermodynamically stable upon Li (de)intercalation. It consists of two components: the reduction limit ( $V_{\text{red}}$ ) during discharge and oxidation limit ( $-V_{\text{ox}}$ ) during charge. The reduction (cathodic) limit of a cathode coating with composition  $A_aB_bC_c\dots$  is defined as the voltage limit at which the material lithiates to  $A_aB_bC_c\dots\text{Li}_\delta$ . The discharge reaction can be expressed as:



where  $[aA,bB,cC,\dots,\delta\text{Li}]$  represents the compositions of the products, which are determined from the stable phases in the relevant phase diagram.  $\delta$  represents a dilute amount of Li, such that  $[aA,bB,cC,\dots,\delta\text{Li}]$  remains within the first phase-region formed by  $A_aB_bC_c\dots$  and other stable phases towards the Li-node of the phase diagram. In this phase-region,  $[aA,bB,cC,\dots,\delta\text{Li}]$  has the lowest Li chemical potential, therefore the highest  $V_{\text{red}}$ , along the composition path from  $A_aB_bC_c\dots$  towards the Li-node of the phase diagram. For a cathodically stable cathode coating,  $V_{\text{red}}$  in eqn (12) should be lower than the discharge cutoff voltage of the cathode as shown in Fig. 1. We set the criterion for  $V_{\text{red}}$  to be 3 V.<sup>19</sup> The oxidation (anodic) limit is defined as the voltage limit at which the material oxidizes and decomposes into one or more phases. The charge reaction can be expressed as:



where  $A^{n+}$  represents the dissolved ion. For a Li-containing compound, we take  $\text{Li}^+$  as the dissolved ion due to its high standard oxidation potential (3.04 V). For a compound that does not contain Li, we determine the dissolved ion by calculating the reaction potentials for all elements in the compound and conservatively selecting the element that leads to the highest reaction potential, thus the highest dissolution tendency. It should be noted that in this study, we assume a one-step single ion dissolution while the actual dissolution process may involve multi-step/multi-ion dissolution. For a non-Li-containing compound with ion dissolution reactions involving other species, we use the oxidation limit of the lithiated, stable compound with the lowest Li chemical potential along the composition path from the compound towards the Li-node of the phase diagram. For example, the dissolution reaction of boron is  $\text{B(s)} + 3\text{H}_2\text{O} \rightarrow \text{B(OH)}_3(\text{aq}) + 3\text{H}^+ + 3e^-$  and the



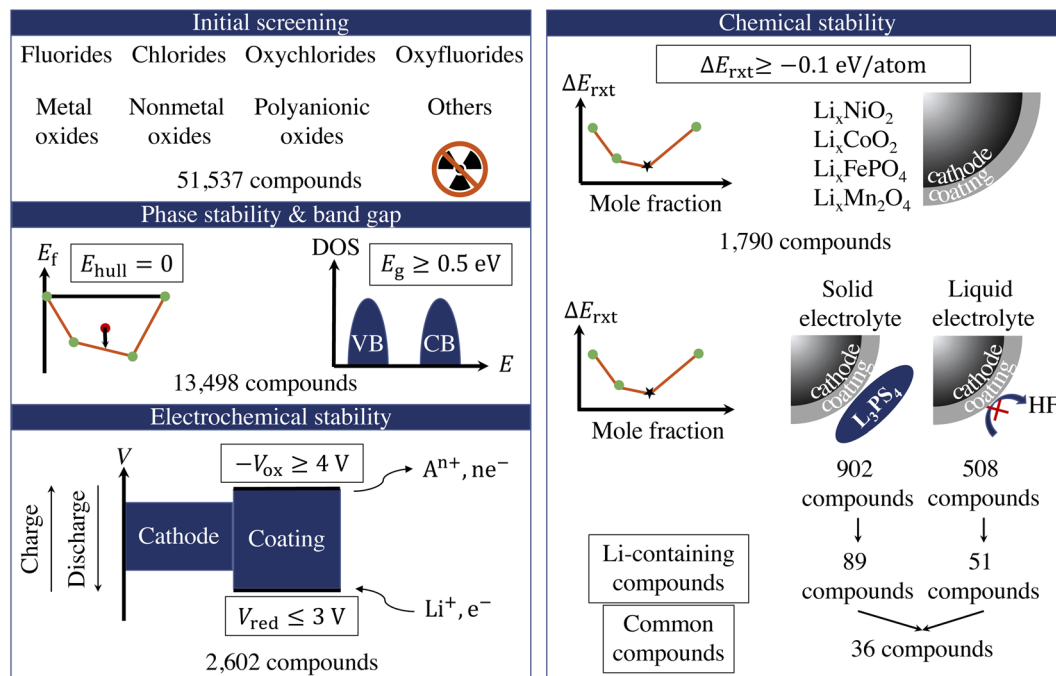


Fig. 1 The flowchart of the high-throughput computational screening of cathode coating materials. Compounds with radioactivity or energy above convex hull ( $E_{\text{hull}}$ ) greater than 0 are excluded. Compounds with band gap ( $E_{\text{g}}$ ) smaller than 0.5 eV are excluded. Compounds with reduction limit ( $V_{\text{red}}$ ) above 3 V or oxidation limit ( $-V_{\text{ox}}$ ) below 4 V are excluded. Compounds with reaction energy ( $\Delta E_{\text{rxt}}$ ) with cathode or electrolyte smaller than  $-0.1$  eV per atom are excluded.

