

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

Citation for published version (APA):

Tezsevin, I., van de Sanden, M. C. M., & Er, S. (2021). High-throughput computational screening of cubic perovskites for solid oxide fuel cell cathodes. *Journal of Physical Chemistry Letters*, 12(17), 4160-4165. <https://doi.org/10.1021/acs.jpcllett.1c00827>

Document license:
TAVERNE

DOI:
[10.1021/acs.jpcllett.1c00827](https://doi.org/10.1021/acs.jpcllett.1c00827)

Document status and date:
Published: 06/05/2021

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

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

Ilker Tezsevin, Mauritius C. M. van de Sanden, and Süleyman Er*

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 4160–4165

Read Online

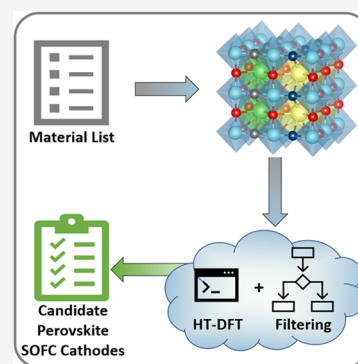
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

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_{vac} data for a pool of all-inorganic ABO_3 and $A^{I}_{0.5}A^{II}_{0.5}BO_3$ 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 between those of 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 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.



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 because of 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 employed as active electrode and electrolyte materials for efficient conversion of clean energy in solid oxide fuel cells (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 ($T = 700–1000$ °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 allowing 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 between those of 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 multipurpose 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} and oxygen reduction,^{3,6,29,31,32} as well as for oxygen ion diffusion through materials.^{22,33}

The catalytic behavior and oxygen permeation performance of perovskites are influenced by the presence of oxygen atom vacancies in their structures.^{22,34} 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

Received: March 14, 2021

Accepted: April 19, 2021

Published: April 23, 2021



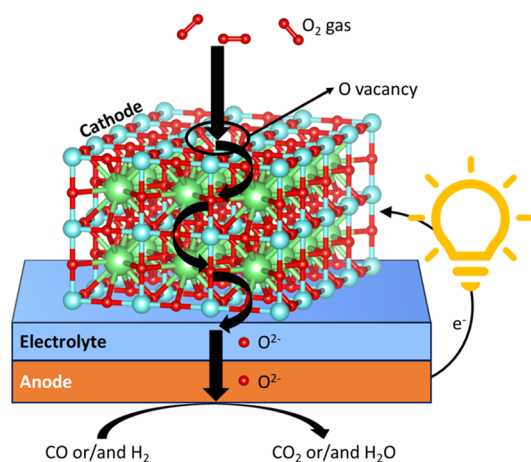


Figure 1. Schematic representation of oxygen utilization in SOFCs. Only the perovskite structure of the cathode material is depicted. Oxygen atoms are shown with red, A-type perovskite atoms with green, and B-type perovskite atoms with blue colored spheres.

of fuel (e.g., CO and/or H₂) then takes place on the surface of the 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, recent experimental work on perovskites attributes the high performance of oxygen exchange to low area-specific resistance (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 application 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 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_{vac} and ASR of experimentally investigated materials and the HT-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.

First, a direct correlation between E_{vac} and the log(ASR) is developed by using the experimental data of Pr_{0.5}Ba_{0.5}CoO_{3-δ} (PBC), La_{0.8}Sr_{0.2}MnO_{3-δ}, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}, and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} perovskites on Gd-doped ceria (GDC) and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}, Pr_{0.5}Ba_{0.5}CoO_{3-δ}, and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} perovskites on Sm-doped ceria (SDC) substrates.^{36–42} To virtually match these experimented

compositions, cubic supercells of Pr₄Ba₄Co₈O₂₄, La₆Sr₂Mn₈O₂₄, Ba₄Sr₄Co₆FeO₂₄, and La₅Sr₃Co₂Fe₆O₂₄, which represent Pr_{0.5}Ba_{0.5}CoO₃, La_{0.75}Sr_{0.25}MnO₃, Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.25}O₃, and La_{0.625}Sr_{0.375}Co_{0.25}Fe_{0.75}O₃ 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.^{2,43} For example, BaTiO₃ 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 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

