Interplay between H$_2$O and CO$_2$ coadsorption and space-charge on Y-doped BaZrO$_3$ surfaces†

Jonathan M. Polfus, Jing Yang and Bilge Yildiz

The present work quantifies the equilibrium defect and adsorbate chemistry on oxide surfaces in the presence of multiple gas components at elevated temperatures and sub-surface space charge. The considerations of chemisorbed H$_2$O and CO$_2$ as well as surface protons and oxygen vacancies were calculated for Y-doped BaZrO$_3$ using a thermodynamic framework with input from first-principles calculations. The overall energy of the system was minimized based on contributions from gas adsorption, interactions between defects and adsorbates, segregation of point defects and space-charge formation, as well as configurational entropy. The coverage dependent adsorption energies were found as $-1.44 + 0.34 \theta_{H_2O}$ eV and $-2.25 + 1.21 \theta_{CO_2}$ eV for chemisorption of H$_2$O and CO$_2$, respectively. The interaction between the adsorbates was found to follow $1.72 \theta_{H_2O} \theta_{CO_2}$ eV. The coverage of surface protons was above 0.3 up to 1000 K under most considered conditions (0.01–1 bar H$_2$O, 4 $\times$ 10$^{-4}$–1 bar CO$_2$) due to a favorable interaction with both surface hydroxide and CO$_2$ adsorbates. Most importantly, the results show that the coadsorption, adsorbate interactions or space-charge formation each played a major role in the obtained defect concentrations and surface coverages. Thus, the approach in this work demonstrates the importance of considering quantitatively each of these aspects in obtaining accurately the surface equilibria on complex catalytic oxides.

1. Introduction

Perovskite oxides based on barium zirconate are applicable as proton conducting ceramic electrolytes for intermediate temperature fuel cells,\textsuperscript{1–4} electrolysis cells\textsuperscript{5,6} and electrochemical catalytic membrane reactors for steam-methane reforming\textsuperscript{2} and dehydrogenation processes.\textsuperscript{5,6} Most of these devices operate at temperatures from about 350 to 800 °C in H$_2$O and CO$_2$ containing atmospheres and the equilibrium surface chemistry can be expected to be significantly affected by the operating environment.\textsuperscript{8,9} It is therefore of importance to understand quantitatively how the surface composition and defect chemistry may influence the properties of the oxide surface for catalytic activity, chemical stability and coke resistance. For instance, Huang et al.\textsuperscript{10} recently demonstrated significantly enhanced CO$_2$ and H$_2$O exchange kinetics on oxide ion conducting perovskites and fluorites, as well as enhanced oxygen exchange rates in the presence of H$_2$O or CO$_2$ in addition to O$_2$ on electronically conducting Sr-doped LaMnO$_3$.\textsuperscript{12,13} Duan et al.\textsuperscript{14} recently reported excellent performance and durability of BaZrO$_3$-based protonic ceramic fuel cells with a range of hydrocarbon fuels and a steam-to-carbon ratio of 2.5 : 1 at 500–600 °C.

As a proton conducting oxide, Y-doped BaZrO$_3$ (BZY) readily dissolves protons from water vapor by hydration of oxygen vacancies.\textsuperscript{15} Both the BaO and ZrO$_2$ terminations of the preferred (0 0 1) surface exhibit strong affinity for H$_2$O, and dissociative adsorption predominates according to computational studies.\textsuperscript{16,17} The hydroxide and protonic species remain at the surface at higher temperatures than in the bulk due to a more exothermic adsorption enthalpy compared to the bulk hydration enthalpy. Furthermore, these charged surface species, OH$^-_{ad}$ and OH$_2^+$ respectively in Kröger–Vink notation,\textsuperscript{18} are central in the formation of space-charge layers at the surface.\textsuperscript{19,20} In this respect, protons have been found to be particularly stable at the surface leading to a positive surface charge that is charge compensated by hydroxide adsorbates and a subsurface space-charge region.

