

High-throughput computational screening of cubic perovskites for solid oxide fuel cell cathodes

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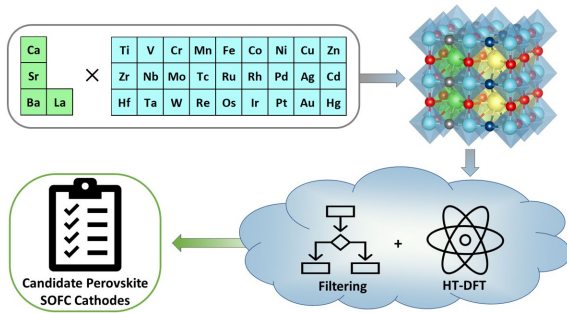
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It is a present-day challenge to design and develop oxygen permeable solid oxide fuel cell (SOFC) electrode and electrolyte materials that operate at low temperatures. Herein, by performing high-throughput density functional theory (HT-DFT) calculations, oxygen vacancy formation energy, E_{vac} , data for a pool of all-inorganic ABO_3 and $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ cubic perovskites is generated. Using E_{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 in between state-of-the-art SOFC cathode and oxygen permeation components. In addition, an intuitive approach to estimate E_{vac} and ASR data of complex perovskites solely by using the easy-to-access data of simple perovskites is shown, which is expected to boost future explorations on perovskite material search space for genuinely diverse energy applications.

TOC GRAPHICS



Technological advances are needed to address the rising demand for clean energy.¹ Perovskites, represented with a basic formula of ABO_3 , attract considerable attention due to their tunable structure-composition-property relationships that facilitate their scalable use as active materials in various energy applications.^{2,3} In addition to catalytic and photovoltaic applications, perovskites are increasingly being more employed as active electrode and electrolyte materials for efficient conversion of clean energy in SOFCs. This is mainly due to their promising features including, stability, electronic conductivity, and oxygen ion permeability.^{3–10} However, to efficiently operate, typical SOFCs require very high temperatures ($T = 700 \sim 1000$ °C). Enabling the operation at low temperatures, thereupon improving the overall energy efficiency of SOFCs, is a present-day challenge.^{10–14} $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) are two families of perovskites that are widely used as cathode materials in SOFCs. The former is a broadly studied SOFC cathode material, whereas the latter is a more recently investigated perovskite for SOFCs. Recent research shows that LSCF offers a good compromise between oxygen transport and thermomechanical features, thereby capacitating its operation at relatively lower temperatures than LSM.^{12,13,15–17} A third perovskite SOFC electrode material that attracted recent research interest is $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.25}O_{3-\delta}$ (BSCF), which shows both superior oxygen permeation and power density at low temperature.^{11,13,15,18} However, BSCF suffers from material stability issues that adversely affect its practical use in SOFC applications.^{15,19,20} This study aims to find perovskites with promising SOFC electrode material features that are predicted to be in between the two state-of-the-art materials of LSCF and BSCF.

In addition to good electrical conductivity, SOFC cathode materials should feature both an active reduction of oxygen molecules on their surfaces and a fast transport of oxygen atoms through their bulk structures.^{21–23} The oxygen vacancy formation energy, E_{vac} , of perovskites is a multi-purpose

descriptor that is extensively used for estimating the stability of compounds and their application-specific behaviors.^{6,22,24,25} In recent studies, E_{vac} is used as a performance descriptor for highly diverse chemical reactions including, carbon dioxide reduction^{3,26,27}, hydrogen evolution^{6,28,29}, nitrous oxide reduction^{6,30}, volatile organic compound oxidation^{3,6}, oxygen reduction^{3,6,29,31,32}, and in addition to all these, for oxygen ion diffusion through materials.^{24,33}

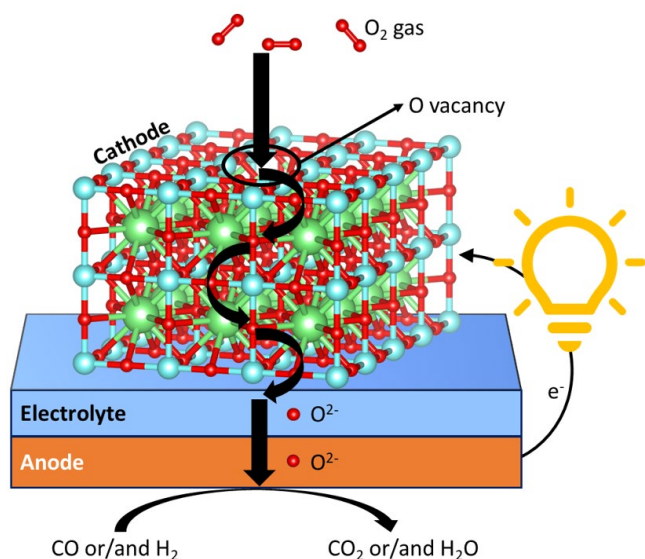


Figure 1. A schematic representation of oxygen utilization in SOFCs. Only the perovskite structure of the cathode material is depicted. Oxygen atoms are shown with red, A-type perovskite atoms with green, and B-type perovskite atoms with blue colored spheres.