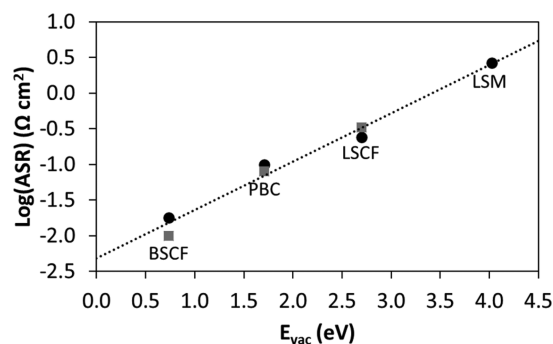


Figure 2. LR between the measured ASR and the calculated E_{vac} data: (●) data set plotted using the available data of materials on GDC and (■) data set plotted using the available data of materials on SDC substrates. All data points are used in the LR model.

linear regression (LR) model is developed for the measured log(ASR) and the DFT-calculated E_{vac} data of materials. The obtained LR equation

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

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.

In the next stage, HT-DFT calculations are employed for building the E_{vac} data for a virtual chemical library of ABO₃ and A^I_{0.5}A^{II}_{0.5}BO₃ family of perovskites. As shown in Figure 3, ABO₃ perovskites have a single group of unique coordination arrangement for all their oxygen atoms, whereas A^I_{0.5}A^{II}_{0.5}BO₃ perovskites have three groups of unique oxygens. In the latter situation, from a total of 24 oxygen atoms in an A^I₄A^{II}₄B₈O₂₄ supercell shown in Figure 3b, four oxygen atoms (gray 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^I₄A^{II}₄B₈O₂₃ supercells. This way, the weighted average oxygen formation energies are calculated for A^I_{0.5}A^{II}_{0.5}BO₃ perovskites.

The optimized lattice parameters and calculated E_{vac} data of perovskites are shown in Supporting Information Figures S1 and S2, respectively. For ABO₃ perovskites with B-type metal

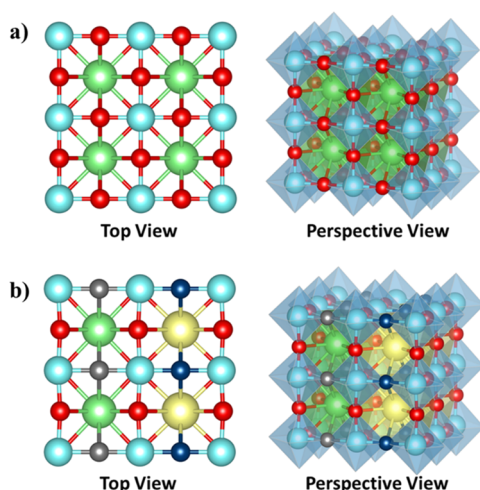


Figure 3. Top and perspective views of (a) $A_8B_8O_{24}$ and (b) $A^{I}_4A^{II}_4B_8O_{24}$ supercells that represent ABO_3 and $A^{I}_{0.5}A^{II}_{0.5}BO_3$ groups of perovskites, respectively. Green and yellow spheres represent A-type (i.e., A, A^I , or A^{II}) metal cations, blue spheres B-type metal cations, and red spheres O atoms. In $A^{I}_4A^{II}_4B_8O_{24}$ supercells, as shown in panel 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, gray, and dark blue spheres.

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, 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.

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 $\log(ASR)$ 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.⁴⁵

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_{vac}^{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_{vac} data of simple perovskites, $A^I BO_3$ and $A^{II} BO_3$, into the following equation

$$E_{vac}^{est} = x \cdot E_{vac}^{A^I BO_3} + (1 - x) E_{vac}^{A^{II} BO_3} \quad (2)$$

where $x = 0.5$ for the present material compositions. Figure 5 shows the observed correlations between the DFT calculated, E_{vac} , and the estimated, E_{vac}^{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_{vac} data are omitted, because a negative E_{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_{vac} and E_{vac}^{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,