oxidation limit of  $\text{B}_2\text{O}_3$  is estimated using the  $-V_{\text{ox}}$  value of  $\text{Li}_3\text{B}_{11}\text{O}_{18}$ . In the ESI,<sup>†</sup> we illustrate the procedures of calculating [ $V_{\text{red}}$ ,  $-V_{\text{ox}}$ ] for  $\text{LiAl}_5\text{O}_8$ ,  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  coatings. For a cathode coating to be electrochemically stable during charge, its  $|V_{\text{ox}}|$  magnitude should be larger than the charge cutoff voltage of the cathode, as shown in Fig. 1. As the oxidation reaction processes are likely to exhibit slow kinetics, an overpotential is expected during the charging cycle. Therefore, we set  $|V_{\text{ox}}|$  to be 4 V, even though a typical cathode material can be charged up to as high as 4.5 V. The use of electrochemical stability descriptor returns 2602 compounds for further consideration. Fig. 2a illustrates the reduction and oxidation limits of the compounds that are thermodynamically stable. The electrochemical stability of each category is denoted by two violin plots: the left and right represent oxidation and reduction limits, respectively. We find that in general, fluorides, such as  $\text{AlF}_3$  and  $\text{LiAlF}_4$ , have the largest electrochemical stability window with high oxidation limits and low reduction limits. On the other hand, metal oxides, such as  $\text{BaO}$  and  $\text{Bi}_2\text{O}_3$ , exhibit low oxidation limit, and nonmetal oxides, such as  $\text{P}_2\text{O}_5$  and  $\text{SeO}_2$ , have high reduction limit. The bar graph in Fig. 2a summarizes the numbers of compounds for each category of materials that pass the electrochemical stability screening. After this screening tier, polyanionic oxides have the largest number of candidates, followed by fluorides and chlorides. There are only 12 metal oxides and 1 nonmetal oxide,  $\text{B}_2\text{O}_3$ , left for further screening.

The fourth attribute we consider is the chemical stability of the cathode coatings. It has been shown that a coating material

can react with cathodes and electrolytes to form new phases at cathode/coating and coating/electrolyte interfaces, respectively.<sup>7,16</sup> Therefore, we screen for cathode coatings that are inert to chemical reactions with both cathodes and electrolytes. The reaction energy  $\Delta E_{\text{rxt}}$  is calculated using DFT-computed energies of the reactants and products, and a more negative  $\Delta E_{\text{rxt}}$  indicates a more reactive chemical reaction. We set the criterion for chemically stable cathode coatings as:  $\Delta E_{\text{rxt}} \geq -0.1$  eV per atom.<sup>21</sup> We calculate  $\Delta E_{\text{rxt}}$  between cathodes and coating materials using the commonly used cathodes, layered  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , spinel  $\text{LiMn}_2\text{O}_4$ , and olivine  $\text{LiFePO}_4$ . Both lithiated and half-lithiated cathodes are considered corresponding to the discharge and charge cycles, respectively. We select the most negative  $\Delta E_{\text{rxt}}$ , *i.e.*, the most favorable chemical reaction, as the  $\Delta E_{\text{rxt}}^{\text{cathodes}}$  for each compound, and we plot  $\Delta E_{\text{rxt}}^{\text{cathodes}}$  for each category that pass the electrochemical stability descriptor in Fig. 2b. In Fig. S2,<sup>†</sup> we also plot  $\Delta E_{\text{rxt}}$  of each selected cathode material. We find that compared with other cathodes,  $\text{LiNiO}_2$  tends to exhibit a more negative  $\Delta E_{\text{rxt}}$ , therefore reacts more favorably with the coating materials. In addition, oxides coatings are less prone to react with cathodes than fluorides and chlorides. Specifically, all the electrochemically stable metal oxides exhibit low reactivity with common cathodes and pass the chemical stability descriptor. This round of screening returns 1790 compounds for further consideration with polyanionic oxides having the largest number of candidates (714).

Similarly, we calculate  $\Delta E_{\text{rxt}}$  between coating materials and representative electrolyte components. In this study, we consider the commonly used  $\text{Li}_3\text{PS}_4$  solid electrolyte and  $\text{LiPF}_6$



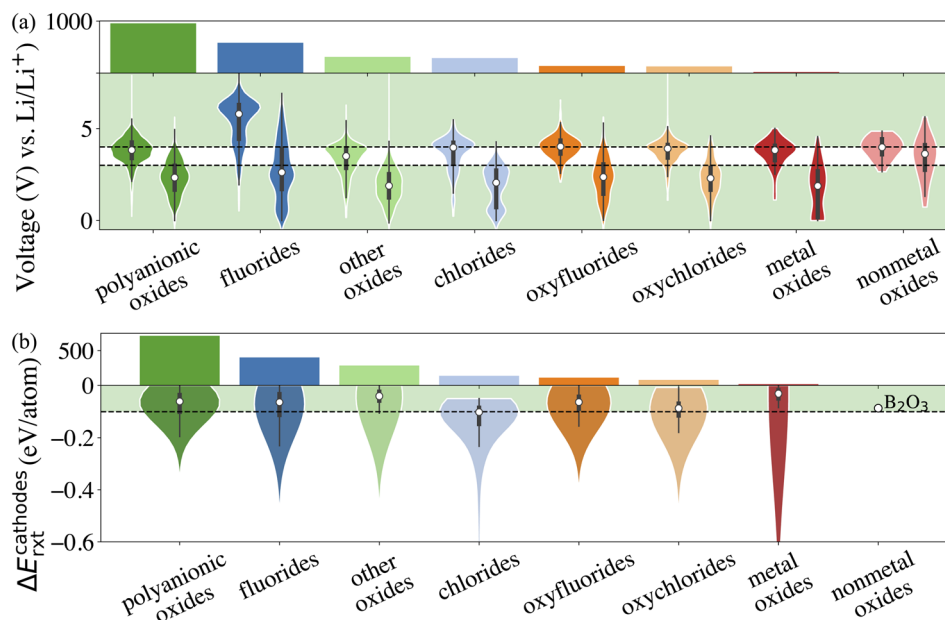


Fig. 2 (a) Distribution of the reduction and oxidation limits for each category that pass thermodynamic stability descriptor. (b) Distribution of the reaction energy  $\Delta E_{\text{rxt}}$  with  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiFeOP}_4$  cathodes for each category that pass electrochemical stability descriptor. Both lithiated and half-lithiated cathodes are evaluated and the most negative  $\Delta E_{\text{rxt}}$  is selected as  $\Delta E_{\text{rxt}}$  with cathodes. The horizontal dash lines represent the limits of the descriptors. The histograms in (a) and (b) illustrate the numbers of compounds for each category that pass the descriptors.