The catalytic behavior and oxygen permeation performance of perovskites are influenced by the presence of oxygen atom vacancies in their structures.^{24,34} Figure 1 shows the adsorption of oxygen molecules on the surface of a SOFC cathode material and their subsequent reduction to oxygen ions. The newly generated oxygen atoms successively fill the vacant sites of the electrode. Similarly, oxygen is triggered to move from a high chemical potential cathode unit to a low

chemical potential anode unit through a solid electrolyte. The oxidation of fuel (e.g. CO and/or H₂) then takes place on the surface of SOFC anode material.¹⁶ 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.^{7,35} In addition to this, recent experimental works on perovskites attribute the high performance of oxygen exchange to low ASR.^{9,13,14} Hence, to estimate the SOFC performance, developing a calculable relationship between E_{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 E_{vac} , creates a risk for the structural integrity of the compound.³ Therefore, in addition to its exercise as a descriptor for the catalytic behavior and the oxygen transport performance of materials, E_{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_{vac} data is formulated. Next, a virtual chemical library of perovskites, which contains 108 ABO₃ and 162 A^I_{0.5}A^{II}_{0.5}BO₃ perovskites, is enumerated. Then, for all the compounds in the library, the E_{vac} data is generated by applying HT-DFT calculations. After that, the ASR data of a total of 270 virtual materials is predicted by using the newly developed relationship between E_{vac} and ASR of experimentally investigated materials and the DFT calculated E_{vac} data. Finally, the most promising candidate materials for SOFC cathodes are singled out and a practical means for accessing the key E_{vac} and ASR data of complex perovskites is presented. The specific aspects of the stages of the study are described below.

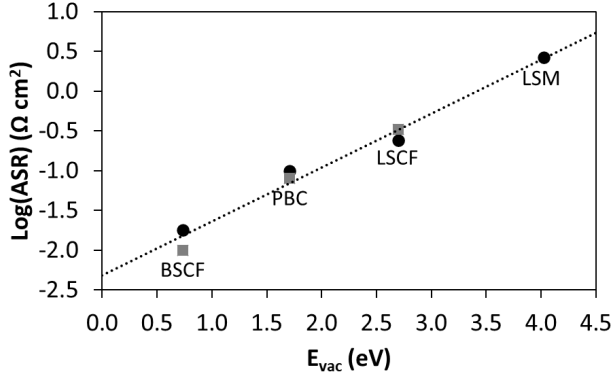


Figure 2. LR between the measured ASR and the calculated E_{vac} data: ● dataset is plotted using the available data of materials on GDC and ■ dataset is plotted using the available data of materials on SDC substrates. All data points are used in the LR model.

First, a direct correlation between E_{vac} and the $\text{log}(ASR)$ is developed by using the experimental data of $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (PBC), $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskites on Gd-doped ceria (GDC) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskites on Sm-doped ceria (SDC) substrates.^{36–42} To virtually match these experimented compositions, cubic supercells of $\text{Pr}_4\text{Ba}_4\text{Co}_8\text{O}_{24}$, $\text{La}_6\text{Sr}_2\text{Mn}_8\text{O}_{24}$, $\text{Ba}_4\text{Sr}_4\text{Co}_6\text{FeO}_{24}$, and $\text{La}_5\text{Sr}_3\text{Co}_2\text{Fe}_6\text{O}_{24}$, which respectively represent, $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$, $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3$, and $\text{La}_{0.625}\text{Sr}_{0.375}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_3$ compositions, are used in DFT calculations. It is known that perovskites that have non-cubic symmetry at room temperature are usually prone to a phase transformation to cubic symmetry at higher temperatures.^{2,43} For example, BaTiO_3 has rhombohedral ($R3m$) symmetry at low temperature, and upon heating, its structure transforms to orthorhombic ($Amm2$) at -90°C , to tetragonal ($P4mm$) at 5°C , and finally to cubic ($Pm3m$) at above 120°C .⁴⁴ Therefore, as a pragmatic reasoning owing to SOFC operation temperatures, all structures considered here are

assumed in cubic symmetry. Also, notably, the weighted average vacancy formation energies are calculated by performing DFT simulations on all of the unique oxygen vacant configurations of perovskite structures. Accordingly, as shown in Figure 2, a linear regression (LR) model is developed for the measured $\log(ASR)$ and the DFT calculated E_{vac} data of materials. The obtained LR equation

$$\log(ASR) = 0.68(E_{vac}) - 2.32 \quad \text{Eq. 1}$$

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.