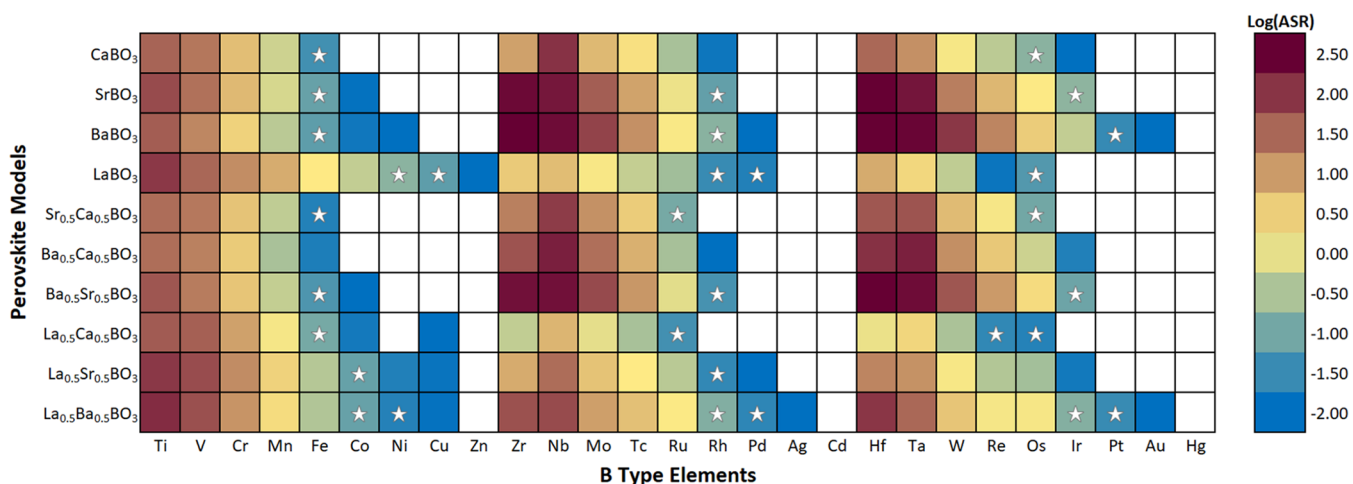


Figure 4. Heat map of perovskites' $\log(ASR)$ data. The most promising compounds are indicated by using a star, whereas the likely unstable perovskites are shown with blank cells.

