



Surface Strontium Segregation of Solid Oxide Fuel Cell Cathodes Proved by In Situ Depth-Resolved X-ray Absorption Spectroscopy

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Little is known about the structures and chemistry of perovskites, occurring from the surface to the bulk, at high temperatures and ambient oxygen pressures. Changes in the composition and electronic structure of (001)-oriented $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC) films were investigated by using in situ depth-resolved X-ray adsorption (XAS) under practical operating conditions of solid oxide fuel cells. Depth-resolved XAS spectra of LSC films, with a depth resolution of ~ 2 nm, revealed that the surface regions of ~ 10 nm were considerably different from the film bulk. The surface regions were enriched in strontium, which can play an important role in governing the oxygen exchange kinetics at the surface.

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Perovskites with mixed high electronic and ionic conductivities have been studied extensively as catalysts for applications in solid oxide fuel cells (SOFCs), metal-air batteries, oxygen permeation membranes, automobile exhaust catalysts, and gas sensors.¹⁻⁵ Oxygen exchange reaction kinetics (i.e., $\text{O}_2 + 4e \rightarrow 2\text{O}^{2-}$) on the surface of these perovskites often limit their performance at elevated temperatures.⁶ Previous work has shown that the concentration of strontium in the perovskite structure can greatly influence the oxygen exchange kinetics at the surface.⁷ Although strontium segregation toward the surface of these oxides has been suggested in a number of studies,⁸⁻¹⁷ little is known about the surface structures and chemistry of perovskites at high temperatures and ambient oxygen pressures, which hampers the research and discovery of highly active perovskite catalysts. Ex situ surface analysis tools^{18,19} fail to capture surface compositions governing the electrocatalytic activity, as the catalyst surface composition may change as a function of temperature and oxygen partial pressure. Conventional in situ compositional surface characterization techniques^{20,21} such as X-ray photoelectron spectroscopy (XPS) at low pressures, may also provide information considerably different from those under ambient oxygen pressure at elevated temperatures relevant to practical device operation.²² Since the simultaneous observation of the structural chemistry occurring from the surface to the bulk under the operating condition of SOFC cathode is still lacking, the changes in the chemical composition and chemical nature of (001)-oriented $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ away from the surface on the nanometer-scale remain obscure.

Recent in situ ambient pressure X-ray photoelectron spectroscopy (APXPS) studies have shown that surface strontium concentration and chemical states (in the perovskite structure versus surface secondary phases), with a penetration depth of ~ 2 nm, can significantly change in the surface region of (001)-oriented $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ upon heating/cooling to/from $\sim 500^\circ\text{C}$, as a function of applied potential under an oxygen partial pressure of up to 10^{-3} atm.^{23,24} As the concentration of oxygen vacancies is expected to decrease from the perovskite surface to the bulk,²³ the concentration of cations, in particular, strontium are expected to change from the surface to the bulk. However, the previous in situ APXPS studies were conducted at a pressure of only up to 10^{-3} atm, which is still not the ambient pressure. Furthermore in the previous XPS measurements, the penetration depth is less than 2 nm, which limits the observation of the difference between the oxide bulk and the surface. Therefore, the changes in the chemical composition and chemical nature of (001)-oriented $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ away from

the surface on the nanometer-scale are not understood due to the lack of techniques that can simultaneously probe both the surface and the bulk under the operating condition.

In this study, we address this by applying depth-resolved X-ray absorption (XAS) under practical SOFC operating conditions. This measurement provides a systematic structural change information from surface to bulk in one depth-resolved XAS measurement. Depth-resolved XAS can provide depth resolution in the order of a few nanometers,^{25,26} and hard X-rays used in the XAS enables in situ measurements under high temperatures and atmospheric pressures. The depth-resolved XAS data in this study can provide systematic structural change information from the surface to the bulk over a depth of 100 nm. Herein we report the electronic structural changes of epitaxial $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC) thin films of three different thicknesses (viz., 20 nm, 45 nm, and 130 nm), at a nanometer depth resolution from the surface to bulk, using in situ depth-resolved hard X-ray absorption spectroscopy upon heating from room temperature to 520°C under an oxygen partial pressure ($p(\text{O}_2)$) of 1 atm.

