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Effects of moisture on (La, A)MnO₃ (A = Ca, Sr, and Ba) solid oxide fuel cell cathodes: a first-principles and experimental study

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One of the major challenges in developing clean, environmentally friendly energy technologies such as solid oxide fuel cells (SOFCs) is performance degradation at higher temperatures. Solid oxide fuel cell (SOFC) cathode degradation in the presence of moisture is one of the major concerns. Combining computational and experimental studies provides a comprehensive picture of the interaction between moisture and lanthanum manganite based SOFC cathodes. To better understand the surface chemistry, (La, A)MnO₃ (A = Ca, Sr and Ba) (001) surfaces are explored using first-principles calculations. This computational study suggests that dissociative adsorption of water molecules is favored on (La, A)Oterminated (001) surfaces. The covalently unsaturated surface terminal O atom (via strong H-bond) attracts one of the H atoms of the water molecule, with a subsequent breakup of the water molecule into H⁺ and OH⁻ groups. The surface should also be significantly enriched with A-site dopants under all realistic conditions, with all the three dopants driven to segregate to the surface over a wide range of T $p_{\rm H,O}$ conditions. Atomic force microscopy reveals just such a segregation of dopants to the surface of doped LaMnO3, enhanced in the presence of moisture. It is hypothesized that the interplay of the resulting oxygen vacancy defects and moisture from the operating environment further drives cationic surface segregation, ultimately degrading catalytic activity. In addition to providing insights into the surface chemistry, this combined experimental and computational investigation opens pathways for designing new materials with enhanced catalytic functionality.

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1. Introduction

One of the critical scientific challenges for contemporary researchers is developing clean, environmentally friendly energy technologies. Solid oxide fuel cells (SOFCs) have been regarded as a promising route for clean and efficient electricity as it provides us with the flexibility to use a wide range of fuels at high operating temperatures (\geq 800 °C). Although, the high operating temperature favors the rapid reaction kinetics (such as anodic reactions, ion transport in the electrolyte and cathodic reactions), it leads to many complications.

One of the major issues with SOFCs is cathode degradation at higher temperatures. The promising cathode materials are strontium doped lanthanum manganite (LSM) and lanthanum

strontium cobalt ferrite (($La_{1-x}Sr_x$)($Co_{\nu}Fe_{1-\nu}$) O_{3-z}). When LSM, which is the state of the art cathode material, is exposed to atmospheric air (during SOFC operation), segregation of strontium oxide at the LSM surface is often observed. This is believed to decrease the oxygen reduction reaction (ORR) rate as well as the transport of ions and electrons to the surface. Atmospheric air contains moisture (\sim 3%), CO₂ (\sim 400 ppm) and sulfur (<1 ppm) as the major impurities. However, the concentration of the impurities may vary with the geographic locations. It has been reported that moisture in air decreases the electrical performance of LSM but the presence of $\leq 0.5\%$ carbon dioxide is not detrimental.^{1,2} A recent study has shown no discernible change in LSM performance in moisture containing air under zero electrical bias but the performance decreases under cathodic bias (negative electrical potential). This finding leads to the conclusion that moisture in air does not block any electrochemically active sites by poisoning the cathode but negatively affects the charge transport kinetics.3 Precipitation of tiny strontium or lanthanum oxides/hydroxides and manganese oxide, and formation of lanthanum zirconate at the cathodeelectrolyte interface were concluded to be responsible for decreasing the performance. A recent study reports that moisture in air favors segregation of strontium oxide/hydroxide and

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Given that reduction of the operation temperature is unfavorable due to adverse effects on electrochemical processes, which are thermally activated and at reduced temperatures become much slower. Hence, optimization of cathode materials becomes essential in order to achieve reasonable performance of SOFCs. Experimental⁴⁻¹¹ and computational^{5,7,9-14} studies have attempted to explain cation segregation in terms of the formation of cation-containing phases,15,16 charge compensation^{6,17} and other degradation mechanisms of conventional cathode materials. Previous experimental studies mainly focus on the optimization of cathode composition and the electrode microstructure,18,19 and control of the electrolyte-cathode interface reactivity.19,20 Computational studies, on the other hand, are aimed at investigating the oxygen exchange processes on various facets of perovskite oxides7,8,15,21,22 and report that the different atomic sizes of the elements cause surface segregation to reduce the free energy of the system.^{13,22,23} Moreover, both experimental and computational studies confirm that cation segregation is a commonly observed phenomenon at the surface of perovskite oxides that affect the cathode reactivity and stability in the ORR under SOFC operating conditions. Still a detailed study for mapping the 'real-world' atmospheric conditions and their effect on the perovskite oxide surfaces is much needed to develop a deeper understanding and to find a suitable replacement for conventional cathode materials. Specifically, insights concerning the interaction of air and water with oxide surfaces and how oxide surface chemistry influences their functionality are much needed.