based non-aqueous liquid electrolytes, respectively, and categorize the coating materials based on their reactivity. In the case of  $\text{LiPF}_6$ -based electrolytes, we calculate  $\Delta E_{\text{rxt}}$  between coating materials and HF, which is known to react strongly with both cathodes and coating materials. Fig. 3 illustrates the distribution of  $\Delta E_{\text{rxt}}$  with  $\text{Li}_3\text{PS}_4$  and HF for the compounds that are chemically stable with the cathodes. We find that most fluorides and chlorides have lower chemical reactivity with both  $\text{Li}_3\text{PS}_4$  and HF than oxides compounds, thus are chemically compatible with both the cathodes and electrolytes. On the other hand, most oxides compounds are not chemically inert in  $\text{LiPF}_6$ -based liquid electrolytes due to a high reactivity with HF. It should be noted that these chemical reactions may only happen at the coating/electrolyte interface and render a partially fluorinated oxides coating layer, which could be beneficial for the cycling performance.<sup>46</sup> Therefore, even though we categorize the coatings based their chemical compatibility with liquid and solid electrolyte, the materials may be effective in both conditions. It should be noted that in  $\text{LiPF}_6$ -based liquid electrolyte systems, besides fluorination of the coating layer from an HF attack, other organic species and  $\text{Li}_2\text{CO}_3$  can also be found on the surface of the coated cathodes. We only consider the HF attack to broadly capture the chemical compatibility between coatings and  $\text{LiPF}_6$ -based liquid electrolytes in a high-throughput fashion. This round of screening returns 902 and 508 coating candidates that are chemically compatible with  $\text{Li}_3\text{PS}_4$  and  $\text{LiPF}_6$  based electrolytes, respectively.

In this study, we are mainly interested in the Li-containing compounds, as lithiated compounds tend to exhibit a higher ionic conductivity.<sup>30</sup> Adding the Li-containing criterion, the

entire screening procedure returns 89 and 51 Li-containing compounds that pass the proposed criteria for stability with respect to  $\text{Li}_3\text{PS}_4$  solid state electrolyte and HF, respectively, with 36 compounds that are chemically compatible with both  $\text{Li}_3\text{PS}_4$  and HF. In Fig. S2,<sup>†</sup> we summarize the numbers of Li-containing compounds for each category that pass the phase stability, electrochemical stability, and chemical stability descriptors. We find that oxides coatings, especially polyanionic oxides, account for the largest number of coatings for  $\text{Li}_3\text{PS}_4$ -based LIB, followed by fluorides and chlorides. On the other hand, the majority of coatings for  $\text{LiPF}_6$ -based LIB are fluorides and chlorides. The common coatings only consist of the fluorides and chlorides. In Table S3,<sup>†</sup> we list the calculated voltage windows, reduction and oxidation reactions, and reaction energies for the 104 Li-containing compounds that pass the screening criteria. In ESI,<sup>†</sup> we list the calculated material attributes of coating candidates.

### Ion diffusion analysis

Our computational screening procedure has narrowed down the coatings of interest to 104 Li-containing compounds. Besides providing facile  $\text{Li}^+$  diffusion pathways, an optimal cathode coating should block  $\text{O}^{2-}$  diffusion such that the oxygen-loss-induced cathode surface reconstruction can be mitigated. Therefore, to evaluate  $\text{Li}^+$  and  $\text{O}^{2-}$  transport in the screened amorphous coatings, we calculate ionic diffusivity, flux, and transport time through the coating materials using *ab initio* molecular dynamics (AIMD) simulations and Onsager transport models, as described in Computational details. Due to the high computational cost of investigating the ionic



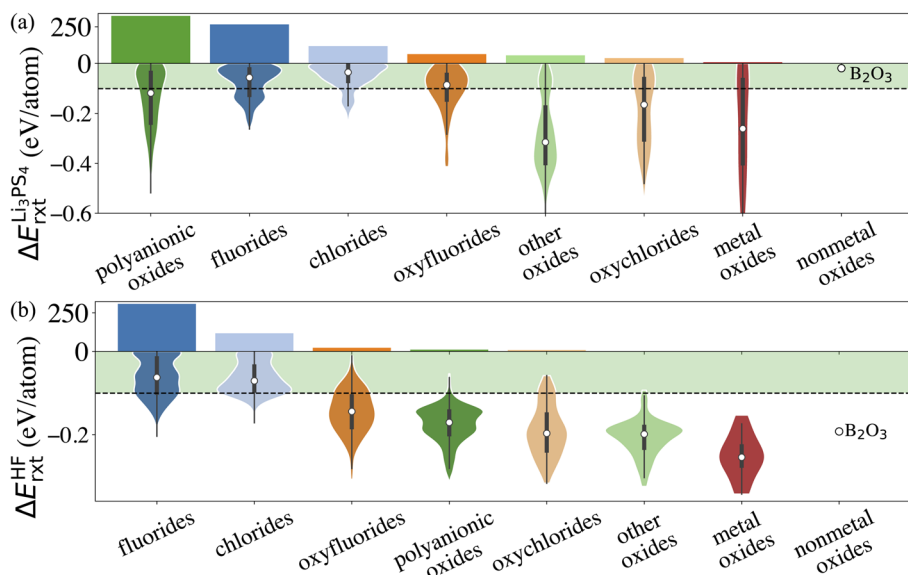


Fig. 3 Distribution of the reaction energy  $\Delta E_{\text{rxt}}$  with  $\text{Li}_3\text{PS}_4$  (a) and HF (b) for each category that pass chemical stability with the cathodes descriptor. The horizontal dash lines represent the limits of the descriptors. The histograms in (a) and (b) illustrate the numbers of compounds for each category that pass the descriptors.

