High-Throughput Computational Screening of Cubic Perovskites for Solid Oxide Fuel Cell Cathodes

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ABSTRACT: It is a present-day challenge to design and develop oxygen-permeable solid oxide fuel cell (SOFC) electrode and electrolyte materials that operate at low temperatures. Herein, by performing high-throughput density functional theory calculations, oxygen vacancy formation energy, $E_{\text{vac}}$, data for a pool of all-inorganic ABO$_3$ and $A_{1-x}A'^{x}O_{3}$ cubic perovskites is generated. Using $E_{\text{vac}}$ data of perovskites, the area-specific resistance (ASR) data, which is related to both oxygen reduction reaction activity and selective oxygen ion conductivity of materials, is calculated. Screening a total of 270 chemical compositions, 31 perovskites are identified as candidates with properties that are between those of state-of-the-art SOFC cathode and oxygen permeation components. In addition, an intuitive approach to estimate $E_{\text{vac}}$ and ASR data of complex perovskites by using solely the easy-to-access data of simple perovskites is shown, which is expected to boost future explorations in the perovskite material search space for genuinely diverse energy applications.

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of fuel (e.g., CO and/or H₂) then takes place on the surface of the SOFC anode material. Therefore, the convenience of perovskites for atomic-scale migrations of oxygen atoms, or similarly for oxygen atom vacancies in the opposite direction, relates to their macroscale oxygen-transfer performance. In addition, recent experimental work on perovskites attributes the high performance of oxygen exchange to low area-specific resistance (ASR). Hence, to estimate the SOFC performance, developing a calculable relationship between \( E_{\text{vac}} \) and ASR data of perovskite-based materials is useful. Typically, the oxygen atom vacancies in perovskites facilitate a fast diffusion of oxygen ions. However, a too strong tendency for O vacancy formation, as evident from a largely negative \( \Delta E_{\text{vac}} \), creates a risk for the structural integrity of the compound. Therefore, in addition to its application as a descriptor for the catalytic behavior and the oxygen transport performance of materials, \( E_{\text{vac}} \) is also useful when estimating the stability of perovskites.

Herein, a group of cubic perovskites is systematically explored for their esteemed use as low-temperature SOFC cathode materials. First, based on the knowledge of existing compounds, a relation between the measured ASR and the computed \( E_{\text{vac}} \) data is formulated. Next, a virtual chemical library of perovskites, which contains 108 \( ABO_3 \) and 162 \( A_{1/2}A_{11/5}B_{1/3}O_3 \) perovskites, is enumerated. Then, for all the compounds in the library, the \( E_{\text{vac}} \) data is generated by applying high-throughput density functional theory (HT-DFT) calculations. After that, the ASR data of a total of 270 virtual materials is estimated by using the newly developed relationship between \( E_{\text{vac}} \) and ASR of experimentally investigated materials and the HT-DFT calculated \( E_{\text{vac}} \) data. Finally, the most promising candidate materials for SOFC cathodes are singled out and a practical means for accessing the key \( E_{\text{vac}} \) and ASR data of complex perovskites is presented. The specific aspects of the stages of the study are described below.

First, a direct correlation between \( E_{\text{vac}} \) and the \( \log(\text{ASR}) \) is developed by using the experimental data of \( Pr_{0.5}Ba_{0.5}CoO_3 \), \( La_{0.75}Sr_{0.25}MnO_3 \), \( Ba_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_3 \) and \( La_{0.8}Sr_{0.2}MnO_3 \), which represent \( Pr_{0.5}Ba_{0.5}CoO_3 \), \( La_{0.75}Sr_{0.25}MnO_3 \), \( Ba_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_3 \) and \( La_{0.8}Sr_{0.2}MnO_3 \) compositions, respectively, are used in DFT calculations. It is known that perovskites that have noncubic symmetry at room temperature are usually prone to a phase transformation to cubic symmetry at higher temperatures. For example, \( BaTiO_3 \) has rhombohedral (R3m) symmetry at low temperature, and upon heating, its structure transforms to orthorhombic (Ammt2) at \(-90^\circ C\), to tetragonal (P4mm) at \( 5^\circ C \), and finally to cubic (Pm3m) at above \( 120^\circ C \). Therefore, as a pragmatic reason owing to SOFC operation temperatures, all structures considered here are assumed to have cubic symmetry. Also, notably, the weighted average vacancy formation energies are calculated by performing DFT simulations on all of the unique oxygen vacancy configurations of perovskite structures. Accordingly, as shown in Figure 2, a linear regression (LR) model is developed for the measured \( \log(\text{ASR}) \) and the DFT-calculated \( E_{\text{vac}} \) data of materials. The obtained LR equation

\[
\log(\text{ASR}) = 0.68(E_{\text{vac}}) - 2.32
\]  

with \( R^2 = 0.98 \) shows a large positive linear association, although the data in experiments were collected by using different, GDC and SDC, substrates.