In this contribution, using density functional theory (DFT) based computations, we illustrate the interaction mechanisms of moisture with the (La, A)MnO₃ (001) surfaces (A = Ca, Sr, and Ba) with/without the presence of oxygen vacancies. The DFT results explain and support the experimental findings that the cathodic bias accelerates the surface segregation due to formation of oxygen vacancies. In addition, we have also studied the role of different A-site dopants on the surface chemistry. In the present work, it is observed that the dopants tend to segregate to the surface over a wide range of $T-p_{H_2O}$ conditions and it is only at rather low $p_{H,O}$ and/or high T that surface segregation is suppressed. Under these conditions, the dopant prefers to remain in the bulk regions accompanied by the appropriate number of charge compensating O vacancies. The favorable agreement of the identified cationic surface segregation behaviors for the chosen dopants with the available experimental data is indicative of the usefulness of such firstprinciples thermodynamic approaches, which can be used next to study other more involved and relevant situations (e.g., surface segregation of a larger variety of dopants in the presence of moisture).15,16

Using atomic force microscopy (AFM), we further experimentally confirm an enhancement in the segregation tendency of dopants to the surface of LMO specimens in the presence of moisture. AFM has previously been used for similar studies with a range of fuel cell materials. In terms of topographic changes due to processing as implemented here, the surface development of Mn doped yttria-stabilized zirconia (YSZ) has been analyzed recently upon thermal treatment in a temperature from 1250 °C to 1400 °C due to Mn dissolution.24 The morphologies of various fuel cell electrodes have also been studied, including Pt on Y stabilized zirconia, as a function of annealing,25 and pre- and post-PA impregnation of carbon electrodes loaded with precious metal nanoparticles.26 Functional properties can be mapped as well with variations of AFM, such as the electrostatic force or scanning surface potential microscopy, to study work function variations in electrodes27 or at interfaces for cross sectioned lanthanum strontium manganite films on YSZ.28 Potential gradients due to anionic oxygen diffusion, with down to nanoscale variations related to grains and grain boundaries, have even been observed at typical operating temperatures for YSZ.29 More specific to lanthanumoxide systems, reversible and irreversible electrochemical phenomena at distinct biases were reported for LaAlO₃-SrTiO₃ based on electrochemical strain microscopy.30 With scanning tunneling microscopy and spectroscopy even finer spatial resolution is achieved, resolving: activation polarization at 580 °C and 10⁻³ mbar oxygen pressure for cation-oxygen bonding with La_{0.7}Sr_{0.3}MnO₃ (LSM);³¹ Sr segregation, oxygen vacancy formation, and the corresponding variations in the electronic structure as a function of tensile and compressive strains via LSM epitaxy on STO and LAO substrates, respectively;11 and variations in the surface morphology and electronic structure of shallow-angle cross-sections of La_{0.65}Sr_{0.35}MnO₃/SrTi_{0.2}Fe_{0.8}O₃ multilayers as a function of distance from the interfaces.32 Incorporating such experimental results, guided by theory, for further refinement of next-stage materials modeling and discovery represents a clear opportunity for future research with LMO and related functional materials systems.

2. Computational and model details

The DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) code,^{33–35} within Perdew–Burke–Ernzerhof (PBE)³⁶ generalized gradient approximation (GGA), the projector-augmented wave approach, and a cutoff energy of 400 eV for the plane wave expansion of the wave functions. Geometries were relaxed using a conjugate gradient algorithm until the forces on all unconstrained atoms became smaller than <0.03 eV Å⁻¹. Appropriate Monkhorst–Pack *k*-point meshes were considered to produce results with an energy convergence of 0.5 meV per atom.

Owing to the fact that under SOFC operating conditions LaMnO₃ has a cubic structure (space group Pm3m) and Jahn-Teller lattice deformation around manganese ions and the related magnetic and orbital orderings may not be critical.12,13,21,37 Thus similar to previous studies, we construct our surface models within the cubic (Pm3m)crystal symmetry.12,13,21,37 The optimized lattice parameter of the bulk cubic LaMnO₃ (3.91 Å) is slightly overestimated with respect to the available experimental results (3.89 Å).³⁸ The overestimation of lattice parameters is also observed in earlier DFT based studies^{39,40} and can be explained in terms of formation of the high spin state of Mn.

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In this work, we restrict our consideration to the (La, A)O terminated (001) surfaces, which are energetically the most stable under typical SOFC operational conditions.12,13,21,37 After considering the tradeoff between the energetic convergences and associated computational time, we adopted a 2×2 surface supercell with 5-layer stoichiometric slabs of (La, A)O-termination (001) surfaces, as shown in Fig. 1. It is worth mentioning that the difference between segregation energies computed using 3 \times 2 and 2 \times 2 surface supercells, with 5-layer and 9layer (La, Sr)O-terminated slabs was negligible (<0.01 eV), indicating that the (2×2) surface supercell size is within the scope of the present study. Moreover, the (2×2) surface supercell size has been reported to be sufficient enough in other studies.41-43 Here, one La atom is substituted at a time with Ca, Sr or Ba, either in the central LaO plane (bulk region), or in the surface LaO plane, corresponding to a dopant concentration of \sim 7.4%. The slabs are separated by a vacuum spacing of 16 Å, chosen by testing the variation in total energy with vacuum distance and the decay of the local potential away from the surfaces. In LSM under SOFC operating conditions, a low concentration of oxygen vacancies is expected.⁴⁴ Therefore, to study the effect of the oxygen vacancy (O_{vac}) on the surface segregation, one Ovac is considered at the adjacent site (first neighboring position) of the dopant.44 In the presence of cationic vacancies, the oxygen vacancies are predicted to be predominant to maintain the charge neutrality. Hence, in the present work we have excluded the cationic vacancies.