Experimental

$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC) thin films with gadolinium-doped ceria (GDC) buffer layer were prepared by pulsed laser deposition (PLD), as reported previously.²⁷ $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ and $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ pellets were used as PLD targets. Single crystalline 8 mol% yttria-stabilized zirconia (YSZ) having (001) orientation (Princeton Scientific Corp.) were used as substrates. Prior to the deposition, platinum (Pt) paste (#6082 BASF Catalysts, Newark, NJ) was painted on the other side of the YSZ substrates and fired at 800°C in air for 1 hour. A KrF excimer laser ($\lambda = 248$ nm, repetition rate of 10 Hz, and energy of 50 mJ per pulse) was used. The distance between the substrates and the targets was 5 cm. Oxygen pressure during deposition was maintained at 10 mTorr. GDC buffer layer was first deposited on YSZ substrates at 450°C for 500 laser pulses. LSC films were then deposited at 680°C for 5,000, 15,000, and 30,000 laser pulses in order to change the film thickness.

X-ray diffraction (XRD) patterns of the films were collected using a Bruker D8 (Karlsruhe, Germany) multipurpose diffractometer using $\text{Cu K}\alpha$ radiation. Surface morphology and film thickness were observed by atomic force microscopy (AFM) using a Veeco Enviroscop (New York, USA). AFM images were analyzed using the Nanoscope software package (Veeco Instruments, Inc. Version 5.30).

In situ depth-resolved X-ray absorption spectroscopy measurements were performed at BL37XU and BL01B1 at Spring-8/JASRI(Japan). The X-ray beam, monochromatized by a Si(111)

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double-crystal, was set incident to the thin films at an angle of 6° . Grazing exit emitted fluorescence was detected by a two-dimensional pixel array detector (PILATUS-100 K detector). By using a PILATUS-100 K detector, 194 different-angle signals were obtained simultaneously. Fluorescence XAS measurements at the Co K -edges were performed. XAS spectra were collected under $p(\text{O}_2) = 1.0$ atm from $T = 25^\circ\text{C}$ to 520°C .

Results and Discussion

Epitaxial LSC thin films of thicknesses (20 nm, 45 nm, and 130 nm) with gadolinium-doped ceria (GDC) buffer layer on (001) oriented yttrium-stabilized zirconium (YSZ) single crystal were prepared by pulsed laser deposition (PLD) as reported previously.^{23,24,27–29} Normal XRD patterns for LSC films (Fig. 1) show only reflections corresponding to the (001)_{pc} diffractions from LSC and (001)_c diffraction from GDC or YSZ, validating the formation of highly (001)_{pc}-oriented LSC thin films (here the subscript “pc” and “c” denote the pseudo-cubic and the cubic notation, respectively). Off-normal phi-scan analysis (Fig. S1) shows that LSC(202)_{pc}, GDC(202)_c and YSZ(202)_c have intense peaks with 4-fold cubic symmetry, indicating that the LSC films were grown epitaxially on GDC and YSZ having in-plane crystallographic relationships between GDC and YSZ (a cube-on-cube alignment), and LSC and GDC (a in-plane 45° rotation).^{27,30} The relaxed lattice parameters of these films are $3.84\text{--}3.85$ Å which are higher than that of LSC bulk (3.83 Å), and in-plane and out-of-plane strains $\sim -0.4 \pm 0.1\%$ and $0.6 \pm 0.15\%$, respectively which are in reasonable agreement with those previously reported (Fig. S2).²⁷ Atomic force microscopy (AFM) in Fig. S3 reveals that these films have low surface roughness with a root-mean-square (rms) of about $1\text{--}4$ nm. The experimental setup for in situ depth-resolved XAS is illustrated in the supporting information (Fig. S4), which is based on the difference of the self-absorption coefficient with exit angles of fluorescence X-ray.³¹ The spectra collected from low-exit angles consist of signals only from the surface of the electrode due to self-absorption of fluorescence X-ray from deeper range, and the spectra collected from high-exit angles include signals from both the surface and bulk. By using the LSC thin films with the GDC buffer layer, the depth resolution of this technique was examined (Fig. S5) and estimated to be ~ 2 nm.

