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Authors

Gao, Ran
Fernandez, Abel
Chakraborty, Tanmoy
et al.

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Correlating Surface Crystal Orientation and Gas Kinetics in Perovskite Oxide Electrodes

Ran Gao, Abel Fernandez, Tanmoy Chakraborty, Aileen Luo, David Pesquera, Sujit Das, Gabriel Velarde, Vincent Thoréton, John Kilner, Tatsumi Ishihara, Slavomír Nemšák, Ethan J. Crumlin, Elif Ertekin, and Lane W. Martin*

Solid–gas interactions at electrode surfaces determine the efficiency of solid-oxide fuel cells and electrolyzers. Here, the correlation between surface–gas kinetics and the crystal orientation of perovskite electrodes is studied in the model system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$. The gas-exchange kinetics are characterized by synthesizing epitaxial half-cell geometries where three single-variant surfaces are produced [i.e., $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}/\text{SrRuO}_3/\text{SrTiO}_3$ (001), (110), and (111)]. Electrochemical impedance spectroscopy and electrical conductivity relaxation measurements reveal a strong surface-orientation dependency of the gas-exchange kinetics, wherein (111)-oriented surfaces exhibit an activity >3-times higher as compared to (001)-oriented surfaces. Oxygen partial pressure (p_{O_2})-dependent electrochemical impedance spectroscopy studies reveal that while the three surfaces have different gas-exchange kinetics, the reaction mechanisms and rate-limiting steps are the same (i.e., charge-transfer to the diatomic oxygen species). First-principles calculations suggest that the formation energy of vacancies and adsorption at the various surfaces is different and influenced by the surface polarity. Finally, synchrotron-based, ambient-pressure X-ray spectroscopies reveal distinct electronic changes and surface chemistry among the different surface orientations. Taken together, thin-film epitaxy provides an efficient approach to control and understand the electrode reactivity ultimately demonstrating that the (111)-surface exhibits a high density of active surface sites which leads to higher activity.

1. Introduction

Strong interactions with gas molecules at the solid–gas interface have made perovskite ABO_3 oxides promising electrode candidates for intermediate-temperature solid-oxide fuel cells and electrolyzers.^[1–3] Nevertheless, the rate of oxygen electrocatalysis at the electrode surface remains one of the major factors that limits device efficiency. Extensive work has been performed to understand the surface–gas kinetics of perovskite electrodes and its correlation with specific properties such that better electrodes can be designed. Compositional screening has identified important electronic factors, such as the occupancy of the *B*-site cation e_g orbitals^[4,5] or the relative position of the oxygen 2*p* band center,^[6] both of which can act as descriptors for predicting high electrochemical activity. As such, controlling the electronic structure of perovskite electrodes via chemical doping has been the prevailing route to optimize gas-exchange kinetics.

Beyond chemistry control, advances in thin-film synthesis now enable researchers

Dr. R. Gao, A. Fernandez, A. Luo, Dr. D. Pesquera, Dr. S. Das, Dr. G. Velarde, Prof. L. W. Martin
Department of Materials Science and Engineering
University of California, Berkeley
Berkeley, CA 94720, USA
E-mail: lwmartin@berkeley.edu

Dr. R. Gao, A. Fernandez, A. Luo, Dr. D. Pesquera, Dr. S. Das, Dr. G. Velarde, Prof. L. W. Martin
Materials Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA

Dr. T. Chakraborty
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana–Champaign
Urbana, IL 61801, USA

Dr. D. Pesquera
Catalan Institute of Nanoscience and Nanotechnology
Campus UAB, Bellaterra, Barcelona 08193, Spain

Dr. V. Thoréton, Prof. J. Kilner, Prof. T. Ishihara
WPI International Institute for Carbon-Neutral Energy Research (WPI-I2CNER)

Kyushu University
Fukuoka 81-0395, Japan

Prof. J. Kilner
Department of Materials
Imperial College London
London SW72AZ, UK

Dr. S. Nemšák, Dr. E. J. Crumlin
Advanced Light Source
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA

Prof. E. Ertekin
Department of Mechanical Science and Engineering
University of Illinois, Urbana-Champaign
Urbana, IL 61801, USA

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202100977>.

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to study surface reactions on an oriented single-crystal facet where extrinsic factors of bulk ceramics can be eliminated, and new methods of structural control can be realized. For instance, epitaxial strain has been found to influence both the surface-gas kinetics and ionic conductivity of perovskites, where the $B-O-B$ bond strength and angle have been identified as important factors affecting both oxygen exchange and mobility.^[7–11] Other studies have focused on the relative importance of both surface-termination and sub-surface chemistry of (001)-oriented perovskite surfaces in dictating electrochemical reaction rates.^[12–15] Perovskite electrodes with different exposed crystallographic orientations have also been reported to have different electrochemical reaction rates.^[16–18] Attempts to study surface-orientation effects on the gas-exchange kinetics of perovskite electrodes have been accomplished by growing single-layer-perovskite electrodes on perovskite substrates, typically employing techniques such as isotope-tracer diffusion, electrical-conductivity relaxation, and solution-based electrochemical cells.^[16–22] Generally, such studies point to faster kinetics on (111) surfaces and slower kinetics on (001) surfaces, whereas (110) surfaces have provided somewhat contradictory results.^[16–18,22] Nevertheless, there remains a need for detailed mechanistic insights on orientation dependence. Here, we focus on the role of surface orientation in dictating the gas-reaction kinetics of perovskite electrodes.

Examining the impact of surface orientations on gas-exchange kinetics requires the construction of well-defined electrode surfaces and a reliable probe of the gas-exchange kinetics. Previous AC-impedance studies on electrochemical cells composed of yttria-stabilized zirconia (YSZ) or other fluoride-based electrolytes with perovskite microelectrodes have provided mechanistic insight about the surface-gas reactions.^[23–25] The structural mismatch, however, between the electrode and electrolyte results in the creation of polycrystalline electrodes and/or the formation of defective heterointerfaces. Such defects can complicate the interpretation of results and limit control of the perovskite-electrode structure (e.g., varying the surface orientations, and/or altering the strain). Here, we bridge the gap between half-cell-based electrochemical-impedance spectroscopy studies and epitaxial thin-film studies by developing an all-perovskite, epitaxial half-cell heterostructure to examine the orientation-dependent gas-exchange kinetics. Both approaches assure the level of synthetic control typically associated with high-quality epitaxial thin films for further quantitative surface analysis.