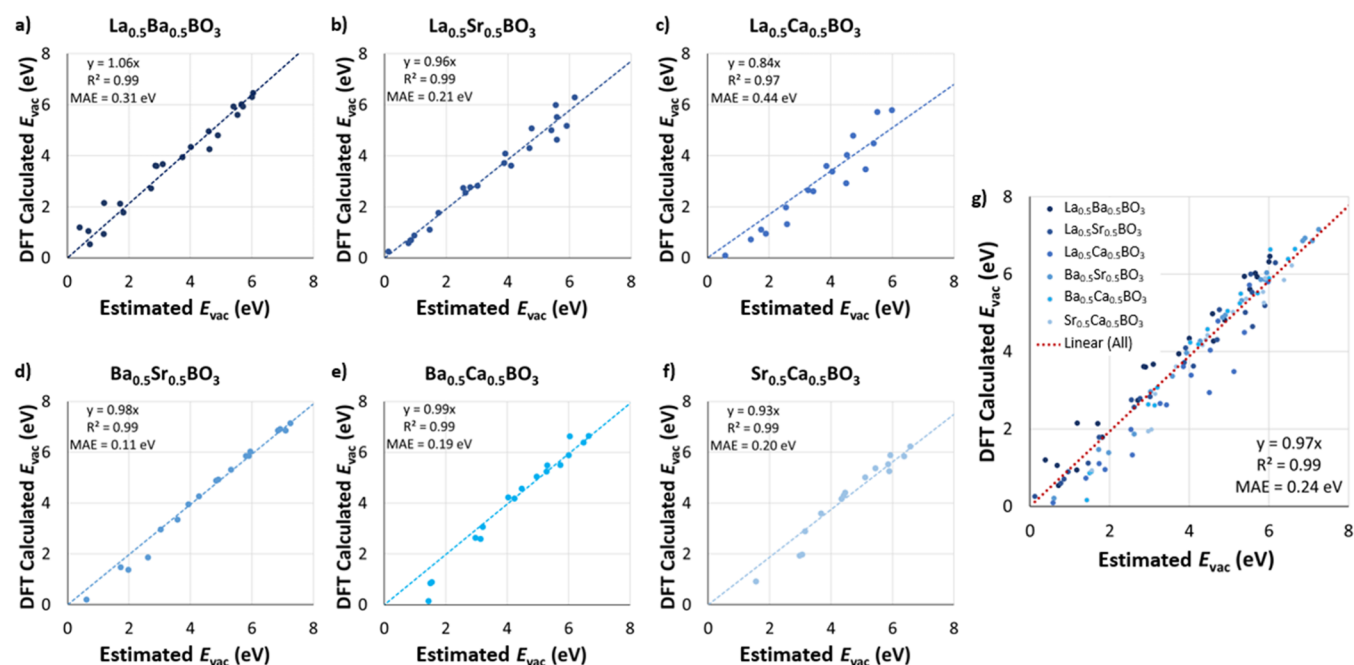


Figure 5. Comparison of DFT calculated and estimated E_{vac} data of $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ perovskites covered in this study. LR results are shown for (a) $\text{La}_{0.5}\text{Ba}_{0.5}\text{BO}_3$, (b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{BO}_3$, (c) $\text{La}_{0.5}\text{Ca}_{0.5}\text{BO}_3$, (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 $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ 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.

respectively. To improve the precision of E_{vac}^{est} data, in comparison to the directly calculated DFT E_{vac} data of $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ perovskites, using the following simple equation is recommended

$$E_{vac} = 0.97(E_{vac}^{\text{est}}) \quad (3)$$

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

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

which allows for the estimation of $\log(\text{ASR})$ data of $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ 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 $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ all-inorganic cubic perovskites, their potential use as electrode materials in SOFCs is scrutinized. E_{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_{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 $\text{A}^{\text{I}}_{0.5}\text{A}^{\text{II}}_{0.5}\text{BO}_3$ perovskites directly from the data of simple $\text{A}^{\text{I}}\text{BO}_3$ and $\text{A}^{\text{II}}\text{BO}_3$ perovskites is propounded.

■ ASSOCIATED CONTENT

SI Supporting Information

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

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

■ AUTHOR INFORMATION

Corresponding Author

Süleyman Er – DIFFER – Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands; CCER – Center for Computational Energy Research, 5612 AJ Eindhoven, The Netherlands; orcid.org/0000-0002-5005-3894; Email: s.er@differ.nl; <https://www.amdmlab.nl>

Authors

Ilker Tezsevin – DIFFER – Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands; CCER – Center for Computational Energy Research, 5612 AJ Eindhoven, The Netherlands; Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0001-5648-3943

Mauritius C. M. van de Sanden – DIFFER – Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands; Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-4119-9971

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcclett.1c00827>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work presented in this Letter is part of the European project KEROGREEN, which has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 763909. S.E. acknowledges funding from the initiative "Computational Sciences for Energy Research" of Shell and The Netherlands Organization for Scientific Research (NWO) Grant No. 15CSTT05. This work was sponsored by NWO Exact and Natural Sciences for the use of supercomputer facilities.