Adsorption of CO$_2$ has recently been shown to be particularly exothermic for the (0 0 1) surfaces by chemisorption of carbonate species, CO$_3^{2-}$.\textsuperscript{21} The calculated surface coverage as functions of temperature and P$_{CO_2}$ showed that a full carbonate overlayer was stable under ambient 400 ppm CO$_2$ up to 400 K and that significant coverage could be retained up to 2000 K.
under 1 bar CO₂. While the overall chemical stability of bulk BaZrO₃ towards CO₂ has been demonstrated, recent studies have shown surface reactivity with CO₂ to form BaCO₃ by accommodating Ba-deficiency in the subsurface region. Considering the strong adsorption of both H₂O and CO₂, interactions between the adsorbed species must be taken into account in order to appropriately describe the equilibrium surface coverages. Furthermore, the defect chemistry of the surface and subsurface must also be accounted for since all surface species – including neutral and charged adsorbates and point defects – interact and compete for the same surface sites. Accordingly, the gas adsorption equilibria will be influenced by the surface defect chemistry, and conversely the subsurface defect chemistry, or the space-charge region, will be affected by the adsorbates.

In the present work, we utilize first-principles calculations to investigate the concentration of adsorbates and defects on the BaO-terminated (0 0 1) surface of BZY under H₂O and CO₂ containing atmospheres. A thermodynamic model comprising gas adsorption equilibria, segregation of point defects and formation of a subsurface space-charge layer was implemented. As a result, surface coverages and subsurface space-charge behavior were obtained as a function of environmental variables. The individual contributions to the overall energy minimization of the system have been discussed in order to understand the interplay between gas adsorption equilibria and surface defect chemistry.

2. Computational approach

The DFT calculations were performed using VASP with the PBE generalized gradient approximation functional and projector-augmented wave pseudopotentials. The plane-wave cut-off energy was 500 eV and the k-point sampling was equivalent to 8 × 8 × 8 for the cubic BaZrO₃ unit cell. BaO-terminated (0 0 1) surfaces were constructed as symmetric 11-layer slabs. Adsorbates were considered at coverages of 0.11, 0.25, 0.5 and 1.0 with 2 × 2 and 3 × 3 expanded slabs (up to 243 atoms), and coadsorbate interaction was evaluated for equal coverages of 0.25 and 0.5 on 2 × 2 slabs, i.e., half and full coverage, respectively. Y-acceptors were not explicitly included in the computational cells since the surface was BaO-terminated and any interactions between adsorbates and subsurface Y-dopants can be expected to be minor compared to interactions between adsorbates or between adsorbates and point defects. The adsorption thermodynamics were evaluated based on the adsorption energy, configurational entropy and vibrational properties of the adsorbates obtained by the finite displacement method. The adsorption energy, ΔE_ads, was calculated as the total energy differences of the adsorption reactions. The equilibrium constant of the adsorption reactions was given by

\[ K = \exp \left( \frac{\Delta H_{ads}}{RT} \right) \exp \left( \frac{\Delta S_{ads}}{T} \right) \]  

(1)

where \( \Delta H_{ads} = \Delta E_{ads}(\Theta_i) + \Delta ZPE \). Bululk parameters including a nominal Y-dopant concentration and surface energies used for the thermodynamic model are listed in Table 1. Further details can be found in our previous work on the same system.20–21

The computed adsorption energies and segregation energies were fed into a thermodynamic framework to obtain the equilibrium concentrations of all adsorbates and defects by minimizing the total energy of the system. Effects of defect interaction and formation of subsurface space-charge layers were taken into account.

The energy of the adsorption layer can be separated into the energy of H₂O adsorbates, CO₂ adsorbates and an interaction term. The energy of the H₂O/CO₂ adsorption layer without interadsorbate interactions was calculated by

\[ E_{int} = \Theta_i (\Delta H_{ads} - \Delta S_{ads} - \Delta \mu_i) \]  

(2)

where \( \Delta \mu_i = kT \ln(p_i/p_0) \) is the chemical potential of the gas phase at varying partial pressure, and the coverage, \( \Theta_i \), represents the number of adsorbed molecules. The interaction between adsorbed H₂O and CO₂ was obtained from the difference in adsorption energy of the coadsorbates and the individual adsorbates (see Table 2), and described as

\[ E_{int} = 1.72 \Theta_{H₂O} \Theta_{CO₂} \]  