Fig. 2a shows X-ray absorption near edge structure (XANES) spectra at Co K -edge collected from the LSC thin film of 45 nm as a function of exit angle from 0.158° (surface) to 0.552° (bulk) measured at 25°C under $p(\text{O}_2) = 1$ atm. The Co K near edge feature results from the transition of core electrons into the $4p$ empty states, and the absorption edge energy shift can be used to determine the oxidation state of cobalt in LSC.¹⁹ The XANES spectra were found to change from the surface region (~ 10 nm from the surface) to the bulk of the LSC thin film with increasing exit angle. When the exit angle is increased from 0.158 to 0.552° , a sharp intense peak referred to as “white line”

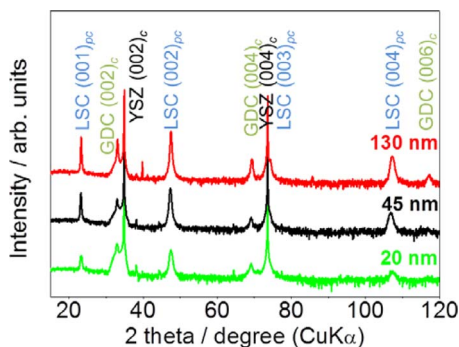


Figure 1. Normal XRD patterns of LSC thin films with varying thicknesses. The peaks are labeled in the pseudo-cubic (pc) LSC, the cubic (c) GDC and the cubic (c) YSZ.

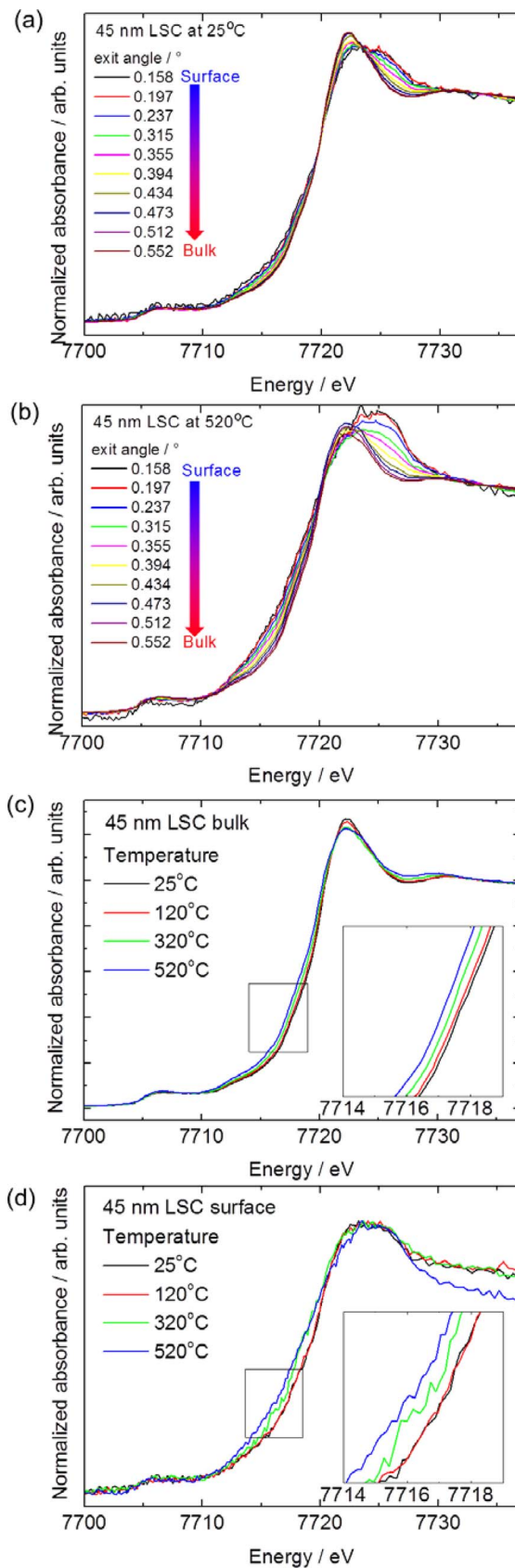


Figure 2. Depth-resolved X-ray absorption near edge structure at Co K -edge of 45 nm LSC thin film measured at (a) 25°C and (b) 520°C under $p(\text{O}_2) = 1$ atm. Temperature dependency of (c) surface and (d) bulk information from depth-resolved X-ray absorption near edge structure at Co K -edge of 45 nm LSC thin film measured under $p(\text{O}_2) = 1$ atm.