We utilize epitaxial thin-films of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) on SrTiO_3 substrates as a model system to probe electrochemical differences between different crystallographic surfaces. Preliminary studies based on electrical-conductivity-relaxation establish that (111) surfaces have the fastest reaction rates, while (001) surfaces are slowest, and (110) surfaces have an intermediate reaction rate. We proceed to develop all-perovskite epitaxial thin-film half-cells of the form 30 nm LSCF (working electrode)/150 nm $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}$ (LSGM, electrolyte)/20 nm SrRuO_3 (counter electrode)/ SrTiO_3 (001), (110), and (111) with the film orientation being set by the substrate. Electrical measurements of the epitaxial half-cells are achieved via microfabrication of the top working electrode (LSCF) into well-defined circular electrodes and applying small

AC voltages between the working and counter electrodes. Electrochemical-impedance spectroscopy reveals that, at 350 °C, the (111) surfaces have a gas-kinetic-rate constant more than 3- and 2-times higher than that of the (001) and (110) surfaces, respectively. Oxygen-partial pressure (p_{O_2}) dependent electrochemical-impedance spectroscopy of the half-cells suggests that the rate-limiting step of the surface reaction is the charge-transfer process to adsorbed oxygen adatoms (for $p_{\text{O}_2} > 1$ Torr) and the absorbance of oxygen molecules (for $p_{\text{O}_2} < 1$ Torr) for all three surface orientations. This indicates that while similar surface reactions occur on all three orientations, the (111) surfaces contain more active reaction sites to account for the differences. Density-functional theory (DFT) calculations reveal that the different surfaces have different stability with respect to the process of vacancy formation and oxygen adsorption, which stabilizes different surface chemistries. This is corroborated by ambient-pressure X-ray photoelectron (AP-XPS) and absorption spectroscopy (AP-XAS), which reveal the presence of different surface chemistries, with the (111) surfaces containing more oxygen vacancies, less surface-strontium segregation, and more near-surface B -site cations. This study reveals the importance of surface versus bulk chemistry and the role that vacancy-formation energy plays in stabilizing surface chemistries that promote oxygen exchange.

2. Results and Discussion

We began by synthesizing single-layer LSCF films on SrTiO_3 (001), (110), and (111) substrates via pulsed-laser deposition (Experimental Section). X-ray diffraction line scans (Experimental Section) reveal single-phase, high-quality, epitaxial films wherein the growth orientation is set by the substrate (Figure 1a). The LSCF composition used in this study was chosen to be closely lattice-matched to the SrTiO_3 substrate, eliminating possible contributions from epitaxial strain and providing a way to closely approximate “bulk-like” LSCF. This lattice-matching is evidenced by the main diffraction conditions from the LSCF thin-films overlapping with the substrate diffraction and only the Laue thickness fringes are visible in the line scan.^[26] The films have smooth surfaces with similar root-mean-squared roughness as revealed by atomic force microscopy (Experimental Section and Figure S1, Supporting Information). Low-energy ion scattering (LEIS; Experimental Section) was used to study of the surface termination and revealed that, for all heterostructures, the outermost layer is A -site cation terminated (Figure S2, Supporting Information). The only nuance being that the (111) surfaces show evidence of a low concentration of exposed B -site cations. This is consistent with previous studies which suggest that the outermost layer is primarily A -site cations, and B -site cations are present only in sub-surface layers.^[27] Thus, the (001) surface should be $(\text{La,Sr})\text{O}$ -terminated and the (111) surfaces should be $(\text{La,Sr})\text{O}_3$ -terminated. The resulting strontium-to-lanthanum peak intensity ratios extracted from the LEIS data are 1.44 and 1.20 for the (001) and (111) surfaces, respectively, both of which are larger than the ideal ratio of 0.25 (Figure S2 inset, Supporting Information). For the (110) surfaces, although the expected termination is $(\text{La,Sr})(\text{Co,Fe})\text{O}$, no detectable B -site cations

Figure 1. Electrical conductivity relaxation on epitaxial $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ thin films. a) X-ray diffraction line-scans reveal high-quality epitaxial $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) on (001)-, (110)-, and (111)-oriented SrTiO_3 substrates. b) Electrical-resistivity-relaxation measurements on single-layer LSCF films demonstrate fast kinetics on (111) surfaces. c) Rate constants extracted from fitting of relaxation measurements indicates the same performance trend as half-cell studies, with the fastest exchange happening on (111) surfaces.

are present, suggesting that some surface reconstruction has taken place, completely masking the *B*-sites with *A*-site cations. Therefore, while the strontium-to-lanthanum peak intensity

ratio for the (110) surface is 0.87, lower than those extracted for (111) or (001), the absence of any *B*-site on the outermost layer of the (110) surface suggests an even larger deviation from the expected surface stoichiometry. This suggests that despite identical growth conditions and strain states, the different crystallographic surfaces stabilize different surface chemistries, which deviate from the expected bulk stoichiometry.

As a first probe of the electrochemical activity of these surfaces, we performed electrical-conductivity-relaxation experiments on the three surface variants (Experimental Section) utilizing a tube-furnace-based measurement setup (Figure S3, Supporting Information). Previous studies have shown different strontium-segregation rates for different perovskite surfaces, and that high levels of segregation can override the intrinsic differences in reactivity of the different crystal surfaces. As such, we performed electrochemical measurements at 350 °C to slow the strontium-segregation kinetics. We measured the relaxation of normalized resistance from the LSCF layers following a step-change in pressure from 380 to 200 Torr (Figure 1b) resulting in the fastest response for (111)-oriented films, with the (001)-oriented films demonstrating the slowest response. The extracted k^{chem} rate constants^[10,28] (Figure 1c), show that (111) surfaces are nearly 5 times as reactive as (110)- and (001) surfaces. The observation of fast kinetics on (111)-oriented surfaces is in agreement with studies on related perovskite systems^[16,17] and the magnitude of k^{chem} is comparable to studies on LSC-based electrodes measured at similar temperatures.^[16,17,29] With the electrochemical trend established, we turn to half-cell-based measurements to further explore the origin of this orientation dependence.

To probe the mechanistic differences governing the oxygen exchange on the different surface variants, we developed an epitaxial, all-perovskite, half-cell device for use in electrochemical impedance spectroscopy experiments based on prior knowledge on epitaxial LSGM electrolytes.^[7] The heterostructures are grown via pulsed-laser deposition and have the form 30 nm LSCF/150 nm LSGM/20 nm $\text{SrRuO}_3/\text{SrTiO}_3$ (001), (110), and (111) (Experimental Section). X-ray diffraction line scans reveal that all heterostructures are composed of single-phase, high-quality, epitaxially grown layers wherein the growth orientation is set by the substrate (Figure 2a–c). RSM studies suggest that all layers are epitaxially aligned and coherently strained (Figure S4, Supporting Information). By developing these epitaxial half-cell heterostructures, we have created a unique platform for studying the LSCF electrode via electrochemical impedance spectroscopy, maintaining the high-quality, single-crystal nature of the LSCF thin films, and creating pristine interfaces between the electrodes and electrolyte, eliminating the convoluting effects of grain boundaries and defective interfaces without sacrificing control of the surface orientation.