diffusivity of all promising coating candidates, we select 9 representative compounds, consisting of polyanionic oxides  $\text{Li}_3\text{B}_{11}\text{O}_{18}$ ,  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{B}_3\text{PO}_8$  and  $\text{LiB}_3\text{O}_5$ , fluorides  $\text{Li}_3\text{AlF}_6$ ,  $\text{LiCaAlF}_6$ ,  $\text{LiYF}_4$  and chloride  $\text{Li}_2\text{ZnCl}_4$ , and analyze their ion diffusion. Fig. 4 illustrates the distribution of  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$  in the selected compounds, along with 7 Li-containing compounds that are filtered out by electrochemical or chemical stability criterion:  $\text{LiNbO}_3$ ,  $\text{Li}_2\text{HfO}_3$ ,  $\text{LiAlO}_2$ ,  $\text{LiTaSiO}_5$ ,  $\text{LiPO}_3$ ,  $\text{LiAlSiO}_4$ , and  $\text{LiSb}_3\text{O}_8$ , and 4 binary oxides:  $\text{Li}_2\text{O}$ ,  $\text{ZnO}$ ,

$\text{Al}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ . Our calculations show that in general,  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion is correlated, *i.e.*, a compound with a higher  $D_{\text{rt}}^{\text{Li}}$  also has a higher  $D_{\text{rt}}^{\text{O}}$ . For example, the  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$  in  $\text{Li}_3\text{PO}_4$  are  $10^{-9}$  and  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , respectively, both of which are higher than those in  $\text{LiAlSiO}_4$  ( $D_{\text{rt}}^{\text{Li}} = 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ,  $D_{\text{rt}}^{\text{O}} = 10^{-23} \text{ cm}^2 \text{ s}^{-1}$ ). The correlation between  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion can be explained by ionic conduction mechanism in amorphous structures. Our previous study<sup>30</sup> showed that  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion consists of discrete vibrational and translational motions. During vibrational motions,  $\text{Li}^+$  is bonded to more  $\text{O}^{2-}$  ions than during translational motions, and its translation to another vibration site is activated by the Li–O bond breaking/formation process, which effectively explains the correlated transport between  $\text{Li}^+$  and  $\text{O}^{2-}$ . In addition, we find that for compounds consisting of the same species, a compound with a higher  $\text{Li}^+$  concentration also has a higher  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion. For example, comparing  $\text{Li}_3\text{B}_{11}\text{O}_{18}$  and  $\text{LiB}_3\text{O}_5$ , we find that  $\text{LiB}_3\text{O}_5$ , which has a higher  $\text{Li}^+$  concentration, exhibits a higher  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$ . Similar behavior is found in  $\text{LiPO}_3$  and  $\text{Li}_3\text{PO}_4$ , relating to their  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$ . Our results are consistent with Xu *et al.*'s work in which they found that a higher  $\text{Li}^+$  solubility will enhance the  $\text{Li}^+$  transport across the coating.<sup>24</sup> In our work, we further demonstrate that, unfortunately, a higher  $\text{Li}^+$  concentration also correlates with increased, detrimental  $\text{O}^{2-}$  transport.

From the calculated  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$ , we evaluate the coating suitability of the selected compounds in terms of their ability to facilitate  $\text{Li}^+$  transport while blocking  $\text{O}^{2-}$  transport. Low  $\text{Li}^+$  diffusivity within the cathode coating layer can increase resistance and capacity loss at higher C-rates due to the resulting large overpotential at higher currents.<sup>47</sup> Thus, for the selected coating compounds, we estimate the overpotential,  $\Delta V$ , at the cathode surface. We set the criterion for overpotential imposed by the coating as  $\Delta V \leq 0.1 \text{ V}$ , above which the  $\text{Li}^+$  transport

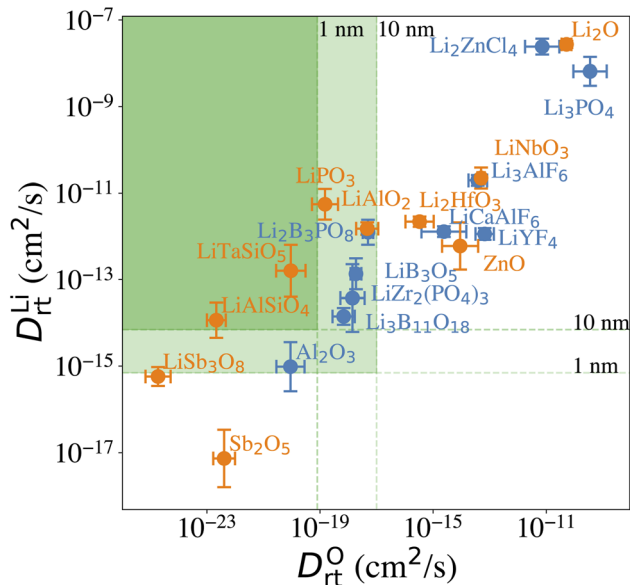


Fig. 4 Calculated room-temperature self-diffusion coefficients of  $\text{Li}^+$  ( $D_{\text{rt}}^{\text{Li}}$ ) and  $\text{O}^{2-}$  ( $D_{\text{rt}}^{\text{O}}$ ) in the selected compounds. The dash lines represent the approximated  $D_{\text{rt}}^{\text{Li}}$  and  $D_{\text{rt}}^{\text{O}}$  limits based on a coating thickness between 1 to 10 nm.