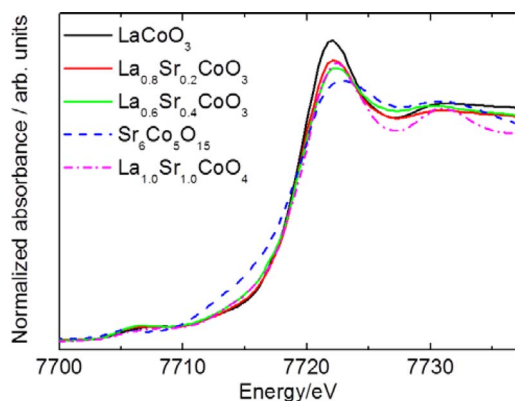


Figure 3. X-ray absorption near edge structure at Co *K*-edge of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$, and strontium cobalt oxide as reference powders.

at around 7723 eV shifts toward lower energy, and the absorption edge structure (edge jump) at around 7716 eV shifts toward higher energy. Such changes became more pronounced for XANES spectra collected at 520°C (Fig. 2b), where the surface region (~10 nm from the surface) becomes increasingly different from bulk at elevated temperatures under $p(\text{O}_2) = 1$ atm. Temperature dependency of surface and bulk XANES spectra is shown in Figs. 2c and 2d, respectively. When the temperature is increased, oxygen vacancy in LSC is further introduced and the valence state of cobalt decreases.^{32,33} The observed energy shift of the absorption edge toward lower energy reflects reduced decrease in the oxidation state of cobalt.¹⁹ Compared with the shift of the edge observed in bulk, the shift in the surface XANES is more pronounced. The result indicates that the surface structure of LSC is preferentially reduced upon increasing the temperature.

The broadened absorption edge feature and the shift of the white line toward higher energy for surface regions of 45 nm LSC thin film are considerably different from those of perovskites including LaCoO_3 , LSC and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, and those of K_2NiF_4 -type phases (including LaSrCoO_4). Interestingly, these features resemble those of $\text{Sr}_6\text{Co}_5\text{O}_{15}$ (Fig. 3) and SrCoO_3 reported previously.³⁴ This observation supports strontium enrichment at the surface of LSC^{35–37}, which includes strontium segregation to the surface in the perovskite structure²³ to yield a $\text{SrCoO}_{3.8}$ -like composition at the LSC surface. As shown in Figs. 2c and 2d, increasing the temperature generates more oxygen vacancies at the perovskite surface than the bulk. This is because the surface of perovskite thin film has a lower energy of vacancy formation than the film bulk (an effect predicted previously by DFT studies).³⁸ Owing to the opposite formal valence change of the oxygen vacancy (2+) and the strontium substitution (1–), the introduction of oxygen vacancy at the surface drives strontium moving in the perovskite structure toward the surface. This effect results in both the reduction in O content and Sr enrichment at the perovskite surface with reduction state associated with increasing temperature.

The difference in the Co *K*-edge of XANES spectra from the surface to bulk collected at 520°C under $p(\text{O}_2) = 1$ atm was found to increase with the LSC film thickness. Figs. 4a and 4b show depth-resolved XANES spectra of 130 and 20 nm LSC thin films, respectively. The changes in the spectra of the LSC with a thickness of 130 nm appears more pronounced than those observed for the 45 nm-thick LSC (Fig. 2b). In contrast, no clear depth dependency was observed for the 20 nm-thick LSC film, and the Co *K*-edge XANES spectra reveals more broadened “white line” similar to those of $\text{Sr}_6\text{Co}_5\text{O}_{15}$ (Fig. 3) and $\text{SrCoO}_{3.8}$.³⁴ These results suggest that thinner films have more strontium-enriched surfaces than thicker films at 520°C under $p(\text{O}_2) = 1$ atm (Fig. S6), which is supported by the fact that the surface oxygen exchange kinetics of the LSC film with a thickness of 20 nm is considerably greater than that of 130 nm (Fig. S7) since the strontium concentration in the perovskite structure is correlated with increased oxygen exchange kinetics at the surface.^{39,40}