The half-cell structures, shown schematically (Figure 2d,e), were subsequently fabricated into real devices (Figure 2f) to enable studies of the electrochemical response (Experimental Section and Figure S5, Supporting Information). As illustrated, the LSCF-working electrodes (diameter 200 μm) are connected to platinum contacts by an arm that just touches the edge of the electrode; negligibly impacting the working area. The platinum contacts are insulated from the rest of the cell by an amorphous, insulating MgO layer. To analyze the impedance

Figure 2. Epitaxial all-perovskite half-cells with controlled surface orientation. a–c) X-ray diffraction line-scans reveal high-quality epitaxial La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O₃ (LSCF)/La_{0.9}Sr_{0.1}Ga_{0.95}Mg_{0.05}O₃ (LSGM)/SrRuO₃ trilayer structures grown on (001)-oriented (a), (110)-oriented (b), and (111)-oriented (c) SrTiO₃ substrates. d) A cross-section of the heterostructure and the corresponding equivalent circuit used for analysis of the half-cell. e) Microfabrication provides many devices to be patterned on a 5 × 5 mm substrate, allowing for statistical analysis of many devices.

response, a lumped-element equivalent circuit is employed, consistent with work elsewhere (Figure 2d).^[30,31] The top part of the circuit is given by parallel elements including a surface resistance R_s and a constant-phase element Q_s , which together describe the surface-reaction process at the electrode-gas interface. Using circular electrodes with 200 μm diameter makes the electrochemical R_s (>10 kΩ) much larger than the ionic-transport impedance across the 150 nm electrolyte with same cross-section (<10 Ω based on the ionic conductivity for single-crystalline LSGM^[7,32] and LSCF^[33]); this allows us to lump the ionic transmission line into a simple resistor given by the ionic-transport impedance R_{ion} . The bottom part of the circuit is the charge-transfer impedance at the LSGM–SrRuO₃ interface which is described by a parallel resistance R_{ct} and a constant-phase element Q_{ct} . Owing to the fact that the SrRuO₃ is metallic and the electrolyte is thin, under small electrical perturbations, the ionic charges at the LSGM–SrRuO₃ interface are expected to be mainly compensated by the stoichiometric change of the LSGM electrolyte. Qualitatively, we assume that such stoichiometry change in the thin LSGM electrolyte is limited by diffusion at dilute concentration, and that the charge-transfer process is expected to show up at much higher frequencies in the impedance spectra compared to the surface-reaction process owing to small R_{ion} . To further validate this assumption

and to confirm that the geometry is surface-reaction-limited, we have performed a set of additional experiments on the half-cells including working-electrode deactivation, electrode-area dependence, and electrolyte-thickness dependence studies, which all suggest that the major potential drop happens at the LSCF–gas interface (Figure S6, Supporting Information). Thus, in this geometry, operation of the half-cell is surface-reaction-limited, providing a platform to isolate and study the active electrode-surface reaction.

Electrochemical-impedance spectroscopy (Experimental Section) of the half-cells with different surface orientations was performed at 350 °C in both air and dry oxygen. Representative spectra for the three half-cell orientations (Figure 3a) reveal that all half-cell variants show a single, well-defined semicircle. The high-frequency intercepts (≈1 kΩ) likely arise from contributions of both ionic-transport (R_{ion}) and charge-transfer (R_{ct}) impedance. The low-frequency endpoints reflect the rate of the surface–gas reaction. Fitting the spectra to the equivalent circuit yields R_s which can be further converted into a surface–gas reaction rate constant $k^g = \frac{kT}{4e^2(R_s \cdot A)c_O}$, where A is the electrode area and c_O is the concentration of oxygen species calculated based on reported values.^[47] The rate constants (in air) reveal that the (111) surfaces have reaction rates >3-times and 2-times

Figure 3. Electrochemical measurements of LSCF cathodes with different surface orientations. a) Representative Nyquist plots from electrochemical-impedance-spectroscopy studies measured on the different surface variants in a dry O_2 environment. b) Rate constants calculated from the extracted R_s values illustrate the large difference in rate constant.

higher than that of the (001) and (110) surfaces, respectively (Figure 3b). In dry oxygen, the trend holds the same for the three orientations except for an overall higher reaction rate due to a richer oxygen concentration. The error bars are determined by measuring multiple devices each on two different sets of half-cell heterostructures; the small deviation indicates good consistency and repeatability.^[48] The results from impedance spectroscopy exhibit the same trend and similar relative magnitudes of kq compared to k^{chem} extracted from electrical-conductivity-relaxation measurements. These two measurements point to the same performance trend: (111) surfaces have gas-reaction-rate constants at least 3- and 2-times higher than the (001) and (110) surfaces.

Although the surface-gas reaction can be decomposed into several elementary steps (e.g., adsorption of oxygen molecules, reduction of adsorbed species, ion incorporation, etc.), it is assumed that at one step will be rate-limiting and dictate the p_{O_2} -dependence of the reaction.^[34–36] The resulting surface-reaction impedance will be related to p_{O_2} according to: $1/R_s \propto (p_{O_2})^m$, where m depends on the nature of the rate-limiting step. To understand the reaction mechanisms, p_{O_2} -dependent electrochemical-impedance spectroscopy (from 0.08 to 760 Torr) was performed (Figure 3c–e and Figure S7, Supporting Information). All three surface variants were found to exhibit essentially the same p_{O_2} dependence, differing only in magnitude of R_s . At low pressures ($p_{O_2} < 1$ Torr), $m \approx 1$ corresponding to a reaction that involves diatomic oxygen. In this case, the reaction may

be limited simply by the surface coverage of adsorbed oxygen molecules (i.e., $O_{2,gas} \rightarrow O_{2,ad}$) or by charge-transfer to the adsorbed oxygen (i.e., $O_{2,ad} \rightarrow O_{2,ad}^- + h^+$ or $O_{2,ad}^- \rightarrow O_{2,ad}^{2-} + h^+$).^[34] At high pressures ($p_{O_2} > 1$ Torr), $m \approx 0.25$ and likely corresponds with a charge-transfer-limited reaction. Here the species involved can be either dissociated, adsorbed oxygen atoms (O_{ad}) or diatomic oxygen in one of three charge states: neutral $O_{2,ad}$, superoxo $O_{2,ad}^-$, or peroxo $O_{2,ad}^{2-}$. In the case of O_{ad} -reduction, this implies a change in the rate-limiting-step from adsorption to charge transfer as p_{O_2} increases, whereas in the latter case, one rate-limiting, charge-transfer step (i.e., $O_{2,ad}^- \rightarrow O_{2,ad}^{2-} + h^+$) dominates the entire pressure regime, and the crossover in m is driven by a change in the surface coverage and resulting electrostatic interactions of charged-surface species.^[49] With all surfaces demonstrating the same crossover, however, it appears there is no mechanistic difference that can explain the differences in reaction rate between the surfaces. Thus, we turn our focus to the details of the adsorption and charge-transfer process that determine the reaction rate.