REFERENCES

- (1) Tezsevin, I.; van de Sanden, M. C. M.; Er, S. Surface Charging Activated Mechanism Change: A Computational Study of O, CO, and CO₂ Interactions on Ag Electrodes. *J. Energy Chem.* **2020**, *50*, 307–313.
- (2) Sebastian, M. T. ABO₃ Type Perovskites. In *Dielectric Materials for Wireless Communication*; Elsevier, 2008; pp 161–203.
- (3) Hwang, J.; Rao, R. R.; Giordano, L.; Katayama, Y.; Yu, Y.; Shao-Horn, Y. Perovskites in Catalysis and Electrocatalysis. *Science* **2017**, *358*, 751–756.
- (4) Labhasetwar, N.; Saravanan, G.; Kumar Megarajan, S.; Manwar, N.; Khobragade, R.; Doggali, P.; Grasset, F. Perovskite-Type Catalytic Materials for Environmental Applications. *Sci. Technol. Adv. Mater.* **2015**, *16*, No. 036002.
- (5) Tyunina, M.; Yao, L.; Chvostova, D.; Dejneka, A.; Kocourek, T.; Jelinek, M.; Trepakov, V.; van Dijken, S. Concurrent Bandgap Narrowing and Polarization Enhancement in Epitaxial Ferroelectric Nanofilms. *Sci. Technol. Adv. Mater.* **2015**, *16*, No. 026002.
- (6) Voorhoeve, R. J. H.; Johnson, D. W., Jr.; Remeika, J. P.; Gallagher, P. K. Perovskite Oxides: Materials Science in Catalysis. *Science* **1977**, *195*, 827–833.
- (7) Himma, N. F.; Wardani, A. K.; Prasetya, N.; Aryanti, P. T. P.; Wenten, I. G. Recent Progress and Challenges in Membrane-Based O₂/N₂ Separation. *Rev. Chem. Eng.* **2019**, *35*, 591–625.
- (8) Kubicek, M.; Bork, A. H.; Rupp, J. L. M. Perovskite Oxides—a Review on a Versatile Material Class for Solar-to-Fuel Conversion Processes. *J. Mater. Chem. A* **2017**, *5*, 11983–12000.
- (9) Gómez, S. Y.; Hotza, D. Current Developments in Reversible Solid Oxide Fuel Cells. *Renewable Sustainable Energy Rev.* **2016**, *61*, 155–174.
- (10) Muñoz-García, A. B.; Ritzmann, A. M.; Pavone, M.; Keith, J. A.; Carter, E. A. Oxygen Transport in Perovskite-Type Solid Oxide Fuel Cell Materials: Insights from Quantum Mechanics. *Acc. Chem. Res.* **2014**, *47*, 3340–3348.
- (11) Duan, C.; Hook, D.; Chen, Y.; Tong, J.; O'Hayre, R. Zr and Y Co-Doped Perovskite as a Stable, High Performance Cathode for Solid Oxide Fuel Cells Operating below 500 °C. *Energy Environ. Sci.* **2017**, *10*, 176–182.
- (12) Ritzmann, A. M.; Muñoz-García, A. B.; Pavone, M.; Keith, J. A.; Carter, E. A. Ab Initio Evaluation of Oxygen Diffusivity in LaFeO₃: The Role of Lanthanum Vacancies. *MRS Commun.* **2013**, *3*, 161–166.
- (13) Li, L.; Yang, H.; Gao, Z.; Zhang, Y.; Dong, F.; Yang, G.; Ni, M.; Lin, Z. Nickel-Substituted Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}: A Highly Active Perovskite Oxygen Electrode for Reduced-Temperature Solid Oxide Fuel Cells. *J. Mater. Chem. A* **2019**, *7*, 12343–12349.
- (14) He, W.; Wu, X.; Yang, G.; Shi, H.; Dong, F.; Ni, M. BaCo_{0.7}Fe_{0.22}Y_{0.08}O_{3-δ} as an Active Oxygen Reduction Electrocatalyst for Low-Temperature Solid Oxide Fuel Cells below 600 °C. *ACS Energy Lett.* **2017**, *2*, 301–305.
- (15) Kotomin, E. A.; Mastrikov, Y. A.; Kuklja, M. M.; Merkle, R.; Roytburd, A.; Maier, J. First Principles Calculations of Oxygen Vacancy Formation and Migration in Mixed Conducting Ba_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_{3-δ} Perovskites. *Solid State Ionics* **2011**, *188*, 1–5.
- (16) Lee, Y.-L.; Morgan, D. Prediction of Surface Oxygen Vacancy Concentrations of (La_{1-x}Sr_x)MnO₃. *ECS Trans.* **2009**, *25*, 2769–2774.
- (17) Ovtar, S.; Søgaard, M.; Norrman, K.; Hendriksen, P. V. Oxygen Exchange and Transport in (La_{0.6}Sr_{0.4})_{0.98}FeO_{3-d}-Ce_{0.9}Gd_{0.1}O_{1.95} Dual-Phase Composites. *J. Electrochem. Soc.* **2018**, *165*, F220–F231.