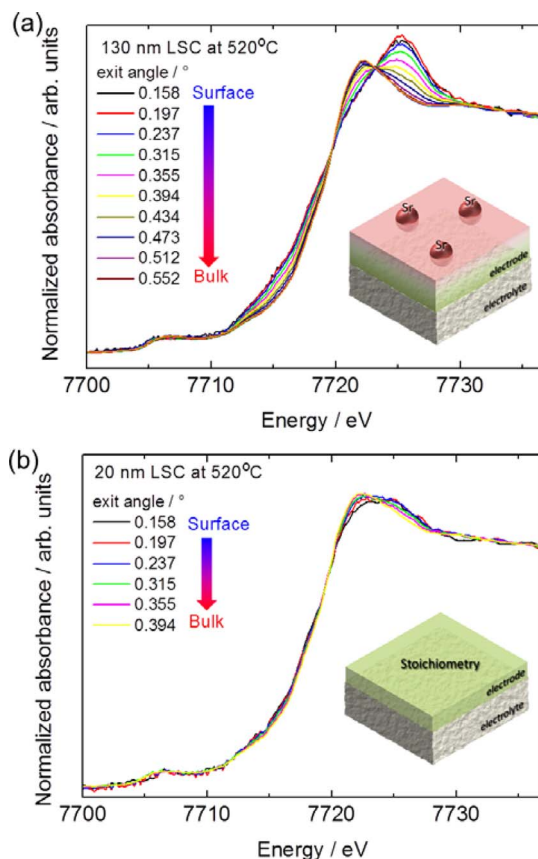


Figure 4. Depth-resolved X-ray absorption near edge structure at Co *K*-edge of (a) 130 nm and (b) 20 nm LSC thin film measured at 520°C under $p(\text{O}_2) = 1$ atm.

Strontium enrichment on the surface of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3.8}$ was reported for bulk^{11,36,41,42} and thin films.^{23,24,37,43} Our previous work has shown that depositing a small amount of SrO coverage on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3.8}$ does not impede surface exchange kinetics, however, increasing SrO coverage eventually results in surface passivation.⁴⁴ The studies relating to the use of epitaxial thin films suggest Sr enrichment in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3.8}$ perovskite structure in addition to the SrO coverage.^{23,43} In this study, we use XAS to probe deeper from the surface relative to previous XPS data,^{11,23,24,36,42,43,45} and report, for the first time, univocal evidence of strontium segregation in the perovskite structure of LSC a few nanometers below the surface, in addition to which composition governs the oxygen exchange kinetics. We do expect that there might be surface species such as $\text{SrO}/\text{Sr}(\text{OH})_2/\text{SrCO}_3$ (not detected in the Co *K*-edge XAS data) as the perovskite surface decomposes and/or reacts with water and CO_2 at ambient atmosphere, which is supported by previous studies of thin films.^{23,43} We surmise that surface impurity phases such as $\text{SrO}/\text{Sr}(\text{OH})_2/\text{SrCO}_3$ exist at the surface as “island” structures and do not fully block the surface reaction.⁴⁴ The previous report hypothesized that these phases may influence the composition of the perovskite structure below.⁴⁴ In this study, we report the much-awaited evidence of Sr segregation in the near surface region of LSC thin films (at a few nanometers from the surface), where Sr changes in LSC were resolved using depth-dependent XAS data. This result builds upon the findings of previous XPS data^{11,23,24,36,42,43,45} that largely probe surface species and have very limited depth resolution, where little understanding exists on how the perovskite composition changes when moving away from the surface.

The physical origin underlying the strontium-enriched surfaces for thinner films is not understood and several possible reasons are discussed here. First, different thicknesses in LSC films grown

epitaxially on GDC/YSZ can yield dissimilar strains profiles within and on the film surface, which may influence the degree of strontium enrichment on the surface. Although the strains calculated from XRD at room temperature are similar among these films of different thicknesses (Fig. S2), the strains in the surface regions and/or at elevated temperatures could be different. Second, the growth of LSC films by PLD may result in increasing strontium concentrations for thinner LSC films, which is ascribed to the lack of depth dependency in the XANES spectra of the 20 nm-thick LSC, considering that all the spectra resemble that of $\text{SrCoO}_{3-\delta}$. Strontium-depleted regions may also exist in the LSC films and if such regions are in the order of ~ 2 nm in thickness, they would not be detected by depth-resolved XAS due to its depth resolution in this study. Future studies are needed to reveal depth-dependent compositions of LSC films grown by PLD and to understand its implication on the oxygen kinetics at the surface as well as the surface stability of these films.

Conclusion

The electronic structural changes of epitaxial LSC thin films with three different thicknesses have been analyzed, at a nanometric depth resolution from the surface to bulk, using in situ depth-resolved XAS upon SOFC operating conditions. The broadened absorption edge features and the shift of the “white line” toward higher energy for the spectra collected from surface regions can be explained by strontium enrichment toward the film surface. Strontium enrichment is most pronounced for the thinnest LSC film, which has the highest surface oxygen exchange kinetics. Our results hint that control of strontium enrichment on the perovskite surface can be critical to develop high active perovskites for solid oxide fuel cells, oxygen permeation membranes and sensor applications.