In the next stage, HT-DFT calculations are employed for building the \( E_{\text{vac}} \) data for a virtual chemical library of \( ABO_3 \) and \( A_{1/2}A_{11/5}B_{1/3}O_3 \) family of perovskites. As shown in Figure 3, \( ABO_3 \) perovskites have a single group of unique coordination arrangement for all their oxygen atoms, whereas \( A_{1/2}A_{11/5}B_{1/3}O_3 \) perovskites have three groups of unique oxygens. In the latter situation, from a total of 24 oxygen atoms in an \( A_4B_{12}O_{24} \) supercell shown in Figure 3b, four oxygen atoms (gray spheres) interact with \( A^2- \) and B-type metal cations, four oxygen atoms (dark blue spheres) interact with \( A^{4-} \) and B-type metal cations, and 16 oxygen atoms (red spheres) interact with all of the \( A^2- \), \( A^{4-} \), and B-type metal cations. Therefore, separate DFT calculations are performed to sample all possible O vacant positions in \( A_4B_{12}O_{24} \) supercells. This way, the weighted average oxygen formation energies are calculated for \( A_{1/2}A_{11/5}B_{1/3}O_3 \) perovskites.

The optimized lattice parameters and calculated \( E_{\text{vac}} \) data of perovskites are shown in Supporting Information Figures S1 and S2, respectively. For \( ABO_3 \) perovskites with B-type metal
cations that are chosen from the same row of the periodic table, an increase in atomic number results in a decrease in $E_{\text{vac}}$ (Figure S2.a). Thus, irrespective of the A-type cation used in the simple perovskites, the minimum $E_{\text{vac}}$ values are always achieved by using B-type atoms from group 12. Likewise, the $E_{\text{vac}}$ data of $A_{I}^{0.5}A_{II}^{0.5}BO_{3}$ perovskites (Figure S2.b) are calculated by considering all possible combinations of A-type cations, where $A = \text{La}, \text{Ba}, \text{Sr},$ and $\text{Ca}$. Similar to simple perovskites, for $A_{I}^{0.5}A_{II}^{0.5}BO_{3}$ perovskites the $E_{\text{vac}}$ decreases when B-type cations of increasing atomic numbers are used from the same row of the periodic table.

To identify candidate materials for SOFC cathodes, ASR extrema values are chosen based on the available information on top-performing perovskite-based SOFC electrode materials, BSCF (ASR = 0.02 $\Omega$ cm$^2$) and LSCF (ASR = 0.24 $\Omega$ cm$^2$). The log(ASR) data of the virtual materials that were estimated by using the LR model shown in eq 1 are provided in Figure S3. Additionally, a heatmap of the log(ASR) data of the likely stable perovskites is shown in Figure 4. Furthermore, the most promising SOFC cathode materials, which have calculated properties that are between those of BSCF and LSCF, are highlighted in Figure 4. From a pool of 270 perovskites investigated in the current study, 31 are shortlisted as candidate SOFC cathode materials. Therefore, to inspect the electrically conductive nature of candidate materials, electronic density of states (DOS) calculations are performed on the optimized structures of perovskites (Figures S5–S8). No apparent electronic band gaps are identified in the DOS analysis of DFT/PBE calculated results (Figures S5 and S6), thus endorsing the use of these promising perovskites as electrodes. In addition, other important factors that are beyond the scope of this study, including the cost and abundance of constituting elements or the synthetic accessibility of materials, can be considered to scale down the list of candidates further.