across the coating will be significantly compromised. In this study, we choose  $\text{LiNiO}_2$  as the relevant cathode material, with density  $\rho = 4.78 \text{ g cm}^{-3}$  and a theoretical capacity  $C = 274 \text{ mA h g}^{-1}$ . Eqn (3) shows that a smaller  $\Delta V$  can be realized by reducing the cathode particle size and coating thickness, and selecting a coating with high  $\text{Li}^+$  diffusivity  $D_{\text{rt}}^{\text{Li}}$  and concentration  $c^{\text{Li}}$ . By assuming a radius  $r = 1 \mu\text{m}$   $\text{LiNiO}_2$  primary particle and a 1C rate current density through the coating, the current density  $J$  is estimated to be  $0.044 \text{ mA cm}^{-2}$ . Finally, using  $D_{\text{rt}}^{\text{Li}}$  and the  $\text{Li}^+$  concentration of the compounds, we calculate the  $\Delta V$  values across a 1 and 10 nm conformal coating, respectively. Fig. 5a shows that for 1 nm surface coatings, all the selected compounds, except  $\text{Sb}_2\text{O}_5$  (23 V) and  $\text{LiSb}_3\text{O}_8$  (0.18 V), result in overpotentials below 0.1 V, which indicates a sufficient  $\text{Li}^+$  transport in these compounds. The overpotential of the  $\text{Al}_2\text{O}_3$  coating is found to be 0.07 V. When the coating thickness is increased to 10 nm, the overpotentials of  $\text{Sb}_2\text{O}_5$ ,  $\text{LiSb}_3\text{O}_8$  and  $\text{Al}_2\text{O}_3$  coatings increase to 230 V, 1.8 V and 0.7 V, respectively, while the overpotentials of other compounds are still below 0.1 V. Using an  $r = 1 \mu\text{m}$   $\text{LiNiO}_2$  primary particle in a 1C rate current density, we estimate the minimum  $\text{Li}^+$  diffusivity  $D_{\text{rt}}^{\text{Li}}$  to meet the overpotential criterion of  $\Delta V \leq 0.1 \text{ V}$ . By assuming a  $\text{Li}^+$  concentration  $c^{\text{Li}} = 10^{22} \text{ cm}^{-3}$ , we find that  $D_{\text{rt}}^{\text{Li}} = 7 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$  and  $7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$  for a 1 and 10 nm cathode coating, respectively, which are represented by the horizontal dashed lines in Fig. 4.

To evaluate the effectiveness of these coatings in blocking  $\text{O}^{2-}$  transport, we estimate the  $\text{O}^{2-}$  flux  $J^{\text{O}}$  and the time  $t$  required for  $\text{O}^{2-}$  to diffuse through the coating. We assume the oxygen-loss-induced surface rocksalt layer mainly consists of  $\text{NiO}$ , which is densified from the layered  $\text{NiO}_2$ . As  $\text{NiO}_2 \rightarrow \text{NiO} + 1/2\text{O}_2$ , we estimate  $t$  for surface  $\text{NiO}_2$  layer to lose half of its oxygen and transform into an  $\text{NiO}$  layer. Let  $c_{\text{max}}^{\text{O}}$  denote the  $\text{O}^{2-}$

concentration in  $\text{NiO}_2$  and  $V_s$  represent the shell volume of the surface  $\text{NiO}$  layer.  $V_s = \frac{4}{3}\pi[r^3 - (r - l_s)^3]$ , where  $l_s$  is the thickness of the surface  $\text{NiO}$  layer. Thus, the upper bound value of the number of  $\text{O}^{2-}$  ions removed from the cathode surface is  $N = 0.5V_s c_{\text{max}}^{\text{O}}$  and the  $\text{O}^{2-}$  diffusion time  $t$  can be expressed as:

$$t = \frac{N}{S_P J^{\text{O}}} = \frac{0.5V_s c_{\text{max}}^{\text{O}}}{S_P J^{\text{O}}} \quad (14)$$

where  $S_P = 4\pi r^2$  is the cathode particle surface area. Combining eqn (14) and (15),  $t$  can be expressed as:

$$t = \frac{0.5V_s}{S_P} \frac{c_{\text{max}}^{\text{O}} l_c}{L^{\text{OO}}(\mu_c^{\text{O}} - \mu_e^{\text{O}})} = \frac{r^3 - (r - l_s)^3}{6(r + l_c)^2} \frac{c_{\text{max}}^{\text{O}} l_c}{L^{\text{OO}}(\mu_c^{\text{O}} - \mu_e^{\text{O}})} \quad (15)$$

$\mu_c^{\text{O}}$  can be estimated from the cathode densification reaction consistent with the phase diagram. At a high charge state, layered  $\text{NiO}_2$  would densify to rocksalt  $\text{NiO}$  and spinel  $\text{Ni}_3\text{O}_4$  with oxygen being released at  $\mu_c^{\text{O}} = -4.95 \text{ eV}$ , which is equal to the DFT-calculated total energy of an  $\text{O}_2$  atom.  $\mu_e^{\text{O}}$  can be estimated from two different conditions: (1) using the condition where the electrolyte reacts with  $\text{O}^{2-}$  and forms a new compound ( $\text{Li}_3\text{PS}_4$  reacts with  $\text{O}^{2-}$  and forms  $\text{Li}_3\text{PO}_4$  at  $\mu_e^{\text{O}} = -8.39 \text{ eV}$ ) and (2) using the condition where  $\text{O}^{2-}$  loses electrons to the carbon network and forms  $\text{O}_2$  (at room temperature and  $P\text{O}_2 = 0.21 \text{ atm}$ ,  $\mu_e^{\text{O}} = -5.24 \text{ eV}$ ). Thus, we estimate  $-8.39 \leq \mu_e^{\text{O}} \leq -5.24 \text{ eV}$ . Eqn (15) indicates that for a given cathode coating and a given size of  $\text{LiNiO}_2$  primary particle, a longer  $\text{O}^{2-}$  diffusion time  $t$  can be realized by a smaller oxygen chemical potential gradient, *i.e.*, higher  $l_c$  and  $\mu_e^{\text{O}}$ . By assuming an  $r = 1 \mu\text{m}$   $\text{LiNiO}_2$  primary particle and an  $l_s = 2 \text{ nm}$  surface  $\text{NiO}$  layer, we estimate the time  $t$  for  $\text{O}^{2-}$  ions to diffuse through the selected coatings (see Fig. 5b). We consider a range of conditions by varying  $l_c$  and  $\mu_e^{\text{O}}$ , with  $l_c = 10 \text{ nm}$ ,  $\mu_e^{\text{O}} = -5.24 \text{ eV}$