To explore possible surface structural and electronic differences that could drive the observed electrochemical differences, we used DFT calculations to understand the driving forces for oxygen exchange on each surface (Experimental Section).^[52,53] We began by simulating the defect-free surfaces for each of the orientations, using A-site terminations enriched with 50% strontium to reflect the LEIS measurements. For (001) and (111) surfaces, this entails AO- and AO_3 -termination, respectively,

Figure 4. a–c) First-principles calculations of surface vacancy formation and oxygen adsorption. DFT calculations illustrate the different formation energy for surface vacancies across the (001) (a), (110) (with both ABO-termination and O_2 -termination) (b), and (111) (c) surface variants. Vacancy formation is unfavorable on (001) surfaces and ABO-terminated (110) surfaces, whereas (111) and O_2 -terminated (110) surfaces have favorable vacancy formation energies.

while for (110) surfaces, we examined both defect-free ABO- and O_2 -terminated surfaces under the assumption that the two terminations are convertible and coexisting by oxygen adsorption/desorption. We calculated the energies of these surfaces following introduction of a surface-oxygen vacancy and subsequently an adsorbed-oxygen molecule and performing these calculations over sites that have either subsurface cobalt or iron allowed for comparison of the relative energies for oxygen exchange for the different B-site species.

The (001) (Figure 4a), (110) (Figure 4b), and (111) (Figure 4c) surfaces were found to exhibit markedly different energy profiles for the hypothesized pathway. Focusing first on vacancy formation, the calculations reveal a sizable increase in energy (2–2.5 eV) when an oxygen vacancy is introduced to the (100) surface (Figure 4a). On the other hand, vacancy formation on (111) surfaces results in a decrease in energy (Figure 4c). This suggests that (111) surfaces are prone to spontaneous vacancy formation, while (100) surfaces limit vacancy formation. For (110) surfaces, the relationship is less clear (Figure 4b). In the case of ABO-termination, vacancy formation results in an increase in energy (4.5 eV) even greater than that for the (100) surface, while vacancy formation on the O_2 -terminated surface results in a significant decrease in energy (0.72–0.9 eV), similar to the (111) surface. In other words, oxygen vacancies on (110) surfaces are unstable in the ABO plane, but are stable above the cations in the O_2 plane.

These trends are consistent with what would be expected from electrostatic considerations of surface polarity. The net charge of a perovskite surface can be estimated by means of a simplistic picture of the formal charge of all the cations (e.g., La^{3+} , Sr^{2+} , and O^{2-}) in an ideal, defect-free surface in order

to understand the electrostatic driving forces that may drive non-stoichiometry at these surfaces. For the (001) surface, an AO-termination with a stoichiometric strontium-to-lanthanum ratio of 1:4 leaves the defect-free surface with a net charge of +0.8 per formula unit. Vacancy formation on this surface would further increase the surface charge, indicating it is unfavorable to form vacancies. Replacing lanthanum with strontium (i.e., strontium segregation) would reduce the net charge thereby electrostatically stabilizing the surface. The stoichiometric ABO-terminated (110) surfaces are similarly positively charged, and vacancy formation would worsen the electrostatic stability. Again, strontium segregation serves to reduce the surface charge and stabilize the surface. Applying the same treatment to the AO_3 -terminated (111) surfaces, the net charge of the surface is –3.2 per formula unit, and thus formation of positively charged oxygen vacancies serves to stabilize the surface polarity, likely explaining the favorability to form such vacancies observed in DFT. Thus, for both the (001) and (110) surfaces, surface charge hinders vacancy formation, and may provide an additional driving force for strontium segregation, in addition to elastic and chemical driving forces.^[37]

Turning to the adsorption of molecular oxygen, the calculations reveal that adsorption at an oxygen-vacancy site results in a lowering of the surface energy in all cases, supporting studies that identify vacancy sites as the primary active site.^[38] Additionally, we note that the bond-length of the adsorbed-oxygen molecule (≈ 1.35 Å) is increased relative to that of molecular oxygen (1.23 Å), indicative of an activated, superoxo $O_{2,ad}^-$ as the stable adsorbed species; lending support to the reaction $O_{2,ad}^- \rightarrow O_{2,ad}^{2-} + h^+$ as the rate-limiting step.^[34,38] Interestingly, when the energies of the different subsurface cations are

weighted by their relative concentration, the (100) and (111) surfaces have similar energy reductions upon adsorption of oxygen molecules (≈ 1.1 eV) suggesting that the stabilization of vacancy sites on (111) surfaces is the main driving force for the increased electrochemical performance. The O_2 -terminated (110) surface has the most favorable energy of adsorption (≈ 1.8 eV) while the ABO-terminated (110) surface has the least favorable adsorption energy (≈ 0.7 eV). Thus, the (110) surface presents a case where the different terminations work in opposition, and the electrochemical results may reflect the competition between the (un)favorable terminations. These results, in conjunction with the absence of surface B-site cations in the LEIS data, merit a deeper study of possible surface reconstructions at these polar surfaces, and particularly on (110) surfaces.

Considering the DFT results, we aimed to directly probe the electronic structure associated with each surface orientation. To do this we performed AP-XAS and AP-XPS which allow for the measurement of elemental-specific spectra at high temperatures and in ambient gas environments (Experimental Section).^[39] For each surface variant, the cobalt and iron *L*-edges and oxygen *K*-edges were probed at 350 °C in oxygen pressures from 10^{-8} to 0.9 Torr to understand how the electronic structure is influenced by the interaction with molecular oxygen (Figure 5a–c). While the XAS results are qualitatively similar across the different surface orientations (Figures S9–S11, Supporting Information), their pressure dependence provides insight into the interaction of these surfaces with oxygen molecules. At low p_{O_2} , both the iron (Figure 5a) and cobalt (Figure 5b) *L*-edge spectra suggest that the cations have predominantly 3+ valence.^[40–42] As oxygen is introduced the iron *L*-edge shows no change, whereas the cobalt *L*-edge broadens to higher photon energies, indicating an increase towards 4+ valence. This agrees with studies in bulk ceramics, where changing oxygen stoichiometry results in larger changes to the cobalt valence.^[43] It has been shown that the electronic structure of iron changes from $3d^5$ to $3d^5L$, where *L* indicates a ligand hole, with increasing oxidation.^[40] As such, changing the oxygen content of the lattice results in hole doping of primarily oxygen 2*p* character, and can be observed in measurements of the oxygen *K* edge (Figure 5c). We observe two broad features at 535 and 542 eV, corresponding to lanthanum/strontium 3*d*–oxygen 2*p* hybridized states, and