A deeper understanding of the influence of 'real-world' atmospheric conditions encountered by the perovskite oxide surfaces is much needed to improve upon the existing cathode materials as well as to design new materials with enhanced catalytic functionality for various technological applications including SOFCs. Here, to get insights into the surface chemistry under SOFC operating conditions we aim to address the following questions: (i) what are the effects of moisture on cation segregation on perovskite oxide surfaces. In other words, does the presence of moisture on the surface suppresses or enhances the tendency for segregation of different dopants? (ii) How strongly does the surface prefers to have oxygen vacancies and how does the presence of oxygen vacancies affects the surface chemistry of cathode materials. (iii) What is the preferred reaction mechanism on the surface to have oxygen vacancies in the presence of moisture? (iv) Does a larger variety of dopants affect the surface segregation in the presence of moisture? For instance, if the presence of water molecules on the surface suppresses the cationic segregation, then the dopant will prefer to remain in the bulk region and the surface chemistry will not depend on the choice of dopants. In this situation, it is fair to consider the slab as a pure LaO-terminated slab and the energy associated with the adsorption of the H₂O molecules on the clean surface will be the binding energy (E_{BE}) of H₂O molecules. On the other hand, if the presence of water molecules on the surface enhances the cationic segregation then the surface chemistry will largely be governed by the choice of dopants.



Fig. 1 Schematic portraying various scenarios considered in the present study. (a) One La atom is substituted with a dopant (A = Ca, Sr and Ba) in the bulk region. (b) Dopant (A) segregation to the surface. (c) Top-view of high-symmetry sites offered by the LaO-terminated (001) surface for the water adsorption. (d) Interaction of water with (La, A)O-terminated (001) surfaces when the slab is exposed to a pure H₂O reservoir. (e) The dissociative adsorption of water molecules on the surfaces. (f) The two adjacent hydroxyl groups are shown, atoms discussed in the text and Table 1 are also labeled.

The scenario when the LaO-terminated slab of La(A)MnO₃ (A = Ca, Sr and Ba) is exposed to the pure H₂O reservoir is portrayed in the schematic shown in Fig. 1. Here, the reference system is shown in Fig. 1a, where one La atom is substituted by one A atom (A = Ca, Sr and Ba) in the bulk region of LaOterminated slab. From our past experience,44 we know that in La(A)MnO₃ dopants have a natural tendency to segregate towards the surface. In this situation, thermodynamically, the whole process can be represented in two parts (i) first the dopant segregates to the surface (segregation energy, E_{Seg}) as shown in Fig. 1b and (ii) then interaction of H₂O molecules on the doped surface takes place (binding energies of the H₂O molecules to the doped surface, $E_{\rm BE}$), see Fig. 1d-f. Here, to capture the zero to full (100%) water coverage, we have varied the number of water molecules from zero to four on the 2 \times 2 (La, A)O terminated (001) surfaces.

3. Experimental details

To support the DFT study, we have thermally treated LSM in atmospheric air and 20% H₂O containing air at 800 °C for 50 hours. The experiment has been conducted in 20% H₂O to accelerate the segregation effect, if any, to identifying above the AFM resolution limit. The surface topography of the (La, A) MnO_3 (A = Ca, Sr and Ba) specimens was imaged with atomic force microscopy (AFM). The commercial instrument (Asylum Research, MFP3d) was used in an AC mode with standard probes (AC160TS) exhibiting a ~380 kHz resonance frequency, spring constant of 42 N m⁻¹, and <10 nm radius of curvature at the apex. Representative 5 µm and 1 µm images are included herein, with 256 imes 256 pixel resolution in order to resolve ${\sim}20$ and 4 nm features, respectively. Scan rates were fixed at 0.5 Hz, with common imaging gain settings of ~10 and an AC-amplitude feedback set-point of ~ 0.5 V (1/2 of the cantilever's free amplitude of 1 V). Images presented in the paper include both topography, as well as the simultaneously acquired AC amplitude (the feedback channel, essentially a derivative of the surface and hence particularly effective for identifying fine feature edges). In this manner, AFM is used to monitor the development of protruding islands of segregates that are hypothesized and calculated to develop at the surface of specimens with a certain composition and processing conditions.

4. Results and discussion

Following the processes shown in Fig. 1a–f, first we carried out systematic DFT calculations for all conceivable (La, A)O terminated (001) slab species with surface- or bulk-substitution of one La atom with one A atom (A = Ca, Sr and Ba).

