

First-principles thermodynamic analysis of  
hydrogen-fluoride scavenging cathode coatings for  
lithium-ion batteries

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A major cause of capacity fade in Li-ion batteries is that hydrofluoric acid (HF) present in LiPF<sub>6</sub>-based electrolytes attacks the cathode particles and aggravates the dissolution of redox-active metal-ion. When applied on the cathode particles, a metal oxide coating can scavenge HF and a metal fluoride layer, which can be a product of the HF-scavenging reaction or a directly applied coating, can serve as a protective barrier that inhibits penetration of HF to the cathode. For a binary metal oxide (M<sub>x</sub>O<sub>1/2</sub>), the HF-scavenging reaction can be written as,



We study 81 binary oxide/fluoride pairs that satisfy the form of this reaction where M is an s-, p- or d-block element. To find the thermodynamically promising HF-scavenger coatings among these materials, we construct a design framework based on four key factors: HF-scavenging reaction enthalpy ( $\Delta H_{HF}$ ), volumetric HF-scavenging capacity, gravimetric HF-scavenging capacity and lithiation voltages of components of the coating. Using Density Functional Theory (DFT) based thermodynamics, we calculate  $\Delta H_{HF}$  and voltages as shown in Fig. 1.

To screen prospective HF-scavenger coating materials, we define the design criteria for the factors embedded in the framework as follows. An oxide coating is expected to preferentially react with HF in presence of the cathode material, and we define a lower bound for the HF-scavenging tendency as shown in Fig. 1, accordingly. This bound is approximated by calculating the enthalpy of a reaction analogous to Eq.1 for a sample cathode chosen as LiCoO<sub>2</sub>. For the voltage of the coating components, an upper bound is defined as the discharge cut-off voltage of the cathode (arbitrarily selected as 3.0 V). Coating materials with a voltage below this bound are not expected to react with the active-Li in the battery. HF-scavenging capacities (moles of HF a coating can scavenge per unit volume or weight) should be maximized. Our calculations show that lithiation voltage of fluorides are often higher than that of the corresponding oxides for a metal M with the same oxidation state (except M = Rb, Cs, K, Sr, Na and Ba fluorides); thus, we select the voltage of the fluoride of M as a design parameter.

Promising coating candidates are in the target region shown in Fig.1. Coating materials that are already known to improve capacity retention experimentally such as Al<sub>2</sub>O<sub>3</sub> and MgO are found to be among the promising screened materials with high HF-scavenging capacities. We finally discuss a potential protection mechanism provided by fluorides, which may scavenge another degradation product of the electrolyte; namely, LiF precipitates that possibly hamper the electron and ion conduction at the cathode.

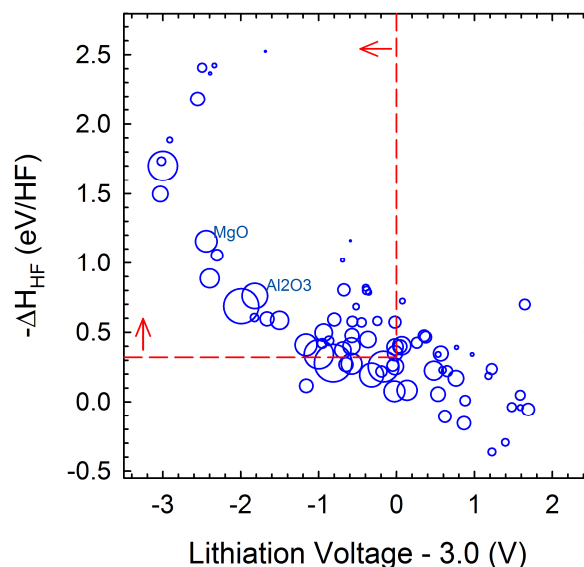


Fig. 1. HF-scavenging tendency ( $-\Delta H_{HF}$ ) of oxides versus lithiation voltage of the corresponding fluoride layers for 81 oxide/fluoride pairs calculated with DFT. Circle sizes are proportional to the gravimetric HF-scavenging capacities. Horizontal dashed-line shows minimum HF-scavenging tendency criterion based on a sample cathode (LiCoO<sub>2</sub>) and the vertical dashed-line shows maximum allowed voltage criterion based on the discharge cut-off of the sample cathode selected as 3.0 V. Arrows point towards the enclosed region where promising coating materials are present.