cobalt/iron 3*p*–oxygen 2*p* hybridized states, respectively; however, the most significant changes are observed around a sharp peak at 530 eV, corresponding to excitations involving cobalt/iron 3*d*–oxygen 2*p* hybridized states. At low p_{O_2} , this peak is relatively sharp, and is attributed to excitation into unoccupied $t_{2g} \downarrow$ states. As the pressure is increased, an increase in intensity at 528 eV is observed, suggesting the depopulation of some $e_g \uparrow$ states^[44,45] (i.e., hole-doping of the oxygen 2*p* states as electrons are transferred to adsorbed oxygen to form the superoxo $\text{O}_{2,\text{ad}}^-$ state). This pre-peak area provides a quantitative marker of oxygen adsorption (i.e., $[h^+]$), and comparison of the rate of pre-peak change for different surface orientations reveals a strong preference for hole doping on (110) surfaces as compared to (001) and (111) surfaces (Figure 5d). The similarity in driving force for oxygen adsorption provided by DFT for the (001) (–1.1 eV) and (111) (–1.37 eV) surfaces is manifested in the similar rate of pre-peak area increase extracted from XAS. The larger slope for the (110) surfaces may point to adsorption in the O_2 -plane rather than the ABO-plane considering the larger driving force for oxygen-molecule adsorption (–1.87 eV). Thus, the distinct bonding environments of each surface orientation give rise to distinct electronic interactions with oxygen.

The understanding gleaned from the LEIS, DFT, and XAS analyses naturally raises the question if different surface chemistries drive the observed electrochemical differences? We also measured the oxygen 1*s*, cobalt/iron 3*p*, strontium 3*d*, lanthanum 4*d*, and valence-band photoelectron excitations with a probing depth of ≈ 1 nm using AP-XPS (Figure S12, Supporting Information). We initially focus on the strontium 3*d* excitation, owing to the well-known deleterious effect of strontium segregation on catalytic reactivity.^[46,47] For all three orientations, we observe the complex peak shapes typically found for strontium 3*d* peaks which are decomposed into a low- and high-binding-energy doublet which we attribute to “lattice-like” and “surface-like” strontium species, respectively (Figure 6a–c and Figures S13–S15, Supporting Information).^[48] A more detailed discussion of the assignment of these peaks is also provided (Supporting Information). The “surface-like” excitation is observed to increase over the duration of the measurement at 350 °C, suggesting active strontium segregation (Figure 6d); however, the (111) surface maintains the lowest “surface-like”

Figure 5. Electronic interactions of cathode surfaces. a–c) Representative X-ray absorption spectra from (110) surfaces as a function of pressure indicate changing surface electronic structure for the iron *L* (a), cobalt *L* (b), and oxygen *K* (c) edges. d) Changing pre-peak area (shaded region in (c)) of the oxygen *K* edge is quantified to demonstrate the different propensities for adsorption and charge-transfer on different surfaces, lines are a guide for the eye.

Figure 6. Evolution of perovskite surface chemistry. a–c) Representative strontium 3d spectra for the (001) (a), (110) (b), and (111) (c) surfaces showing the different contributions of “surface” and “lattice” components. d) In situ observation of strontium segregation is quantified using the relative intensities of the “surface” and “lattice” components of the strontium 3d excitation as a function of gas pressure. e) XPS chemical analysis reveals that the different surface orientations have differing quantities of B-site cations in the near-surface region.

contribution throughout. This supports the notion that the (111) surfaces have an electrostatic driving force originating from the surface polarity that limits strontium segregation compared to the other surfaces, in agreement with previous studies.^[49] This strontium-enriched surface can be confirmed without invoking the “surface-like” assignment by comparing the total ratio of strontium to A-site species in the near-surface region (Figure 6e). Thus, while the LEIS data suggests that the (110) surface has the lowest strontium-to-lanthanum ratio at the outermost atomic layer, the concentration of strontium in top-most 5–6 cationic layers (≈ 1 nm) probed by XPS is higher than that in either the (110) and (111) surfaces. Thus, said another way, while all surface orientations have a higher strontium concentration than the bulk stoichiometry, the (111) surface has the lowest overall concentration of near-surface strontium.

Both the AP-XPS and LEIS point to significant deviations of the surface chemistry from the bulk stoichiometry. As such, we aimed to understand how these deviations impact the near-surface B-site chemistry, which is expected to impact the available reaction sites. We quantify the B-site chemistry using the integrated peak areas from the core-level excitations for all cations, scaled appropriately by their respective photoionization cross-sections (Supporting Information).^[50] The (111) surfaces have the largest fraction of near-surface B-site cations (Figure 6f), supporting the observation of B-site-derived peaks in the LEIS measured only on (111) surfaces. The trends in the fraction of B-site cations track closely with the trends in electrochemical

response, whereas solely looking at the segregated strontium does not. It is interesting to note that, despite similar surface terminations among the three surfaces, a high degree of near-surface or subsurface B-site cations still enhances the catalytic reactivity.^[14,15] Ultimately, these differences in surface chemistry explain the lack of mechanistic differences among the three surfaces. With a charge-transfer-limited reaction, surface vacancies and near-surface B-site cations are needed for the formation of $O_{2,ad}$ and subsequent reduction. Stabilizing high oxygen-vacancy concentration and a “large” number of B-site cations near the surface and limiting the electrostatic driving force for strontium segregation that quenches these sites results in faster reaction rates for the (111) surfaces.

3. Conclusion

We have demonstrated epitaxial all-perovskite half-cells that serve as a platform to study the electrochemical response of perovskite cathodes. Such epitaxial control allows for study of the electrochemical response of the different surfaces, revealing large differences in electrochemical activity. While (001), (110), and (111) surfaces exhibit the same rate-limiting step for oxygen exchange, combined DFT and spectroscopic analyses reveal that the local bonding environment at the surface stabilizes distinct (non-bulk-like) surface chemistries. These results highlight the importance of understanding the possible surface

reconstructions, and how deviations from bulk stoichiometry at surfaces may hinder otherwise favorable reaction kinetics. Fast reaction kinetics are found at (111) surfaces that exhibit a balance of important factors such as vacancy concentration, favorable adsorption energy, low strontium segregation, and high B-site availability. Whereas many studies have pursued performance optimization by tuning the bulk stoichiometry, new avenues for engineering can be envisioned whereby the materials chemistry is engineered to effect favorable surface chemistries and therefore higher catalytic activities.