A. Cation segregation

The segregation energy, E_{seg} , can be defined as

$$E_{\text{Seg}} = E_{n_{O_{\text{Vac}}}}^{\text{D}_{\text{Surf}}} - E_{n_{O_{\text{Vac}}}}^{\text{D}_{\text{Bulk}}}$$
(1)

where $E_{n_{Ovac}}^{D_{Surf}}$ and $E_{n_{Ovac}}^{D_{Bulk}}$ are the DFT total energies of the system with one dopant at the surface and the bulk, respectively. $n_{O_{uac}}$ is

the number of oxygen vacancies, in the present work which is either zero or one.

The segregation energy, defined as the energy difference between the horizontal lines (Fig. 2) corresponding to the bulk and surface dopant situations, is -0.04, -0.17 and -0.26 eV per atom, respectively, for Ca, Sr and Ba, which is in favorable agreement with the available experimental^{5,8} and *ab initio* results.⁵ It is noteworthy that beyond a certain dopant cation concentration, segregation may lead to the formation of new phases, which in fact has been seen in experiments.⁵

B. Effects of moisture

(i) Active adsorption sites. Owing to the fact that dopants considered here tend to segregate to the surface,^{10,11,45} all surfaces adopt La(A)O-termination (A = Ca, Sr and Ba). The interaction of H₂O with La(A)O-terminated (001) surfaces is investigated using adsorbate-slab calculations. It is well known that surface adsorption processes are affected by surface active sites. In the present work, using a (2×2) surface unit cell and water coverage of 0.25 monolayer (ML), which is equivalent to one water molecule per unit cell on the considered La(A)Oterminated (001) slab. We studied various configurations of the water molecule on the stoichiometric La(A)O-terminated (001) surfaces. Particularly the La(A)O-terminated (001) surfaces are optimized by placing one water molecule at various active sites, including "La on-top", "3-fold", "O-top", "La-La/(A) bridge", and "O-O bridge" sites. A schematic top view of these highsymmetry sites offered by the LaO terminated (001) surface for the water adsorption geometry is depicted in Fig. 1c. Moreover, for each adsorption site two orientations are considered; in one the hydrogen atoms are parallel to the surface whereas in the other the hydrogen atoms are perpendicular to the surface.

(ii) Adsorption of water. As illustrated in Fig. 1e and f, the La(A)O-terminated (001) surface prefers the dissociative adsorption of water molecules where a water molecule dissociates into two adjacent hydroxyl groups. This can be schematically represented by the chemical equation $H_2O + O^{2-} \rightarrow$ 20H⁻. In this geometry the molecular H₂O breaks into a H⁺ and an OH⁻ group that binds to a surface O ion and at the middistance (bridge site) between two La ions, respectively.46 As is depicted in Fig. 1e, at the La-La bridge site (between two surface La cations) the O1 and H1 atoms form the first hydroxyl group. The bond length of free OH (distance between O1 and H1) is found to be 0.97 Å, invariant to the choice of dopants. In fact, for other oxide (001) surfaces *i.e.* LaMnO₃, BaTiO₃,⁴⁷ and SrTiO₃ (ref. 41 and 48) the free OH bond length resulting from water molecule dissociation is found to be 0.97 Å. The split-off H^+ (H2 in Fig. 1e) atom of the dissociated water molecule attracts and lifts the lattice oxygen anion (O2 in Fig. 1e) out of the surface plane to form the second hydroxyl group. Moreover, the two hydroxyl groups are tilted toward each other, suggesting the formation of a hydrogen bond. Selected bond distances in the dissociated adsorption geometry at the LaO-terminated (001) surface are listed in Table 1 and compared with other available perovskite oxide (001) surface bond lengths. For the energetically most favorable geometry of water adsorbed on the La(A)O



Fig. 2 Energetics as a function of the H_2O chemical potential for the dissociative adsorption of water molecules on the La(A)O-terminated (001) surface, where A is (a) Ca, (b) Sr, and (c) Ba. Different colors correspond to different water coverages. The dash and solid lines correspond to the situation where the dopant is in the bulk or surface region, respectively. To capture the surface chemistry under SOFC operating conditions, the dependence of the H_2O chemical potential in the gas phase is translated into the pressure scales at 1000 K and 1300 K. In the inset of (a), the widths of the highlighted parts in black and red indicate the segregation energy in the absence and presence of water (with O_{vac}), respectively. In (a–c), the shaded part in blue represents the region above the H_2O -rich limit, it sets an upper boundary to the chemical potential of water at the experimental critical point.⁴¹

surfaces, the top layer can be seen as chemically modified into a layer of dopant hydroxides since it forms a composition A(OH)₂. Both hydroxyl groups are hydrogen bonded to each other. Available computational and experimental studies provide significant evidence for the surface hydroxylation on the AO-terminated (001) surfaces. For example in the presence of water the top most layers of the AO-terminated (001) surfaces of $BaHfO_3$,⁴⁶ $BaZrO_3$,⁴⁶ $SrTiO_3$,^{41,49–51} $BaTiO_3$,⁴⁷ $SrMO_3$ (M = Ti, Zr, and Hf)⁵² LaNiO₃,⁵³ and double perovskite oxides A₂-FeMoO_{6- δ} (A = Ca, Sr and Ba)⁵⁴ are found to be hydroxylated confirming the formation of A(OH)₂ and both OH were hydrogen bonded to each other. Moreover, surface hydroxylation is also experimentally observed for SrTiO₃, and the adsorption of water on TiO2- and SrO-terminated domains, attributed to surface hydroxylation, was experimentally measured for a range of water exposures.49-51