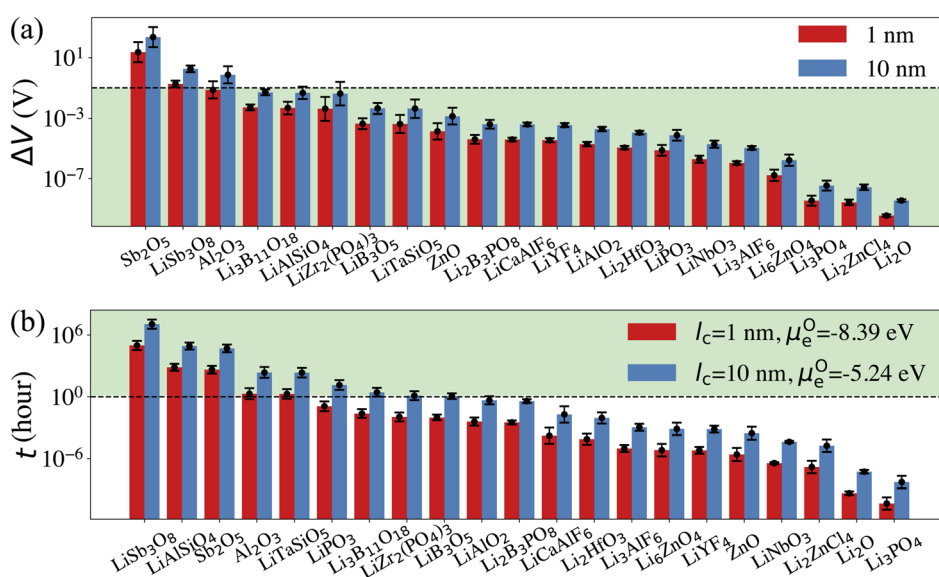


Fig. 5 (a) Calculated overpotentials ( $\Delta V$ ) for a current density of  $0.044 \text{ mA cm}^{-2}$  across room temperature cathode coatings of  $l_c = 1$  and  $10 \text{ nm}$ . The dashed line represents  $\Delta V = 0.1 \text{ V}$ . (b) Calculated  $\text{O}^{2-}$  diffusion time  $t$  in the selected compounds assuming a  $r = 1 \mu\text{m}$  primary particle and an  $l_s = 2 \text{ nm}$  surface rocksalt phase. The dashed line represents  $t = 1 \text{ h}$ .





corresponding to the slowest  $O^{2-}$  diffusion and  $l_c = 1$  nm,  $\mu_e^O = -8.39$  eV corresponding to the fastest  $O^{2-}$  diffusion. Fig. 5b shows the calculated  $O^{2-}$  diffusion time  $t$  in the selected compounds. We select the compounds with an estimated  $O^{2-}$  diffusion time longer than 1 h such that not all  $O^{2-}$  ions that are evolved from surface  $NiO_2$  layer have diffused through the coating under 1C rate. We find that  $LiSb_3O_8$ ,  $LiAlSiO_4$ ,  $Sb_2O_5$ ,  $Al_2O_3$ ,  $LiTaSiO_5$ ,  $LiPO_3$ ,  $Li_3B_{11}O_{18}$ ,  $LiZr_2(PO_4)_3$  and  $LiB_3O_5$  exhibit an estimated  $O^{2-}$  diffusion time longer than 1 h. Next, we estimate the upper limit of  $O^{2-}$  diffusivity to have  $t \geq 1$  h. As mentioned earlier, we approximate  $L_{rt}^{OO} \approx L_{rt, self}^{OO}$ . Using eqn (6), we can directly calculate  $L_{rt}^{OO}$  from self-diffusion coefficient  $D_{rt}^O$ :

$$L_{rt}^{OO} = \frac{D_{rt}^O c^O}{k_B T} = \frac{r^3 - (r - l_s)^3}{6(r + l_c)^2} \frac{c_{max}^O l_c}{t(\mu_c^O - \mu_e^O)} \quad (16)$$

Next, we use the same cathode particle configuration and assume an  $O^{2-}$  concentration  $c^O = 10^{22}$   $cm^{-3}$  in a coating layer. We find that  $D_{rt}^O = 8 \times 10^{-20}$   $cm^2 s^{-1}$  for  $l_c = 1$  nm,  $\mu_e^O = -8.39$  eV and  $D_{rt}^O = 1 \times 10^{-17}$   $cm^2 s^{-1}$  for  $l_c = 10$  nm,  $\mu_e^O = -5.24$  eV, which are represented by the vertical dashed lines in Fig. 4. Therefore, the green region in Fig. 4 represents the favorable  $Li^+$  and  $O^{2-}$  diffusivity window, and a compound falling on the top left area is more desirable in terms of facilitating  $Li^+$  transport while blocking  $O^{2-}$  transport. It should be noted that the effect of different cathode materials on  $\Delta V$  and  $t$  is marginal (see Fig. S4†). Therefore, the calculated  $\Delta V$ ,  $t$ , and  $Li^+$  and  $O^{2-}$  diffusivity window are applicable for other cathodes, such as Ni-based NMC and  $LiCoO_2$ .