4. Experimental Section

Synthesis of Epitaxial Thin-Films and Half-Cell Structures: The thin-film heterostructures were synthesized via pulsed-laser deposition using a KrF excimer laser (248 nm; LPX 305, Coherent, Inc.) on SrTiO₃ (001), (110), and (111) substrates (Crystec, GmbH). The SrRuO₃ bottom electrode layers were deposited from a ceramic target (Praxair) of the same chemistry deposited at a heater temperature of 700 °C in a dynamic P_{O_2} of 100 mTorr with a laser fluence of 1.3 J cm⁻² and a repetition rate of 15 Hz. Following the growth of the SrRuO₃, the LSGM layers were deposited from a ceramic target of the same chemistry (La_{0.9}Sr_{0.1}Ga_{0.95}Mg_{0.05}O₃) at a heater temperature of 800 °C in a dynamic P_{O_2} of 40 mTorr with a laser fluence of 1.7 J cm⁻² and repetition rate of 5 Hz. Following the growth of the LSGM, the LSCF films were grown from a ceramic target (Praxair) of the same chemistry (La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ}) at a heater temperature of 700 °C in a dynamic P_{O_2} of 150 mTorr with a laser fluence of 1.6 J cm⁻² and repetition rate of 5 Hz. Following deposition, the films and heterostructures were cooled in a static P_{O_2} of 700 Torr at 10 °C min⁻¹. For the single-layer LSCF films, the growth conditions were maintained as noted above, but growth was completed directly on the SrTiO₃ (001), (110), and (111) substrates.

Film Crystal Structure, Surface, and Surface Stoichiometry Characterization: X-ray studies were conducted with a high-resolution X-ray diffractometer (X'pert Pro3, PANalytical). θ -2 θ line scans were used to probe the out-of-plane orientation of both single-layer films and tri-layer heterostructures from 10–70°. Two-dimensional reciprocal space mapping (RSM) studies were carried out to verify the epitaxy and strain state of the heterostructures. For the (001), (110), and (111) surfaces, the 103-, 221-, and 312-diffraction conditions were chosen, respectively, to obtain in-plane structural information for each heterostructure type. Surface topography was studied using an atomic force microscope (MFP-3D, Asylum Research). The outermost surface chemistry of the LSCF films was examined by low-energy ion scattering (LEIS) using a QTAC 100 (IONTOF). Prior to measurement the sample was cleaned in a preparation chamber in flowing oxygen for 40 min. before loading into the measurement chamber. The spectra were recorded with a 6 keV neon beam (1 nA) over a 1 mm² area in static conditions.

Electrical-Conductivity-Relaxation Measurements: Electrical-conductivity-relaxation measurements were performed on 40-nm-thick, single-layer LSCF films with four platinum contacts deposited at the corners. The platinum contacts were then gold-wire bonded to a Cerdip chip carrier, which was subsequently loaded in the measurement setup. The measurement setup includes a home-built, tube-furnace-based measurement setup (Figure S3, Supporting Information). An Al₂O₃ tube was sealed using KF flanges on both ends, with one end connected to a mechanical pump and the other with a customized KF-type flange through which sample connection, gas inlet, and temperature monitoring were accomplished. An alumina bar is mounted on the flange to hold the Cerdip chip carrier, and four silver wires with thermal shields were used to connect the chip carrier with external BNC ports via electrical feedthroughs. A Keithley 2400 current-voltage source was used (driving at 10 mV for current measurements) to monitor the electrical resistance change of the sample after a step change in pressure. The

step change in P_{O_2} is controlled by a sudden open and close of the outlet pumping port, while the pressure was monitored simultaneously.

Fabrication of Half-Cell Structures: Half-cell fabrication was carried out via a series of pulsed-laser deposition and photolithography steps (Figure S5, Supporting Information). Initially, a bilayer consisting of the SrRuO₃ counter-electrode layer and the LSGM electrolyte were synthesized in situ via pulsed-laser deposition. A photolithography step is used to define the circular area that will define the LSCF electrodes. The patterned sample is then returned to the pulsed-laser deposition chamber, and a room-temperature deposition of 80 nm of MgO followed by 30 nm of ZnO is deposited using a laser fluence of 2.0 J cm⁻² at a repetition rate of 15 Hz and a pressure of 5 mTorr in both cases. Following ZnO/MgO deposition, the photoresist is removed with acetone and isopropanol rinses, leaving a hard mask to define the LSCF electrodes,^[51] with the LSGM surface exposed. The LSGM surface is then plasma-cleaned for 60 sec. and immediately returned to the pulsed-laser deposition chamber. LSCF top electrodes are then deposited using the same conditions as the single-layer films. Following deposition, a continuous LSCF layer covers the entire structure. Liftoff of the underlying ZnO layer with a NaOH etch selectively dissolves the ZnO and removes excess LSCF that is not defined by the circular areas of the hardmask leaving the MgO insulating layer, and exposed circular electrodes of LSCF. A final photolithography step is performed to define the platinum pads which are used for wire-bonded electrical connection to the LSCF electrode. Liftoff of the excess photoresist with acetone leaves well-defined platinum pads that contact the edge of the LSCF electrode, completing the half-cell heterostructure.

Electrochemical-Impedance-Spectroscopy Studies: Electrochemical-impedance-spectroscopy measurements were carried out in the same home-built, tube-furnace-based measurement setup (Figure S3, Supporting Information). A PARSTAT 3000 potentiostat was used to perform the electrochemical-impedance-spectroscopic measurements from 0.5 Hz to 500 kHz using a 10 mV excitation. For temperature control, an additional thermocouple was placed immediately adjacent to the sample holder to measure temperature near the sample surface. During the measurement, the temperature is monitored via the internal thermocouple mounted in proximity to the chip carrier and the PID setting of the heater was tuned to assure stable temperatures for this sample geometry. P_{O_2} was controlled by fixing the inlet flow of oxygen (flow rate at 4 sccm), while the outlet pumping speed was adjusted by changing the opening of the outlet pumping port to achieve target pressure. Using this setup, pressure control from 80 to 760 Torr is achievable. Before measuring, the samples were allowed to equilibrate at each pressure and temperature for 20 min.

Density-Functional-Theory Calculations: All total-energy calculations were performed using plane-wave density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).^[52–54] The Perdew–Burke–Ernzerhof (PBE) approximation to the exchange-correlation functional and projector augmented wave^[55] pseudopotentials were used. The Hubbard U (GGA+ U)^[56,57] term was included to improve the description of the localized cobalt and iron 3d, with $U = 5$ eV for both. For the plane-wave basis a cutoff energy of 520 eV was used. Brillouin zone sampling was sufficient in all cases to converge total energies to within 0.01 eV per slab. All calculations were spin-polarized and initialized with a ferromagnetic configuration of cobalt and iron atoms, which was allowed to relax. The atomic coordinates and the volume of all the surfaces were fully relaxed during the simulations until the Hellmann-Feynman forces on each atom were below 0.01 eV Å⁻¹. Graphical visualization package VESTA^[58] was used for all the surface models.