The 0 K binding energies, $E_{\rm BE}$, associated with various dissociative adsorption configurations of water molecules are calculated as

$$E_{\rm BE} = E_{\{n_{\rm H_2O}, n_{\rm O_{vac}}\}}^{\rm D_{surf}} - E_{\{n_{\rm O_{vac}}\}}^{\rm D_{surf}} - n_{\rm H_2O} \times E_{\rm H_2O}$$
(2)

Table 1 Selected bond distances in the dissociated adsorption geometry at the LaO-terminated (001) surface (in Å). The labels for the individual atoms are defined in Fig. 1f

			La(A)MnO ₃		
	SrTiO ₃ (ref. 41)	LaMnO ₃	Ca	Sr	Ва
H1-O1	0.97	0.97	0.97	0.97	0.97
H2-O2	1.01	1.03	1.05	1.05	1.03
H2-O1	1.6	1.49	1.43	1.46	1.52
01–A	2.59	2.74	2.49	2.61	2.75

here, $E_{\{n_{\rm H_2O}, n_{\rm O_{Vac}}\}}^{\rm D_{Surf}}$ is the total energy of the doped surface covered with dissociated water molecules, $E_{\{n_{\rm O_{Vac}}\}}^{\rm D_{Surf}}$ is the total energy of the doped surface, and $n_{\rm O_{vac}}$ is the number of oxygen vacancies which is either zero or one in the present work. $E_{\rm H_2O}$ is the DFT total energy of an isolated H₂O molecule. $E_{\rm H_2O}$ is calculated in a 20 × 20 × 20 Å supercell resulting in an optimized OH-bond length of 0.99 Å which is found to be compared well with the available theoretical (0.99 Å)⁴¹ and experimental (0.96 Å)^{55,56} values. Here, all zero-point energies are neglected under the assumption that entropic contributions from the solids to the free energy difference are insignificant.⁵⁷

(iii) Surface phase diagram. Now, with the assumption that the (La, A)MnO₃ (001) surfaces (A = Ca, Sr, and Ba) are exposed to a water vapor reservoir, we combine the energetics of adsorbed water (zero to full coverage) on the La(A)O-surfaces within a first-principles atomistic thermodynamics framework. In this approach, we assume the surface to be in equilibrium with the surrounding water vapor environment characterized by a chemical potential μ_{H_2O} . So far, eqn (2) that represents the DFT total energy based 0 K binding energetics does not account for the temperature (*T*) and pressure (p_{H_2O}) dependence of the H₂O chemical potential, $\mu_{H_2O}(T, p_{H_2O})$, which can be written as

$$\mu_{\rm H_2O}(T, p_{\rm H_2O}) = E_{\rm H_2O}^{\rm DFT} + \Delta \mu_{\rm H_2O}(T, p_{\rm H_2O})$$
(3)

where, $\Delta \mu_{\rm H_2O}(T,p_{\rm H_2O})$ is the variation of the H₂O chemical potential due to the temperature and pressure of the surrounding water vapor atmosphere.

After including *T* and $p_{\rm H_2O}$ dependence of the H₂O chemical potential, eqn (2) can be written as

$$\begin{split} E_{\rm BE} &= \left[E_{\{n_{\rm H_{2O}}, n_{\rm O_{vac}}\}}^{\rm D_{\rm Surf}} - E_{\{n_{\rm O_{vac}}\}}^{\rm D_{\rm Surf}} - n_{\rm H_{2O}} \times E_{\rm H_{2O}}^{\rm DFT} \right] - n_{\rm H_{2O}} \\ &\times \Delta \mu_{\rm H_{2O}} (T, p_{\rm H_{2O}}) \end{split}$$
(4)

In eqn (4), the last term accounts for the *T* and $p_{\rm H_2O}$ dependence, which includes contributions from the translational, rotational and vibrational degrees of freedom of the H₂O molecule, and can be determined *via* statistical thermodynamics or from thermochemical JANAF Tables.⁵⁸ Using the results of our *ab initio* computations the phase diagrams showing the interaction of water molecules with different La(A) O-terminated (001) surface coverage configurations are portrayed in Fig. 2.