Five observations can be made from the high-throughput screening results and the estimated overpotential  $\Delta V$  and  $O^{2-}$  diffusion time  $t$ :

(1) Among the nine Li-containing compounds that pass the computational screening, only  $Li_3B_{11}O_{18}$ ,  $LiZr_2(PO_4)_3$  and  $LiB_3O_5$  have been found to exhibit both  $\Delta V \leq 0.1$  V and  $t \geq 1$  h. However, the thickness of the considered coatings should be large enough (e.g. 10 nm) to improve their oxygen-retaining ability. Experimentally, Zhang *et al.* demonstrated that an amorphous  $Li_3B_{11}O_{18}$  coating layer with a few nanometers thickness exhibits excellent chemical/electrochemical stability and can significantly improve the capacity retention of NMC cathodes.<sup>11</sup> However, the surface structure of NMC particles still evolved from a layered phase to a rocksalt phase after cycling. Our recent calculations showed facile  $O^{2-}$  transport in the amorphous  $Li_3B_{11}O_{18}$  material, which leads to an oxygen-loss induced surface phase transition. In this work, we predict that a thicker  $Li_3B_{11}O_{18}$  coating layer (e.g. 10 nm) is beneficial to mitigate the oxygen-loss induced surface densification and further improve the cycling performance of NMC cathodes. In addition, Wang *et al.* reported that amorphous  $LiZr_2(PO_4)_3$  coated  $LiCoO_2$  exhibits better capacity retention and rate performance than bare  $LiCoO_2$ .<sup>48</sup> The enhanced cycling performance was attributed to an enhanced Li-ion diffusion and a significantly mitigated chemical reactions between  $LiCoO_2$  and sulfide-based solid electrolytes by the protective  $LiZr_2(PO_4)_3$  coating layer, which agrees well with our ion

diffusion and chemical stability analysis. However, based on our  $O^{2-}$  diffusion in amorphous  $LiZr_2(PO_4)_3$  analysis, we expect that the 2 nm  $LiZr_2(PO_4)_3$  coating used in their study is not thick enough to mitigate oxygen loss from  $LiCoO_2$  surface and it's likely that the  $LiCoO_2$  cathodes still suffer from oxygen-loss induced surface reconstruction at prolonged cycling and high charge.<sup>49</sup> Therefore, we predict that a thicker  $LiZr_2(PO_4)_3$  coating (e.g. 10 nm) could further improve the cycling performance of  $LiCoO_2$ .

(2) Among the nine Li-containing compounds that do not pass the computational screening,  $LiPO_3$ ,  $LiSb_3O_8$ ,  $LiAlSiO_4$  and  $LiTaSiO_5$  can also be considered as promising cathode coatings mainly because of their exceptional oxygen retaining ability.  $LiPO_3$  exhibits a high oxidation limit (4.9 V) and a reaction energy  $\Delta E_{rxn} = -0.11$  eV per atom with  $LiNiO_2$  to form  $LiNiPO_4$  and  $Li_3PO_4$ , therefore is screened out by our chemical stability criterion:  $\Delta E_{rxn} \geq -0.1$  eV per atom. However, both  $LiNiPO_4$  and  $Li_3PO_4$  coatings have been reported to enhance the rate capability and cycle performance of cathode materials<sup>50,51</sup> and the chemical reaction may only happen at the interface of  $LiPO_3$  and  $LiNiO_2$  considering the sluggishness of solid state reactions. Experimentally, Chong *et al.*<sup>8</sup> coated  $LiNi_{0.5}Mn_{1.5}O_4$  (LNM) particles with a 1 nm thickness of amorphous  $LiPO_3$  and found that the  $LiPO_3$  coating can significantly reduce the cell impedance and facilitate  $Li^+$  ion transport, which is in good agreement with our calculations.  $LiSb_3O_8$  also exhibits a high oxidation limit (5.0 V), but its predicted reduction limit (3.2 V) is higher than our reduction limit criterion:  $V_{red} \leq 3$  V. However, its lithiated compound  $LiSbO_3$  is expected to exhibit a higher  $Li^+$  diffusion, which may offset its relatively high overpotential. In addition,  $LiSb_3O_8$  reacts favorably with both HF and  $Li_3PS_4$ , *i.e.*  $\Delta E_{rxn} \leq 0.1$  eV per atom. We note that these chemical reactions may only happen at the coating/electrolyte interface and the reaction products could form a passivation layer to prevent further reactions.  $LiAlSiO_4$  exhibits excellent oxygen retention, but its oxidation limit ( $|V_{ox}| = 3.9$  V) is lower than our oxidation limit criterion:  $|V_{ox}| \geq 4$  V. However,  $LiAlSiO_4$  decomposition involves the  $O_2$  evolution reaction, which is likely to have sluggish kinetics.<sup>52,53</sup> Therefore, the overpotential of the  $LiAlSiO_4$  decomposition reaction may increase its oxidation limit, *i.e.*,  $|V_{ox}| \geq 4$  V. Experimentally, Deng *et al.*<sup>54</sup> cycled an amorphous  $LiAlSiO_4$ -coated LNM cathode with an electrochemical window from 3.5 to 4.9 V for 150 cycles and found improved capacity retention, lower Mn-dissolution and faster  $Li^+$  transport in  $LiAlSiO_4$ -coated LNM, compared to uncoated LNM. Our calculated  $Li^+$  diffusivity in  $LiAlSiO_4$ ,  $1.16 \times 10^{-14}$   $cm^2 s^{-1}$ , is also in good agreement with their reported value,  $7.96 \times 10^{-15}$   $cm^2 s^{-1}$ . Therefore, despite its limitations, we include  $LiAlSiO_4$  in the list of promising cathode coatings. Similarly,  $LiTaSiO_5$  is another potentially effective cathode coating, despite its low oxidation limit ( $|V_{ox}| = 3.9$  V).

(3) Fluoride and chloride materials exhibit exceptional electrochemical and chemical stability as well as low overpotentials due to their fast  $Li^+$  transport. However, our calculations also show that the fluoride and chloride coatings are  $O^{2-}$  transparent, which means that halide-coated cathode surfaces will be



prone to oxygen loss and are likely to transform over time into a densified rocksalt phase.