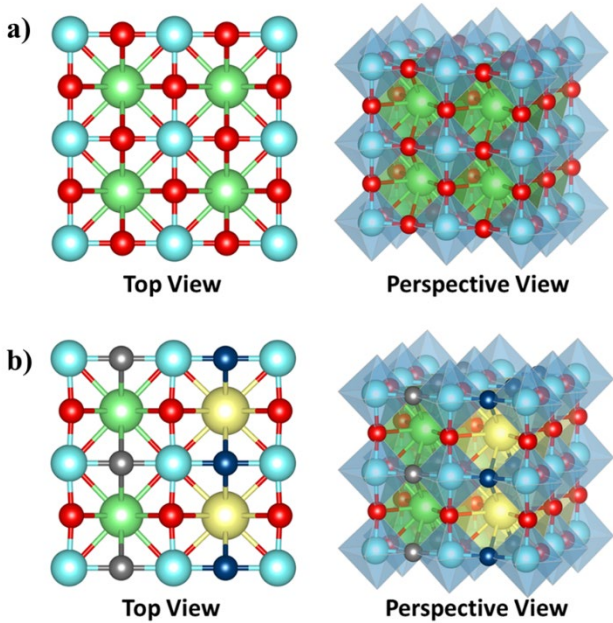


Figure 3. Top and perspective views of **a)** $A_8B_8O_{24}$ and **b)** $A_4A^I_4A^{II}_4B_8O_{24}$ supercells that represent ABO_3 and $A^{I}_{0.5}A^{II}_{0.5}BO_3$ group of perovskites, respectively. Green and yellow spheres represent A-type (i.e., A, A^I , or A^{II}) metal cations, blue spheres represent B-type metal cations, and red

spheres represent O atoms. In $A^I_4A^{II}_4B_8O_{24}$ supercells, as shown in **b**), O atoms are categorized into three different groups in relation to their coordination to first order neighboring metal atoms. For an improved visual perception, these different groups of O atoms are shown with red, grey, and dark blue spheres.

In the next stage, HT-DFT calculations are employed for building the E_{vac} data for a virtual chemical library of ABO_3 and $A^{I}_{0.5}A^{II}_{0.5}BO_3$ 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 $A^{I}_{0.5}A^{II}_{0.5}BO_3$ perovskites have three groups of unique oxygens. In the latter situation, from a total of 24 oxygen atoms in an $A^I_4A^{II}_4B_8O_{24}$ supercell shown in Figure 3.b, four oxygen atoms (grey spheres) interact with A^I - and B-type metal cations, four oxygen atoms (dark blue spheres) interact with A^{II} - and B-type metal cations, and 16 oxygen atoms (red spheres) interact with all of the A^I -, A^{II} -, and B-type metal cations. Therefore, separate DFT calculations are performed to sample all possible O vacant positions in $A^I_4A^{II}_4B_8O_{23}$ supercells. This way, the weighted average oxygen formation energies are calculated for $A^{I}_{0.5}A^{II}_{0.5}BO_3$ perovskites.

The optimized lattice parameters and calculated E_{vac} data of perovskites are shown in Supporting Information Figure 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_{vac} (Figure S2.a). Thus, irrespective of the A-type cation used in the simple perovskites, the minimum E_{vac} values are always achieved by using B-type atoms from group 12. Likewise, the E_{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 $A = La, Ba, Sr, \text{ and } Ca$. Similar to simple

perovskites, for $A^{I}_{0.5}A^{II}_{0.5}BO_3$ perovskites the E_{vac} decreases when B-type cations of increasing atomic numbers are used from the same row of the periodic table.