Fig. 2(a–c) summarize the surface energetics as a function of the H₂O chemical potential for the dissociative adsorption of a range of water coverages on the La(A)O-terminated (001) surface, where A is Ca, Sr, and Ba. In Fig. 2, the dash and solid lines correspond to the situation where one La atom is substituted with one dopant (A = Ca, Sr, and Ba) in the bulk or in the surface region, respectively. On the energy scale the difference between these two lines is the segregation energy, E_{seg} , as described in eqn (1). It is evident from Fig. 2(a-c) that with the increasing ionic size mismatch between the dopant and host cations, E_{seg} increases. The ionic radius of Ca (1.34 Å) is almost identical to that of La (1.36 Å), correlating well with the very small surface segregation energy. In fact, recent experiments confirm that the Ca-doped LaMnO₃ films showed a relatively smaller amount of dopant segregation than the Srdoped variety.⁵ While in the case of Sr (1.44 Å) and Ba (1.61 Å) a larger surface segregation is observed. With increasing ion size, Ca < Sr < Ba, the increase in surface segregation energies provides an indication that the ion size is one of the dominating factors which control the surface segregation. Another important factor which plays a crucial role in determining the stability and the host site of a dopant is the mismatch of the oxidation states⁵⁹ between the dopant with respect to the host atom. In the present case, the oxidation state is not critical as the nominal oxidation state of all the three considered dopants (Ca, Sr, and Ba) is +2. Thus, the observed variation in surface segregation is primarily dominated by the size mismatch between the dopant (Ca, Sr, and Ba) and host cations (La).

Next, we address the effect of water on the surface segregation energy results and trends on the type of dopant. To capture the surface chemistry under SOFC operating conditions, the dependence of the H₂O chemical potential in the gas phase is translated into the pressure scales at 1000 K and 1300 K. In Fig. 2, the shaded part represents the regions above the H_2O rich limit, *i.e.*, it sets an upper boundary for the chemical potential of water at the experimental critical point and the present approach assuming equilibrium with water vapor is no longer strictly applicable.41,60 In the region where the chemical potential of $\mu_{H,O}$ is high, the water coverage of 1 ML is most stable, which is far away from the conditions considered during the experiments.^{61,62} As we move towards the region where the chemical potential of μ_{H_2O} is low, the hydroxylated geometries become increasingly less favorable. Furthermore, the water absorption increases for higher water partial pressures, which is found to be in agreement with the available experimental results on strontium-doped lanthanum cobaltite.63

With increasing ion size, Ca (above $\mu_{\rm H_2O} = -2.8$) < Sr (above $\mu_{\rm H_2O} = -2.5$) < Ba (above $\mu_{\rm H_2O} = -1.8$), the surface remains

significantly enriched with the dopants. Moreover, the phase diagrams shown in Fig. 2 also indicate that near ambient pressure conditions (1 atm), at a higher temperature (1300 K), the surface segregation of dopants with the ion size similar to the host atom (Ca and Sr) is not affected by the surrounding environment. Under similar pressure conditions (1 atm), segregation of dopants with a larger ionic size (Ba) is favored even at 1000 K. The primary insight that emerges from this study is that the cation size dominates the segregation tendency.

(iv) Oxygen vacancy. Next, we made an attempt to understand the role of oxygen vacancy (Ovac) on the surface segregation under humid conditions. To portray this, we considered several configurations of the O vacancy in the vicinity of the dopant in the above-described model. From our past experience, we know that the lowest-energy site occurs in the adjacent site (first neighboring position) of the dopant.44,59 In the presence of O_{vac} the segregation energy, E_{seg} , (shown in Fig. 1a and b) is calculated as the energy difference between the total energies corresponding to the bulk and surface dopant situations with an O_{vac} in the neighborhood. Binding energies (E_{BE}) are calculated for all thermodynamically possible water molecule dissociation mechanisms that the La(A)O-terminated (001) surface with Ovac can adopt. The energy profile of possible water molecule dissociation mechanisms on the O deficient La(A)Oterminated slab is plotted in Fig. 3. The considered mechanisms are: (Case 1) OH from the La-La bridge site (between two surface La cations) occupies the Ovac site, (Case 2) OH remains at the La–La bridge site with the O_{vac} in the neighborhood of the dopant and (Case 3) the oxygen atom dissociates from H₂O and occupies the Ovac site. Here onwards, these dissociation mechanisms are further referred as Case 1, Case 2 and Case 3, respectively. Our self-consistent DFT total energy based energy profile indicates that among the considered dissociation mechanisms the increasing order of stability is Case 1 > Case 2 >



Fig. 3 Energy profile of the possible water dissociation mechanisms on the O_{vac} defected La(A)O-terminated slab, here A is Ca, Sr and Ba. The different considered mechanisms are: (i) OH from the La–La bridge site (between two surface La cations) occupies the O_{vac} site, (ii) OH remains at the La–La bridge site with the O_{vac} in the neighborhood of the dopant and (iii) the oxygen atom dissociates from H₂O and occupies the O_{vac} site. Possibilities for water dissociation mechanisms on the O deficient La(A)O-terminated slab are also shown. La, Mn, O, H and A atoms are shown in blue, purple, cyan, orange and brown, respectively.