(4) Although non-Li containing,  $\text{Al}_2\text{O}_3$  can be considered as a promising cathode coating. We estimate that the diffusion time of oxygen in an  $\text{Al}_2\text{O}_3$  coating varies between 2 to 227 h, depending on  $l_c$  and  $\nabla\mu^{\text{O}}$  (see Fig. 4). Thus, we predict that an NMC cathode coated with a thin  $\text{Al}_2\text{O}_3$  coating layer, such as 1 nm, is still prone to surface oxygen loss, especially when cycled at low C-rate. This result could explain why a 3 nm  $\text{Al}_2\text{O}_3$  surface coating is not sufficient to stabilize NMC cathode surface when cycled at C/7.<sup>18</sup> On the other hand, a thicker  $\text{Al}_2\text{O}_3$  coating layer can effectively mitigate  $\text{O}^{2-}$  transport, which results in a better cathode surface protection; David *et al.* showed that an  $\text{Al}_2\text{O}_3$  ALD coating can effectively prevent surface reconstruction of NMC cathodes even after 760 cycles,<sup>55</sup> which indicates that a thick and conformal  $\text{Al}_2\text{O}_3$  coating was applied on the NMC cathodes in their study.

(5) An optimal amorphous cathode coating should not only exhibit sufficient thermodynamic stability, electrochemical stability and chemical stability, but also a low  $\text{O}^{2-}$  diffusivity and a high  $\text{Li}^+$  diffusivity to achieve oxygen-retaining and surface-protective functions while avoiding significant losses in rate capability. However, the correlation between  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion in amorphous coatings highlights the inherent contradiction in identifying cathode coating materials with optimal  $\text{Li}^+$  transport as well as  $\text{O}^{2-}$  blocking ability. In general,  $\text{Li}^+$  diffusion in Li-containing compounds is fast enough to avoid a large overpotential. As a higher  $\text{Li}^+$  diffusion may compromise a coating's ability to block  $\text{O}^{2-}$  diffusion, for compounds with same chemistry, a compound with a lower  $\text{Li}^+$  concentration is thus preferred. For example, the  $\text{Li}^+$  concentrations in  $\text{LiPO}_3$  and  $\text{Li}_3\text{PO}_4$  are 20% and 37.5%, respectively. Fig. 4 shows that both  $\text{LiPO}_3$  and  $\text{Li}_3\text{PO}_4$  exhibit a facile  $\text{Li}^+$  diffusion, but  $\text{LiPO}_3$  exhibits an improved oxygen retention as compared to  $\text{Li}_3\text{PO}_4$ . In addition, the oxidation limit of  $\text{LiPO}_3$  (4.9 V) is higher than that of  $\text{Li}_3\text{PO}_4$  (4.0 V).

## Conclusions

In summary, we have carried out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for Li-ion battery applications. Our high-throughput screening includes descriptors to evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, and ionic diffusion in the cathode coatings. We consider reactivity with the commonly used  $\text{Li}_3\text{PS}_4$  solid state electrolyte and with HF as a particularly detrimental representative of liquid electrolyte degradation. We find that polyanionic oxides account for the largest number of cathode coatings for  $\text{Li}_3\text{PS}_4$ -based LIB, followed by fluorides and chlorides. On the other hand, the majority of cathode coatings that are inert to chemical reactions with HF are fluorides and chlorides. Combining the screening results and ionic diffusion analysis of 20 selected compounds, we summarize the promising cathode coatings and general materials design principles:

(1)  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion are highly correlated, therefore, a higher  $\text{Li}^+$  transport promotes higher  $\text{O}^{2-}$  transport. In Li-containing compounds, the  $\text{Li}^+$  diffusion rate is generally fast enough to avoid a large overpotential. When selecting a cathode coating with same chemistry, a compound with a lower Li concentration is preferred, as it exhibits an improved oxygen retention as well as a higher oxidation limit.

(2) Mitigating  $\text{O}^{2-}$  diffusion is a formidable challenge when selecting an ideal cathode coating as most thin conformal coatings will transport oxygen under prolonged cycling and high voltage. Our results show that in addition to the four experimentally confirmed cathode coatings:  $\text{Li}_3\text{B}_{11}\text{O}_{18}$ ,  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{LiPO}_3$  and  $\text{LiAlSiO}_4$ , we also identify three new promising cathode coatings:  $\text{LiB}_3\text{O}_5$ ,  $\text{LiSb}_3\text{O}_8$  and  $\text{LiTaSiO}_5$ .

(3) Based on our ionic diffusion analysis, we find that  $\text{BO}_x^{y-}$ ,  $\text{SiO}_x^{y-}$ ,  $\text{PO}_x^{y-}$  and  $\text{SbO}_x^{y-}$  anion groups tend to exhibit an improved oxygen retention. Therefore, we expect that compounds such as  $\text{LiBa}(\text{B}_3\text{O}_5)_3$ ,  $\text{LiAl}(\text{Si}_2\text{O}_5)_2$ ,  $\text{LiTi}_2(\text{PO}_4)_3$ ,  $\text{LiScP}_2\text{O}_7$ ,  $\text{LiK}(\text{PO}_3)_2$ , and  $\text{LiCs}(\text{PO}_3)_2$  could also be potentially effective cathode coatings. On the other hand,  $\text{F}^-$  and  $\text{Cl}^-$  anion groups tend to exhibit faster  $\text{Li}^+$  and  $\text{O}^{2-}$  diffusion as compared to the oxides. Thus, they are not ideal for high-voltage cathode coatings where the driving force for oxygen loss is high. However, their inherent fast  $\text{Li}^+$  diffusivity may render them promising candidates as the solid-state electrolytes or lithium metal coatings.

(4) A non-Li-containing compound generally exhibits slower  $\text{Li}^+$  diffusion but better oxygen retention ability as compared to its lithiated counterpart. We mainly consider Li-containing compounds in this study, however, we expect that effective cathode coatings can also be found in non-lithiated compounds, such as  $\text{Al}_2\text{O}_3$ . Based on our identified anion groups above, we expect that compounds, such as  $\text{ScBO}_3$ ,  $\text{HfSiO}_4$ ,  $\text{ZrP}_2\text{O}_7$  and  $\text{AlPO}_4$ , could be potentially effective cathode coatings. A follow-up study on non-Li-containing coatings will be presented in a later report.

## Conflicts of interest

There are no conflicts to declare.

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