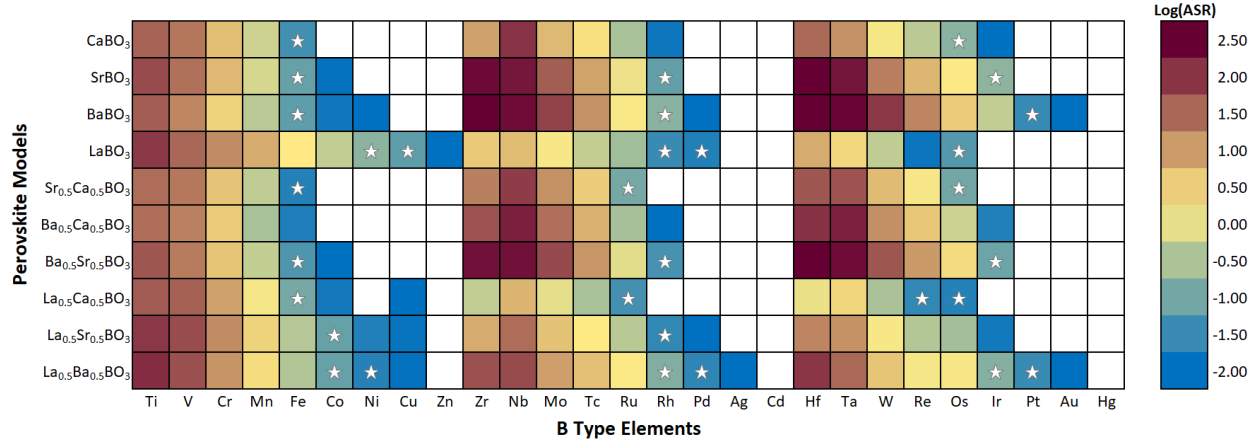


Figure 4. A heat map of perovskites' $\log(ASR)$ data. The most promising compounds are indicated by using a star sign, whereas the likely unstable perovskites are shown with blank cells.

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 ($ASR = 0.02 \Omega \text{ cm}^2$)³⁷ and LSCF ($ASR = 0.24 \Omega \text{ cm}^2$).⁴² The calculated $\log(ASR)$ data of virtual materials is provided in Figure S3 and a heatmap of $\log(ASR)$ data of the likely stable perovskites is shown in Figure 4. Additionally, the most promising SOFC cathode materials, which have calculated properties that are in between 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. Furthermore, to inspect the electrically conductive nature of candidate materials, electronic density of states (DOS) calculations are performed on the optimized structures of perovskites. No apparent electronic band gaps are identified in the DOS analysis. Thus, endorsing the use of these promising perovskites as electrodes. Withal, 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.⁴⁵