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Case 3. The calculated most favorable water adsorption geometry on the La(A)O-terminated (001) surfaces is Case 3, where the vacancy site is occupied by the oxygen atom dissociated from the H₂O molecule. The remaining H₂ molecule is weakly bound to the surface with the total energy increasing by 0.1 eV with the removal of the molecule from the surface. In Table 2, all the calculated adsorption energies (in eV) for possible water molecule dissociation mechanisms on the La(A)O-terminated (001) surfaces with the O_{vac} in the neighborhood of the dopant are tabulated. It is observed that our calculated adsorption energies, reported in Table 2, indeed show good agreement with the available values of the SrO-terminated (001) surface.⁴⁸

In light of these results, we revisit the surface phase diagram in Fig. 2. The phase diagram reveals that the most notable effect of hydrogenation is to stabilize the surface over a wide range of *T*- $p_{H,O}$ conditions. It is only at rather low $p_{H,O}$ pressures and/or high T that the effect of moisture is suppressed. For the $T-p_{H_{2}O}$ conditions that SOFC systems encounter, such as 1 to 10^{-6} atm (for both choices of T), a surface segregation devoid of O_{vac} is favored. Fig. 2(a-c) also depict that in the high chemical potential region, the tendency of the cations to segregate towards the surface not only depends on the size of the dopant but also depends on the surrounding chemical environment as well as on the presence of the defects on the surface. In the insets of Fig. 2(a-c), we have zoomed into the low chemical potential region (H₂O-poor region) of the phase diagram. The widths of the highlighted parts in black and pink indicate the segregation energy in the absence and presence of moisture, respectively (see the insets of Fig. 2(a-c)). Under SOFC operating conditions (such as 1 to 10^{-6} atm for both choices of *T*) with the increasing cation size the presence of moisture (devoid of O vacancies) has less effect on the surface segregation, as depicted in Fig. 2(a-c). However, under similar conditions the low concentration of O_{vac} is found to be capable of stabilizing a nonstoichiometric surface terminated by either hydroxyl groups or water like species. The present finding is analogous to the observations made for various oxide surfaces *i.e.* α -Al₂O₃ (0001),64 and RuO₂ (110).60 Furthermore, experimental studies also suggest that at high T and low $p_{H,O}$ pressures, OH coverage diminishes and surface hydroxide species become more

Table 2 Calculated adsorption energies (in eV) for water molecule dissociation mechanisms on the La(A)O-terminated (001) surfaces with the O_{vac} in the neighborhood of the dopant. The considered mechanisms are: (Case 1) OH from the La–La bridge site (between two surface La cations) occupies the O_{vac} site, (Case 2) OH remains at the La–La bridge site with the O_{vac} in the neighborhood of the dopant and (Case 3) the oxygen atom dissociates from H₂O and occupies the O_{vac} site

Discussion			La(A)MnO ₃ ^{<i>a</i>}		
mechanisms	SrTiO ₃ (ref. 41)	LaMnO ₃ ^a	Ca	Sr	Ва
Case 1		-1.26	-1.63	-1.38	-1.29
Case 2		-1.64	-1.70	-1.52	-1.52
Case 3	-2.71	-2.86	-2.55	-2.58	-2.60

^a Present work.

Another possibility is that the oxygen vacancy concentration may increase during the hydration, which has not been considered in the present study. It is observed that cathodic bias during the SOFC operation accelerates the extent of surface segregation. Cathodic bias increases the oxygen vacancy in the LSM bulk and the surface and subsequent surface segregation. Both Fig. 2 and 3 confirm that under humid environments the surface chemistry of La(A)O-terminated surfaces with defects is largely governed by oxygen vacancies and the dopant shows a tendency for segregation.

(v) Atomic force microscopy measurements. In support of the DFT study, we have prepared LSM samples by sintering in air at 1200 °C for 2 hours for morphological investigations by AC-mode AFM. After thermally treating half of these specimens in atmospheric air at 800 °C for 50 hours, topographic grain boundary grooving as deep as ~200 nm, as well as nano-down to atomic-scale steps, develop as expected (Fig. 4A). Multiple fine terraces are especially visible at the bottom right of the simultaneously acquired AFM-amplitude image in Fig. 4B, which highlights the feature edges as shown. Technically such amplitude images convey amplitude deviations during the scanning of the tapping AFM probe from a nominal amplitude in free air (A_0) of approximately 50 nm. The grain surfaces themselves are essentially featureless, however, as is evident in the higher magnification (1 µm) and finer contrast scale images of Fig. 4C and D. Fine particles are nevertheless visible heterogeneously scattered on the LSM surface, which are not visible for the un-annealed specimens (not shown for brevity),



Fig. 4 AFM images of the LSM surface sintered in air: 5 μ m topography (A) and amplitude (B) images, and 1 μ m topography (C) and amplitude images (D).

suggesting an occasional formation of second phases for segregants even in these moderate (atmospheric air) annealing/ sintering.

Identically prepared LSM specimens were also exposed to 20% H₂O, again at 800 °C for 50 h, causing two important modifications to the surface morphology. First, a higher density and greater homogeneity of atomic steps become apparent, even in large scale topographic images (Fig. 5A). Second, closer inspection (Fig. 5C) reveals numerous uniformly distributed particles at the surface that did not develop without the presence of moisture during annealing. A previous study identifies such particles as SrO/Sr(OH)2.4 Again, the edges of these various fine features are accentuated in the AFM amplitude images (Fig. 5B and D), which as shown in Fig. 4 indicate amplitude variations from a nominal free amplitude of \sim 50 nm. Notably, the scales in Fig. 4 and 5 for panels A-D, respectively, are identical for direct comparison, emphasizing the extensive differences in the surface evolution as a function of exposure without or with 20% H₂O.