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References

- S. B. Adler, *Chem. Rev.*, **104**, 4791 (2004).
- C.-s. Chen, S.-j. Feng, S. Ran, D.-c. Zhu, W. Liu, and H. J. M. Bouwmeester, *Angew. Chem. Int. Ed.*, **42**, 5196 (2003).
- V. Neburchilov, H. Wang, J. J. Martin, and W. Qu, *J. Power Sources*, **195**, 1271 (2010).
- Y. Teraoka, T. Nobunaga, K. Okamoto, N. Miura, and N. Yamazoe, *Solid State Ionics*, **48**, 207 (1991).
- J. Suntivich, H. A. Gasteiger, N. Yabuuchi, H. Nakanishi, J. B. Goodenough, and Y. Shao-Horn, *Nature Chem.*, **3**, 546 (2011).
- T. Kawada, J. Suzuki, M. Sase, A. Kaimai, K. Yashiro, Y. Nigara, J. Mizusaki, K. Kawamura, and H. Yugami, *J. Electrochem. Soc.*, **149**, E252 (2002).
- L. M. van der Haar, M. W. den Otter, M. Morskatte, H. J. M. Bouwmeester, and H. Verweij, *J. Electrochem. Soc.*, **149**, J41 (2002).
- S. P. Simmer, M. D. Anderson, M. H. Engelhard, and J. W. Stevenson, *Electrochem. Solid-State Lett.*, **9**, A478 (2006).
- Y. Chen, W. Jung, Z. H. Cai, J. J. Kim, H. L. Tuller, and B. Yildiz, *Energ. Environ. Sci.*, **5**, 7979 (2012).
- W. Jung and H. L. Tuller, *Energ. Environ. Sci.*, **5**, 5370 (2012).
- D. Oh, D. Gostovic, and E. D. Wachsman, *J. Mater. Res.*, **27**, 1992 (2012).
- S. Li, W. Jin, P. Huang, N. Xu, J. Shi, and Y. S. Lin, *J. Membr. Sci.*, **166**, 51 (2000).
- H. Yokokawa, H. Tu, B. Iwanschitz, and A. Mai, *J. Power Sources*, **182**, 400 (2008).
- M. Finsterbusch, A. Lussier, J. A. Schaefer, and Y. U. Idzerda, *Solid State Ionics*, **212**, 77 (2012).
- A. K. Huber, M. Falk, M. Rohnke, B. Luerssen, L. Gregoratti, M. Amati, and J. Janek, *Phys. Chem. Chem. Phys.*, **14**, 751 (2012).
- A. E. Becerra-Toledo and L. D. Marks, *Surf. Sci.*, **604**, 1476 (2010).
- H. Ding, A. V. Virkar, M. Liu, and F. Liu, *Phys. Chem. Chem. Phys.*, **15**, 489 (2013).
- G. J. la O, R. F. Savinell, and Y. Shao-Horn, *J. Electrochem. Soc.*, **156**, B771 (2009).
- Y. Orikasa, T. Ina, T. Nakao, A. Mineshige, K. Amezawa, M. Oishi, H. Arai, Z. Ogumi, and Y. Uchimoto, *J. Phys. Chem. C*, **115**, 16433 (2011).
- M. Imamura, N. Matsubayashi, and H. Shimada, *J. Phys. Chem. B*, **104**, 7348 (2000).
- B. Luerssen, E. Mutoro, H. Fischer, S. Gunther, R. Imbühl, and J. Janek, *Angew. Chem. Int. Ed.*, **45**, 1473 (2006).
- C. Zhang, M. E. Grass, A. H. McDaniel, S. C. DeCaluwe, F. El Gabaly, Z. Liu, K. F. McCarty, R. L. Farrow, M. A. Linne, Z. Hussain, G. S. Jackson, H. Bluhm, and B. W. Eichhorn, *Nature Mater.*, **9**, 944 (2010).
- E. J. Crumlin, E. Mutoro, Z. Liu, M. E. Grass, M. D. Biegalski, Y. L. Lee, D. Morgan, H. M. Christen, H. Bluhm, and Y. Shao-Horn, *Energ. Environ. Sci.*, **5**, 6081 (2012).