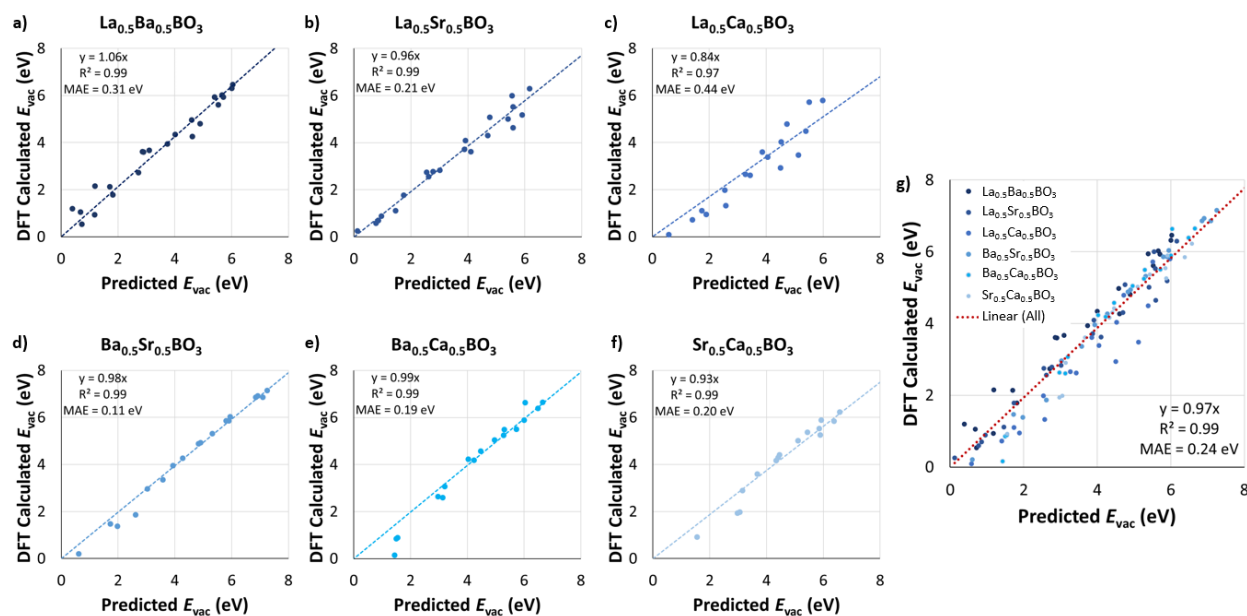


Figure 5. Comparison of DFT calculated and predicted E_{vac} data of $A^{\text{I}}_{0.5}A^{\text{II}}_{0.5}\text{BO}_3$ perovskites covered in this study. LR results are shown for **a)** $\text{La}_{0.5}\text{Ba}_{0.5}\text{BO}_3$, **b)** $\text{La}_{0.5}\text{Sr}_{0.5}\text{BO}_3$, **c)** $\text{La}_{0.5}\text{Ca}_{0.5}\text{BO}_3$, **d)** $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{BO}_3$, **e)** $\text{Ba}_{0.5}\text{Ca}_{0.5}\text{BO}_3$, **f)** $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{BO}_3$, and **g)** all $A^{\text{I}}_{0.5}A^{\text{II}}_{0.5}\text{BO}_3$ compounds. In here, only the likely stable candidate materials are conceded, and the complete data including also the likely unstable compounds is shown in Figure S4.

To help forward the material screening efforts on complex perovskites beyond the current work, a regression analysis is performed for investigating the relationships between the utterly DFT calculated and the predicted oxygen vacancy formation energy data of materials. For the latter,

$E_{\text{vac}}^{\text{pred}}$ of the comparably more complex, $A^{\text{I}}_{0.5}A^{\text{II}}_{0.5}\text{BO}_3$ perovskites, are predicted by incorporating the DFT calculated E_{vac} data of simple perovskites, $A^{\text{I}}\text{BO}_3$ and $A^{\text{II}}\text{BO}_3$, into the following equation

$$E_{\text{vac}}^{\text{pred}} = x * E_{\text{vac}}^{A^{\text{I}}\text{BO}_3} + (1 - x) * E_{\text{vac}}^{A^{\text{II}}\text{BO}_3} \quad \text{Eq.2}$$

where $x = 0.5$ for the present material compositions. Figure 5 shows the observed correlations between the DFT calculated, E_{vac} , and the predicted, $E_{\text{vac}}^{\text{pred}}$, data on a group of complex perovskites. In this analysis, $A^{\text{I}}_{0.5}A^{\text{II}}_{0.5}\text{BO}_3$ perovskites with negative E_{vac} data are omitted, since a negative E_{vac} indicates that the assumed perovskite structure is likely unstable. As shown in Figure 5.a-f, for any complex perovskite constructed by a combination of A-type atoms, the calculated versus predicted data produce linear fits with $R^2 = 0.97\sim 0.99$. Figure 5.g shows the correlation between E_{vac} and $E_{\text{vac}}^{\text{pred}}$ 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, respectively. To improve the precision of $E_{\text{vac}}^{\text{pred}}$ data, in comparison to the directly calculated DFT E_{vac} data of $A^{\text{I}}_{0.5}A^{\text{II}}_{0.5}\text{BO}_3$ perovskites, using the following simple equation is recommended

$$E_{\text{vac}} = 0.97(E_{\text{vac}}^{\text{pred}}) \quad \text{Eq.3}$$

Thus, by combining Equations 1-3, the following equation is obtained

$$\log(\text{ASR}) = 0.33 \left[\left(E_{\text{vac}}^{A^{\text{I}}\text{BO}_3} + E_{\text{vac}}^{A^{\text{II}}\text{BO}_3} \right) \right] - 2.32 \quad \text{Eq.4}$$

which allows for the prediction of $\log(ASR)$ data of $A^I_{0.5}A^{II}_{0.5}BO_3$ 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 $A^I_{0.5}A^{II}_{0.5}BO_3$ all-inorganic cubic perovskites, their potential use as electrode materials in SOFCs is scrutinized. E_{vac} and ASR information of 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 in between the two state-of-the-art SOFC active materials of BSCF and LSCF. Additionally, the complex perovskites showed markedly linear E_{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_{vac} and ASR data of complex $A^I_{0.5}A^{II}_{0.5}BO_3$ perovskites directly from the data of simple $A^I BO_3$ and $A^{II} BO_3$ perovskites is propounded.

ASSOCIATED CONTENT

Supporting Information. Calculated oxygen vacancy formation energies, optimized lattice parameters of structures, area-specific polarization resistance data, comparison of calculated and predicted E_{vac} data for $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ perovskites considered in this study, and computational methodology.

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Notes

The authors declare no competing financial interest.

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