The DFT slab composition was La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O₃ which is close to the experimentally synthesized sample. (La,Sr)O-, O₂-, and (La,Sr)O₃-terminated surfaces were simulated for (001)-, (110)-, and (111)-surface orientations, respectively. For all surface models, symmetric slabs were used to avoid surface-dipole moments, with a vacuum region of 15 Å. The A- and B-site cation sublattices were occupied by lanthanum/strontium and iron/cobalt in an ordered manner for simplicity. For the (001) surface, there were a total of seven layers, four AO and three BO₂

layers, containing 136 atoms in the supercell. For the (110) surface, there were a total of nine layers, four ABO and five O₂ layers, containing 88 atoms in the supercell. For the (111) surface, there were a total of 13 layers, seven AO₃ and six B layers, containing 136 atoms in the supercell. A $2 \times 2 \times 1$ gamma-point *k*-mesh was used for the (001) and (111) surfaces and a $2 \times 3 \times 1$ *k*-mesh for the (110) surface. The slab energies were converged to within 5 meV per formula unit with respect to the *k*-points and energy cutoff.

The oxygen vacancy formation energy $E[V_O]$ and the energy of the surface with the oxygen molecule adsorbed at the vacancy site $E[O_2^{ads}]$ are referenced to the as-cleaved surface and, respectively, given by

$$E[V_O] = E[\text{surface} + V_O] - E[\text{surface}] + \frac{1}{2}\mu_{O_2} \quad (1)$$

$$E[O_2^{ads}] = E[\text{surface} + V_O + O_2] - E[\text{surface}] - \frac{1}{2}\mu_{O_2} \quad (2)$$

where $E[\text{surface}]$, $E[\text{surface} + V_O]$, $E[\text{surface} + V_O + O_2]$ are the total energies of the as-cleaved slabs, slabs with an oxygen vacancy present, and slabs with an oxygen molecule adsorbed into the vacant site, respectively. The quantity $\frac{1}{2}\mu_{O_2}$ is the chemical potential of oxygen, obtained here for standard conditions; note that the corrected value for the DFT-computed oxygen molecule energy was used owing to the fact that PBE is known to overbind the molecule.

Ambient-Pressure X-ray Absorption and Photoelectron Spectroscopy: AP-XAS and AP-XPS measurements were carried out on 20-nm-thick LSCF single-layer films at Beamline 9.3.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory.^[39] Following alignment, samples were cleaned by heating to 350 °C in 10 mTorr of oxygen while observing the carbon 1s peak shrink. After cleaning, the chamber was again pumped to 10^{-8} Torr and measurements were performed with increasing P_{O_2} . A photon energy of 670 eV was used for all AP-XPS measurements. Each measurement sequence took approximately 3 h to obtain high-resolution oxygen 1s, strontium 3d, lanthanum 4d, and cobalt/iron 3p spectra in addition to the oxygen *K*-, cobalt *L*-, and iron *L*-edge absorption spectra. All XPS spectra were calibrated to the lanthanum 4d 5/2 excitation at 104.5 eV. Curve-fitting of the obtained XPS spectra was performed using the CasaXPS software with a symmetric line shape produced from a Gaussian/Lorentzian product function, after subtracting a Shirley-type background. For strontium 3d fitting of the spin-orbit split doublet, a fixed branching ratio of 3:2 and energy separation of 1.8 eV was used. For lanthanum 4d fitting, a branching ratio of 3:2 and energy separation of 2.8 eV was used. Analysis of the surface stoichiometry was performed by scaling the integrated area of the peak of interest with its respective photoionization cross-section. The cobalt and iron *L*-edge XAS spectra were normalized to the peak intensity of the white line, without any pre-edge subtraction. The oxygen *K* edge was normalized by scaling the difference in background intensity before (≈ 525 eV) and after (≈ 548 eV) the main features in order to consistently normalize without the molecular oxygen adsorption at ≈ 530 eV influencing normalization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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- [1] S. J. Skinner, *Int. J. Inorg. Mater.* **2001**, 3, 113.
- [2] C. Sun, R. Hui, J. Roller, *J. Solid State Electrochem.* **2010**, 14, 1125.
- [3] J. A. Kilner, M. Burriel, *Mater. Res.* **2014**, 44, 365.
- [4] J. Suntivich, H. A. Gasteiger, N. Yabuuchi, H. Nakanishi, J. B. Goodenough, Y. Shao-Horn, *Nat. Chem.* **2011**, 3, 546.
- [5] Z. Shao, S. M. Haile, *Nature* **2004**, 431, 170.
- [6] Y.-L. Lee, M. J. Gadre, Y. Shao-Horn, D. Morgan, *Phys. Chem. Chem. Phys.* **2015**, 17, 21643.
- [7] R. Gao, A. C. P. Jain, S. Pandya, Y. Dong, Y. Yuan, H. Zhou, L. R. Dedon, V. Thoréton, S. Saremi, R. Xu, A. Luo, T. Chen, V. Gopalan, E. Ertekin, J. Kilner, T. Ishihara, N. H. Perry, D. R. Trinkle, L. W. Martin, *Adv. Mater.* **2020**, 20, 1905178.
- [8] M. Kubicek, Z. Cai, W. Ma, B. Yildiz, H. Hutter, J. Fleig, *ACS Nano* **2013**, 7, 3276.
- [9] A. Kushima, B. Yildiz, *J. Mater. Chem.* **2010**, 20, 4809.
- [10] B. Koo, H. Kwon, Y. Kim, H. G. Seo, J. W. Han, W. Jung, *Energy Environ. Sci.* **2017**, 11, 71.
- [11] K. A. Stoerzinger, W. S. Choi, H. Jeon, H. N. Lee, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2015**, 6, 487.
- [12] Y.-L. Lee, J. Kleis, J. Rossmeisl, D. Morgan, *Phys. Rev. B* **2009**, 80, 224101.
- [13] Y. A. Mastrikov, R. Merkle, E. A. Kotomin, M. M. Kuklja, J. Maier, *J. Mater. Chem. A* **2018**, 6, 11929.
- [14] C. J. Eom, D.-Y. Kuo, C. Adamo, E. J. Moon, S. J. May, E. J. Crumlin, D. G. Schlom, J. Suntivich, *Nat. Commun.* **2018**, 9, 4034.
- [15] A. R. Akbashev, L. Zhang, J. T. Mefford, J. Park, B. Butz, H. Luftman, W. C. Chueh, A. Vojvodic, *Energy Environ. Sci.* **2018**, 11, 1762.
- [16] K. Kerman, C. Ko, S. Ramanathan, *Phys. Chem. Chem. Phys.* **2012**, 14, 11953.