To help progress the material screening efforts on complex perovskites beyond the current work, a regression analysis is performed for investigating the relationships between the entirely DFT-calculated and the estimated oxygen vacancy formation energy data of materials. For the latter, $E_{\text{vac}}^\text{est}$ of the comparably more complex $A_{I}^{0.5}A_{II}^{0.5}BO_{3}$ perovskites are estimated by incorporating the DFT-calculated $E_{\text{vac}}$ data of simple perovskites, $A_{I}^{0.5}BO_{3}$ and $A_{II}^{0.5}BO_{3}$ into the following equation

$$E_{\text{vac}}^\text{est} = x E_{\text{vac}}^A + (1 - x) E_{\text{vac}}^B,$$

where $x = 0.5$ for the present material compositions. Figure 5 shows the observed correlations between the DFT calculated, $E_{\text{vac}}$, and the estimated, $E_{\text{vac}}^\text{est}$, data on a group of complex perovskites. In this analysis, $A_{I}^{0.5}A_{II}^{0.5}BO_{3}$ perovskites with negative $E_{\text{vac}}$ data are omitted, because a negative $E_{\text{vac}}$ indicates that the assumed perovskite structure is likely unstable. As shown in Figure 5a–f, for any complex perovskite constructed by a combination of A-type atoms, the calculated versus estimated data produce linear fits with $R^2 = 0.97$–0.99. Figure 5g shows the correlation between $E_{\text{vac}}$ and $E_{\text{vac}}^\text{est}$ for the merged data of all complex perovskites considered here, which yields an $R^2$ and a mean absolute error (MAE) of 0.99 and 0.24 eV.

Figure 4. Heat map of perovskites’ log(ASR) data. The most promising compounds are indicated by using a star, whereas the likely unstable perovskites are shown with blank cells.
respectively. To improve the precision of $E_{\text{vac}}$ data, in comparison to the directly calculated DFT $E_{\text{vac}}$ data of AI$_{0.5}$AII$_{0.5}$BO$_3$ perovskites, using the following simple equation is recommended

$$E_{\text{vac}} = 0.97(E_{\text{vac}}^{\text{est}})$$

(3)

Thus, by combining eqs 1−3, the following equation is obtained

$$\log(\text{ASR}) = 0.33[(E_{\text{vac}}^{\text{BO}} + E_{\text{vac}}^{\text{BO}})] - 2.32$$

(4)

which allows for the estimation of $\log(\text{ASR})$ data of AI$_{0.5}$AII$_{0.5}$BO$_3$ perovskites directly from the computed oxygen vacancy formation energies of the simple perovskites.

In summary, by performing HT-DFT calculations on a virtual chemical library of 108 ABO$_3$ and 162 AI$_{0.5}$AII$_{0.5}$BO$_3$ all-inorganic cubic perovskites, their potential use as electrode materials in SOFCs is scrutinized. $E_{\text{vac}}$ and ASR information on the compounds is used as principal chemical descriptors for evaluating the thermodynamic stability, catalytic behavior, and oxygen ion permeation performance of the newly generated virtual materials. A total of 31 candidate perovskites are predicted to show properties that are between those of the two state-of-the-art SOFC active materials of BSCF and LSCF. Additionally, the complex perovskites showed markedly linear $E_{\text{vac}}$ profiles against their ancestral simple perovskite data. Thus, with an attempt to expedite future in silico and in lab explorations on the vast chemical space of candidate perovskites, a screening strategy that relies on deriving $E_{\text{vac}}$ and ASR data of complex AI$_{0.5}$AII$_{0.5}$BO$_3$ perovskites directly from the data of simple ABO$_3$ and A$^5$BO$_3$ perovskites is propounded.

**Figure S5.** Comparison of DFT calculated and estimated $E_{\text{vac}}$ data of AI$_{0.5}$AII$_{0.5}$BO$_3$ perovskites covered in this study. LR results are shown for (a) La$_{0.5}$Ba$_{0.5}$BO$_3$, (b) La$_{0.5}$Sr$_{0.5}$BO$_3$, (c) La$_{0.5}$Ca$_{0.5}$BO$_3$, (d) Ba$_{0.5}$Sr$_{0.5}$BO$_3$, (e) Ba$_{0.5}$Ca$_{0.5}$BO$_3$, (f) Sr$_{0.5}$Ca$_{0.5}$BO$_3$, and (g) all AI$_{0.5}$AII$_{0.5}$BO$_3$ compounds. Here, only the likely stable candidate materials are shown, and the complete data including also the likely unstable compounds is shown in Figure S4.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00827.

Optimized lattice parameters of structures, calculated oxygen vacancy formation energies, area-specific polarization resistance data, comparison of calculated and estimated $E_{\text{vac}}$ data for AI$_{0.5}$AII$_{0.5}$BO$_3$ perovskites considered in this study, density of states plots, and computational methodology (PDF).

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Notes
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