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Interpreting Intrinsic Nature of Proton-Conducting Oxides for Solid Oxide Fuel Cells Using High-Throughput Computation and Machine Learning

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Abstract

Developing highly proton-conductive solid electrolytes is essential for improving the performance of solid oxide fuel cells (SOFCs). Here, we performed high-throughput *ab initio* calculations of hydration energies of host compounds and solution energies of dopants in the host compounds, and constructed their explainable machine-learned models by random-forest regression and Sharpley additive explanations (SHAP). The results gave the design principles of acceptor doping and hydration, and the principles were demonstrated by the experimental discovery of proton incorporation and conduction in an unreported non-perovskite oxide.

1. Introduction

Proton-conducting oxides have attracted considerable attention as electrolytes for environmentally friendly electrochemical devices including SOFCs. The perovskites have been the focus of development of proton-conducting oxides, from the first discovery of $SrCeO_3$ in 1981[1] to now highly proton-conductive Sc-doped $BaZrO_3$[2]. In contrast, non-perovskite proton-conducting oxides are scarcely known[3], mainly limited to rare-earth based oxides such as $LaNbO_4$ and $La_2Zr_2O_7$. This is due to the complex nature of proton-conducting oxides, which need to have an acceptor dopant to create oxygen vacancies, hydrate via oxygen vacancies, have crystal structure where protons migrate easily, and be chemically stable. Among them, finding a good combination of a host compound and a dopant is the most time-consuming task, because of the explosive number of their combinations. Developing design principles for proton-conducting oxides covering not only perovskite oxides but also non-perovskite oxides are highly demanding.

Fig.1 Constitute elements of oxides considered in this study (yellow elements).

2. Method

We constructed random-forest models for hydration energies of host compounds and solution energies of dopants in the host compounds. The SHAP[4] method was applied to interpret the constructed models and to develop design principles for acceptor doping and hydration. These

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models were trained using the data obtained from high-throughput *ab initio* calculations. Initial collections of host compounds with more than 60 prototype cubic structures were taken from Inorganic Crystal Structure Database (ICSD) (Fig. 1). We note that it is practically impossible to calculate solution energies for all the combinations of candidate hosts and possible dopants due to the computational cost. Thus, our computational scheme was designed to efficiently obtain the data essential for proton-conducting oxides, by narrowing down the target compounds based on the properties including bandgap, hydration, proton migration, thermodynamics stability, avoiding the explosive number of host-dopant combinations.

3. Results and discussion

The computational results shows that there are many compounds that can hydrate if oxide-ion vacancies are successfully introduced, but most of them cannot form proton migration paths and have no appropriate dopants that dissolve easily. The SHAP analyses quantitatively indicates how host compounds and dopants should be selected, in terms of ionic size, electronegativity, crystal structure, and stability in phase diagram. For example, a crystal structure needs to have sufficient space to incorporate protons, but excess space (low number density of atoms) does not make hydration easier. The gained design principles led to perform the proof-of-concept synthesis of an as-yet-reported non-perovskite oxide, demonstrating its proton incorporation and conduction.

4. Conclusions

We obtained and verified the design principles of acceptor doping and hydration in oxides by the combination of high-throughput *ab initio* calculations, machine learning and experimental synthesis and measurements. The design principles are applicable to both perovskite and non-perovskite oxides, accelerating the discovery of novel proton-conducting oxides.

References

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