- E. Mutoro, E. J. Crumlin, H. Popke, B. Luerssen, M. Amati, M. K. Abyaneh, M. D. Biegalski, H. M. Christen, L. Gregoratti, J. Janek, and Y. Shao-Horn, *J. Phys. Chem. Lett.*, **3**, 40 (2012).
- T. Okumura, T. Nakatsutsumi, T. Ina, Y. Orikasa, H. Arai, T. Fukutsuka, Y. Iriyama, T. Uruga, H. Tanida, Y. Uchimoto, and Z. Ogumi, *J. Mater. Chem.*, **21**, 10051 (2011).
- D. Takamatsu, T. Nakatsutsumi, S. Mori, Y. Orikasa, M. Mogi, H. Yamashige, K. Sato, T. Fujimoto, Y. Takanashi, H. Murayama, M. Oishi, H. Tanida, T. Uruga, H. Arai, Y. Uchimoto, and Z. Ogumi, *J. Phys. Chem. Lett.*, **2**, 2511 (2011).
- G. J. la O, S. J. Ahn, E. Crumlin, Y. Orikasa, M. D. Biegalski, H. M. Christen, and Y. Shao-Horn, *Angew. Chem. Int. Ed.*, **49**, 5344 (2010).
- Z. X. Feng, E. J. Crumlin, W. T. Hong, D. Lee, E. Mutoro, M. D. Biegalski, H. Zhou, H. Bluhm, H. M. Christen, and Y. Shao-Horn, *J. Phys. Chem. Lett.*, **4**, 1512 (2013).
- E. J. Crumlin, S. J. Ahn, D. Lee, E. Mutoro, M. D. Biegalski, H. M. Christen, and Y. Shao-Horn, *J. Electrochem. Soc.*, **159**, F219 (2012).
- E. J. Crumlin, E. Mutoro, S. J. Ahn, G. J. la O, D. N. Leonard, A. Borisevich, M. D. Biegalski, H. M. Christen, and Y. Shao-Horn, *J. Phys. Chem. Lett.*, **1**, 3149 (2010).
- T. Noma, H. Miyata, and S. Ino, *Jpn. J. Appl. Phys., Part 2*, **31**, L900 (1992).
- M. H. R. Lankhorst, H. J. M. Bouwmeester, and H. Verweij, *J. Solid State Chem.*, **133**, 555 (1997).
- J. Mizusaki, Y. Mima, S. Yamauchi, K. Fueki, and H. Tagawa, *J. Solid State Chem.*, **80**, 102 (1989).
- R. Le Toquin, W. Paulus, A. Cousson, C. Prestipino, and C. Lamberti, *J. Am. Chem. Soc.*, **128**, 13161 (2006).
- R. Bertacco, J. P. Contour, A. Barthélemy, and J. Olivier, *Surf. Sci.*, **511**, 366 (2002).
- P. A. W. van der Heide, *Surf. Interface Anal.*, **33**, 414 (2002).
- M. Kubicek, A. Limbeck, T. Frömling, H. Hutter, and J. Fleig, *J. Electrochem. Soc.*, **158**, B727 (2011).
- Y.-L. Lee, J. Kleis, J. Rossmeisl, and D. Morgan, *Phys. Rev. B: Condens. Matter*, **80**, 224101 (2009).
- L. M. van der Haar, M. W. den Otter, M. Morskatte, H. J. M. Bouwmeester, and H. Verweij, *J. Electrochem. Soc.*, **149**, J41 (2002).
- J. Zhao, J. Sunarso, W. Zhou, Z. P. Shao, R. Ran, and S. M. Liu, *J. Electrochem. Soc.*, **158**, H299 (2011).
- E. Bucher and W. Sitte, *Solid State Ionics*, **192**, 480 (2011).
- E. Bucher, W. Sitte, F. Klauser, and E. Bertel, *Solid State Ionics*, **208**, 43 (2012).
- Z. Cai, M. Kubicek, J. Fleig, and B. Yildiz, *Chem. Mater.*, **24**, 1116 (2012).
- E. Mutoro, E. J. Crumlin, M. D. Biegalski, H. M. Christen, and Y. Shao-Horn, *Energ. Environ. Sci.*, **4**, 3689 (2011).
- M. Kubicek, A. Limbeck, T. Frömling, H. Hutter, and J. Fleig, *J. Electrochem. Soc.*, **158**, B727 (2011).