- (18) Baumann, S.; Serra, J. M.; Lobera, M. P.; Escolástico, S.; Schulze-Küppers, F.; Meulenbergh, W. A. Ultrahigh Oxygen Permeation Flux through Supported Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} Membranes. *J. Membr. Sci.* **2011**, *377*, 198–205.
- (19) Arratibel Plazaola, A.; Cruellas Labella, A.; Liu, Y.; Badiola Porras, N.; Pacheco Tanaka, D.; Sint Annaland, M.; Gallucci, F. Mixed Ionic-Electronic Conducting Membranes (MIEC) for Their Application in Membrane Reactors: A Review. *Processes* **2019**, *7*, 128.
- (20) Kharton, V. V.; Yaremchenko, A. A.; Kovalevsky, A. V.; Viskup, A. P.; Naumovich, E. N.; Kerko, P. F. Perovskite-Type Oxides for High-Temperature Oxygen Separation Membranes. *J. Membr. Sci.* **1999**, *163*, 307–317.
- (21) Uberuaga, B. P.; Pilia, G. Effect of Cation Ordering on Oxygen Vacancy Diffusion Pathways in Double Perovskites. *Chem. Mater.* **2015**, *27*, 5020–5026.
- (22) Mayeshiba, T.; Morgan, D. Strain Effects on Oxygen Vacancy Formation Energy in Perovskites. *Solid State Ionics* **2017**, *311*, 105–117.
- (23) Chen, G.; Buck, F.; Kistner, I.; Widemeyer, M.; Schiestel, T.; Schulz, A.; Walker, M.; Weidenkaff, A. A Novel Plasma-Assisted Hollow Fiber Membrane Concept for Efficiently Separating Oxygen from CO in a CO₂ Plasma. *Chem. Eng. J.* **2020**, *392*, 123699.
- (24) Kim, C.; Eom, T.; Jee, M. S.; Jung, H.; Kim, H.; Min, B. K.; Hwang, Y. J. Insight into Electrochemical CO₂ Reduction on Surface-Molecule-Mediated Ag Nanoparticles. *ACS Catal.* **2017**, *7*, 779–785.
- (25) Emery, A. A.; Wolverton, C. High-Throughput DFT Calculations of Formation Energy, Stability and Oxygen Vacancy Formation Energy of ABO₃ Perovskites. *Sci. Data* **2017**, *4*, 170153.
- (26) Maiti, D.; Hare, B. J.; Daza, Y. A.; Ramos, A. E.; Kuhn, J. N.; Bhethanabotla, V. R. Earth Abundant Perovskite Oxides for Low Temperature CO₂ conversion. *Energy Environ. Sci.* **2018**, *11*, 648–659.
- (27) Maiti, D.; Daza, Y. A.; Yung, M. M.; Kuhn, J. N.; Bhethanabotla, V. R. Oxygen Vacancy Formation Characteristics in the Bulk and across Different Surface Terminations of La_(1-x)Sr_xFe_(1-y)Co_yO_(3-δ) Perovskite Oxides for CO₂ conversion. *J. Mater. Chem. A* **2016**, *4*, 5137–5148.
- (28) Guan, D.; Zhou, J.; Huang, Y.-C.; Dong, C.-L.; Wang, J.-Q.; Zhou, W.; Shao, Z. Screening Highly Active Perovskites for Hydrogen-Evolving Reaction via Unifying Ionic Electronegativity Descriptor. *Nat. Commun.* **2019**, *10*, 3755.
- (29) Montoya, J. H.; Doyle, A. D.; Nørskov, J. K.; Vojvodic, A. Trends in Adsorption of Electrocatalytic Water Splitting Intermediates on Cubic ABO₃ Oxides. *Phys. Chem. Chem. Phys.* **2018**, *20*, 3813–3818.
- (30) Beppu, K.; Hosokawa, S.; Asakura, H.; Teramura, K.; Tanaka, T. Role of Lattice Oxygen and Oxygen Vacancy Sites in Platinum Group Metal Catalysts Supported on Sr₃Fe₂O_{7-δ} for NO-Selective Reduction. *Catal. Sci. Technol.* **2018**, *8*, 147–153.
- (31) Cherkas, S. L.; Kalashnikov, V. L. A Solution of the Discrete Wheeler-Dewitt Equation in the Vicinity of Small Scale Factors and Quantum Mechanics in the Space of Negative Constant Curvature. *Nonlinear Phenom. Complex Syst.* **2014**, *17*, 358–363.
- (32) Li, X.; Wang, H.; Cui, Z.; Li, Y.; Xin, S.; Zhou, J.; Long, Y.; Jin, C.; Goodenough, J. B. Exceptional Oxygen Evolution Reactivities on CaCoO₃ and SrCoO₃. *Sci. Adv.* **2019**, *5*, No. eaav6262.
- (33) Lee, Y. L.; Kleis, J.; Rossmel, J.; Shao-Horn, Y.; Morgan, D. Prediction of Solid Oxide Fuel Cell Cathode Activity with First-Principles Descriptors. *Energy Environ. Sci.* **2011**, *4*, 3966–3970.
- (34) Huang, W. L.; Zhu, Q.; Ge, W.; Li, H. Oxygen-Vacancy Formation in LaMO₃ (M = Ti, V, Cr, Mn, Fe, Co, Ni) Calculated at Both GGA and GGA + U Levels. *Comput. Mater. Sci.* **2011**, *50*, 1800–1805.