The chemical formula of the LSM specimens is nominally (La_{0.8}Sr_{0.2})_{0.98}MnO₃. For strontium doped lanthanum manganite (LSM), as well as undoped LaMnO₃, oxygen non-stoichiometries including both excess and deficiency of oxygen have been observed for the temperature and oxygen pressures considered theoretically and experimentally, cation vacancies (oxygen excess) would be predominant if the LSM was not A-site deficient.⁶⁵⁻⁶⁸ For A-site deficient LSM as investigated herein, oxygen vacancies are predicted to be predominant to maintain charge neutrality. In a previous study,4 we showed that the surface segregation decreases in the presence of oxygen vacancies when sintered in air (800 °C, 0.21 atm p_{O_2}). But in the presence of 20% H₂O-air at 800 °C, the DFT calculations and the direct AFM observations in Fig. 5 confirm surface segregation as compared to that under atmospheric air conditions (Fig. 4).



Fig. 5 AFM images of the LSM surface aged at 800 °C for 50 hours in 20% H₂O containing air: 5 μ m topography (A) and amplitude (B) images, 1 μ m topography (C) and amplitude (D) images.

5. Limitations of the present work

It is noteworthy that moisture is only one of the performancelimiting factors. Even for this case, the present work considered only the thermodynamics of the process. Other crucial factors, such as the influence kinetics, other degradation mechanisms, etc., were excluded. This suggests that a more complex picture, involving surface species (hydroxide, superoxide, peroxide, etc.) or coverage effects (the surface oxygen vacancy concentration, molecular absorbates, hydration and related intermediate species), may arise at higher temperatures and higher coverage. The aim of this study, however, is to investigate the role and reactivity and effect of moisture on catalytic functionality of cathode materials in SOFCs. Secondly, in our computational study we do not consider the effect of the support, which certainly is not negligible; however, the dependence of the energetics of the cationic segregation process on the properties of the cathode alone is better revealed by the approach adopted here.

For strongly correlated systems, due to the errors associated with the on-site Coulomb and exchange interactions,⁶⁹ the standard DFT is not enough to estimate the electronic structure for strongly correlated systems such as late transition metal oxides^{70,71} and rare-earth compounds.^{72,73} However, in the particular case of LaMnO₃, the adsorption energy difference between DFT and DFT+U levels for the O₂–LaMnO₃ species is within the uncertainty of the DFT methods (~less than 0.05 eV).⁷⁴ Even in the present study, the theoretical predictions for the interaction of isolated water molecules on perovskite oxide surfaces is consistent with the experimental observations for this system, which indicates that the theory at the standard DFT-level qualitatively captures a reasonable description of the surface chemistry.

6. Conclusions

To summarize, we provide a comprehensive picture of the impact of various dopants on the surface cation chemistry of doped (La, A)MnO₃ (A = Ca, Sr and Ba), as well as the effect of moisture under SOFC operating conditions, by combining DFT calculations and atomic force microscopy measurements. Specifically, cation segregation towards the surface in the presence of moisture is investigated using the first-principles thermodynamics approach. Our computational study suggests that for a humid environment with (La, A)O-terminated (001) surfaces, the dissociative adsorption of water molecules is energetically favored. The covalently unsaturated surface terminal oxygen atom attracts one of the hydrogens from a water molecule via the strong H-bond, with the water molecule breaking into a H⁺ and an OH⁻ group. DFT predicts that the presence of such moisture enhances the tendency for cation segregation, which is further confirmed with the atomic force microscopy of (La, A)MnO₃ specimens exposed to various environmental conditions. Based on theory, the surface should remain significantly enriched with the dopants under all realistic operating conditions for fuel cells, a tendency that is

qualitatively unaffected by the dopants or the specific $T-p_{\rm H_2O}$ conditions.

Based on DFT we also propose an interaction mechanism of moisture with the (La, A)MnO₃ (001) surfaces (A = Ca, Sr, and Ba) with and without the presence of oxygen vacancies. The interplay of moisture and Ovac at a surface modulates the cationic surface segregation, causing degradation in catalytic activity at the surface. This complex predicted scenario also suggests that the surface prefers to exhibit oxygen vacancies, which significantly accelerate cation segregation even further and thereby affect the surface chemistry of cathode materials. This is consistent with the reported experimental studies that a cathodic bias increases oxygen vacancies in the (La, Sr)MnO₃ bulk corresponding to the surface segregation. Furthermore, a similar approach can also be adopted to understand the durability of lanthanum strontium cobalt ferrite ((La_{0.60}- $Sr_{0.40})_{0.95}(Co_{0.20}Fe_{0.80})O_{3-x})$ cathodes under SOFC operating conditions.75

The present study thereby not only provides insights into surface chemistry under 'real-world' chemical environments for fuel cells, but also suggests approaches for designing new materials with enhanced catalytic functionality for various technological applications.

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