- [17] L. Yan, K. R. Balasubramaniam, S. Wang, H. Du, P. A. Salvador, *Solid State Ionics* **2011**, 194, 9.
- [18] Y. Miyahara, K. Miyazaki, T. Fukutsuka, T. Abe, *Chemelectrochem* **2016**, 3, 214.
- [19] K. A. Stoerzinger, L. Qiao, M. D. Biegalski, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2014**, 5, 1636.
- [20] K. A. Stoerzinger, O. Diaz-Morales, M. Kolb, R. R. Rao, R. Frydendal, L. Qiao, X. R. Wang, N. B. Halck, J. Rossmeisl, H. A. Hansen, T. Vegge, I. E. L. Stephens, M. T. M. Koper, Y. Shao-Horn, *ACS Energy Lett.* **2017**, 2, 876.
- [21] M. Burriel, J. Peña-Martínez, R. J. Chater, S. Fearn, A. V. Berenov, S. J. Skinner, J. A. Kilner, *Chem. Mater.* **2012**, 24, 613.
- [22] S. Fearn, J. C. H. Rossiny, J. A. Kilner, J. R. G. Evans, *Solid State Ionics* **2012**, 271, 51.
- [23] F. S. Baumann, J. Fleig, H.-U. Habermeier, J. Maier, *Solid State Ionics* **2006**, 177, 3187.
- [24] J. Fleig, F. S. Baumann, V. Brichzin, H.-R. Kim, J. Jamnik, G. Cristiani, H.-U. Habermeier, J. Maier, *Fuel Cells* **2006**, 6, 284.
- [25] J. Fleig, H.-R. Kim, J. Jamnik, J. Maier, *Fuel Cells* **2008**, 8, 330.
- [26] J. E. Readman, A. Olafsen, Y. Larring, R. Blom, *J. Mater. Chem.* **2005**, 15, 1931.
- [27] M. Burriel, S. Wilkins, J. P. Hill, M. A. Muñoz-Márquez, H. H. Brongersma, J. A. Kilner, M. P. Ryan, S. J. Skinner, *Energy Environ. Sci.* **2013**, 7, 311.
- [28] R. Merkle, J. Maier, *Angew. Chem., Int. Ed.* **2008**, 47, 3874.
- [29] M. Kubicek, T. M. Huber, A. Welzl, A. Penn, G. M. Rupp, J. Bernardi, M. Stöger-Pollach, H. Hutter, J. Fleig, *Solid State Ionics* **2014**, 256, 38.
- [30] E. Mutoro, E. J. Crumlin, M. D. Biegalski, H. M. Christen, Y. Shao-Horn, *Energy Environ. Sci.* **2011**, 4, 3689.
- [31] E. J. Crumlin, E. Mutoro, S.-J. Ahn, G. J. la O', D. N. Leonard, A. Borisevich, M. D. Biegalski, H. M. Christen, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2010**, 1, 3149.
- [32] T. Ishihara, H. Matsuda, Y. Takita, *J. Am. Chem. Soc.* **1994**, 116, 3801.
- [33] J. A. Lane, S. J. Benson, D. Waller, J. A. Kilner, *Solid State Ionics* **1999**, 121, 201.
- [34] J. Fleig, R. Merkle, J. Maier, *Phys. Chem. Chem. Phys.* **2007**, 9, 2713.
- [35] A. Schmid, G. M. Rupp, J. Fleig, *Chem. Mater.* **2018**, 30, 4242.
- [36] S. B. Adler, *Chem. Rev.* **2004**, 104, 4791.
- [37] W. Lee, J. W. Han, Y. Chen, Z. Cai, B. Yildiz, *J. Am. Chem. Soc.* **2013**, 135, 7909.
- [38] A. Staykov, H. Téllez, T. Akbay, J. Druce, T. Ishihara, J. Kilner, *Chem. Mater.* **2015**, 27, 8273.
- [39] M. E. Grass, P. G. Karlsson, F. Aksoy, M. Lundqvist, B. Wannberg, B. S. Mun, Z. Hussain, Z. Liu, *Rev. Sci. Instrum.* **2010**, 81, 053106.
- [40] M. Abbate, F. M. F. de Groot, J. C. Fuggle, A. Fujimori, O. Strelbel, F. Lopez, M. Domke, G. Kaindl, G. A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, S. Uchida, *Phys. Rev. B* **1992**, 46, 4511.
- [41] M. Abbate, J. C. Fuggle, A. Fujimori, L. H. Tjeng, C. T. Chen, R. Potze, G. A. Sawatzky, H. Eisaki, S. Uchida, *Phys. Rev. B* **1992**, 47, 16124.
- [42] M. Merz, P. Nagel, C. Pinta, A. Samartsev, H. v. Löhneysen, M. Wissinger, S. Uebe, A. Assmann, D. Fuchs, S. Schuppler, *Phys. Rev. B* **2010**, 82, 174416.
- [43] Y. Orikasa, T. Ina, T. Nakao, A. Mineshige, K. Arnezawa, M. Oishi, H. Arai, Z. Ogumi, Y. Uchimoto, *Phys. Chem. Chem. Phys.* **2011**, 13, 16637.
- [44] D. N. Mueller, M. L. Machala, H. Bluhm, W. C. Chueh, *Nat. Commun.* **2015**, 6, 6097.
- [45] N. Tsvetkov, Q. Lu, L. Sun, E. J. Crumlin, B. Yildiz, *Nat. Mater.* **2016**, 15, 1010.
- [46] Y. Chen, H. Téllez, M. Burriel, F. Yang, N. Tsvetkov, Z. Cai, D. W. McComb, J. A. Kilner, B. Yildiz, *Chem. Mater.* **2015**, 27, 5436.
- [47] H. Wang, K. J. Yakal-Kremski, T. Yeh, G. M. Rupp, A. Limbeck, J. Fleig, S. A. Barnett, *J. Electrochem. Soc.* **2016**, 163, F581.
- [48] E. J. Crumlin, E. Mutoro, Z. Liu, M. E. Grass, M. D. Biegalski, Y.-L. Lee, D. Morgan, H. M. Christen, H. Bluhm, Y. Shao-Horn, *Energy Environ. Sci.* **2012**, 5, 6081.
- [49] F. Pişkin, R. Bliem, B. Yildiz, *J. Mater. Chem. A* **2018**, 6, 14136.
- [50] J. J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* **1985**, 32, 1.
- [51] J. Karthik, A. R. Damodaran, L. W. Martin, *Adv. Mater.* **2012**, 24, 1610.
- [52] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.* **1996**, 6, 15.
- [53] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, 54, 11169.
- [54] G. Kresse, D. Joubert, *Phys. Rev. B* **1998**, 59, 1758.
- [55] P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
- [56] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [57] J. Hubbard, *Proc. R. Soc. London, Ser. A* **1963**, 276, 238.
- [58] VESTA, <http://www.jp-minerals.org/vesta/en/> (accessed: August 2019).