(35) Zhang, L.; Liu, B.; Zhuang, H.; Kent, P. R. C.; Cooper, V. R.; Ganesh, P.; Xu, H. Oxygen Vacancy Diffusion in Bulk SrTiO₃ from Density Functional Theory Calculations. *Comput. Mater. Sci.* **2016**, *118*, 309–315.

(36) Shao, Z.; Haile, S. M. A High-Performance Cathode for the next Generation of Solid-Oxide Fuel Cells. *Nature* **2004**, *431*, 170–173.

(37) Chen, C.-H.; Chang, C.-L.; Hwang, B.-H. Electrochemical and Microstructure Characteristics of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) Cathodes Prepared by Citrate Precursor Method for SOFCs. *Mater. Chem. Phys.* **2009**, *115*, 478–482.

(38) Perry Murray, E. (La,Sr)MnO₃–(Ce,Gd)O_{2-x} Composite Cathodes for Solid Oxide Fuel Cells. *Solid State Ionics* **2001**, *143*, 265–273.

(39) Kim, G.; Wang, S.; Jacobson, A. J.; Reimus, L.; Brodersen, P.; Mims, C. A. Rapid Oxygen Ion Diffusion and Surface Exchange Kinetics in PrBaCo₂O_{5+x} with a Perovskite Related Structure and Ordered A Cations. *J. Mater. Chem.* **2007**, *17* (24), 2500.

(40) Chen, D.; Ran, R.; Zhang, K.; Wang, J.; Shao, Z. Intermediate-Temperature Electrochemical Performance of a Polycrystalline PrBaCo₂O_{5+δ} Cathode on Samarium-Doped Ceria Electrolyte. *J. Power Sources* **2009**, *188*, 96–105.

(41) Jiang, S. A Comparison of O₂ Reduction Reactions on Porous (La,Sr)MnO₃ and (La,Sr)(Co,Fe)O₃ Electrodes. *Solid State Ionics* **2002**, *146*, 1–22.

(42) Esquirol, A.; Brandon, N. P.; Kilner, J. A.; Mogensen, M. Electrochemical Characterization of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ Cathodes for Intermediate-Temperature SOFCs. *J. Electrochem. Soc.* **2004**, *151*, A1847.

(43) Lee, Y. L.; Kleis, J.; Rossmeisl, J.; Morgan, D. Ab Initio Energetics of LaBO₃(001) (B = Mn, Fe, Co, and Ni) for Solid Oxide Fuel Cell Cathodes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 224101.

(44) Johnsson, M.; Lemmens, P. Crystallography and Chemistry of Perovskites. *Handb. Magn. Adv. Magn. Mater.* **2007**, *4*, 1–9.

(45) Kuhar, K.; Pandey, M.; Thygesen, K. S.; Jacobsen, K. W. High-Throughput Computational Assessment of Previously Synthesized Semiconductors for Photovoltaic and Photoelectrochemical Devices. *ACS Energy Lett.* **2018**, *3*, 436–446.