(3)

when the surface was considered to be neutral, i.e., \( \Theta_{H₂O} \) denoting paired surface proton and hydroxide species, OH⁰ and OH², respectively. For charged surfaces, the concentration of excess surface protons segregated from bulk was defined as \( \Theta_{OH} = \Theta_{OH} - \Theta_{OH²} \), when \( \Theta_{OH} > \Theta_{OH²} \), and zero otherwise. The \( E_{int} \) interaction energy was then described as

Table 1. Bulk parameters (Y-dopant concentration, lattice constant, relative permittivity and enthalpy and entropy of hydration) and surface segregation energies of protons and oxygen vacancies used in the thermodynamic model

<table>
<thead>
<tr>
<th>Y-dopant/mol%</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant/Å</td>
<td>4.214 (DFT)</td>
</tr>
<tr>
<td>v</td>
<td>75 (exp)²²</td>
</tr>
<tr>
<td>ΔHhydration/eV</td>
<td>−0.97 (exp)²²</td>
</tr>
<tr>
<td>ΔShydration/eV K⁻¹</td>
<td>−1.1 × 10⁻³ (exp)²²</td>
</tr>
<tr>
<td>ΔE hydration/fat/mol%</td>
<td>−0.96 (DFT)²⁹</td>
</tr>
<tr>
<td>ΔE hydration/eV</td>
<td>−0.42 (DFT)²⁹</td>
</tr>
</tbody>
</table>

Table 2. Energetics for dissociative adsorption of H₂O and chemisorption of CO₂ on pristine BaO-terminated BaZrO₃ (0 0 1) and parameters describing the interaction between surface species. The coverage dependent adsorption energies were obtained from linear fits with \( R² = 0.999 \) for CO₂ and \( R² = 0.997 \) for H₂O.

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔEads/eV</td>
<td>−1.44 + 0.34 ΘH₂O</td>
<td>−2.25 + 1.21 ΘCO₂</td>
</tr>
<tr>
<td>ΔZPE/eV</td>
<td>0.091</td>
<td>0.117</td>
</tr>
<tr>
<td>ΔSads/eV</td>
<td>−6.37 × 10⁻⁴</td>
<td>−8.78 × 10⁻⁴</td>
</tr>
<tr>
<td>ΔE hydration/fat/mol%</td>
<td>1.72 ΘH₂O ΘCO₂</td>
<td></td>
</tr>
<tr>
<td>ΔE hydration/eV</td>
<td>−0.31 eV (ref. 21)</td>
<td></td>
</tr>
<tr>
<td>Adsorption site</td>
<td>Ba + O</td>
<td>O</td>
</tr>
</tbody>
</table>

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where the second term corresponds to a favorable interaction between surface protons and adsorbed CO$_2$ as determined in our previous work.$^{21}$ The energies of the excess surface protons and oxygen vacancies were given by their segregation energies and electrostatic interaction with the surface potential, $\phi_0$, according to

$$E_{\text{exc}} = \Theta_{\text{OH}_\text{o}} \Theta_{\text{CO}_2} - 0.31 \Theta_{\text{OH}_\text{o}} \Theta_{\text{CO}_2}$$

(4)

where the coverage, $\Theta$, represents the number of surface species. For a given surface potential the electrostatic potential distribution from surface to bulk was obtained by solving Poisson’s equation

$$\frac{d^2 \phi}{dx^2} = -e \left( c_{\text{V}_\text{o}} - c_{\text{V}_\text{O}} - c_{\text{V}_\text{ZO}_2} \right)$$

(7)

where $c_{\text{V}_\text{o}}$, $c_{\text{V}_\text{O}}$, and $c_{\text{V}_\text{ZO}_2}$ denote the subsurface concentrations of oxygen vacancies, protons and $Y$-dopants, respectively. $V_{\text{O}}$ and $\text{OH}_\text{o}$ were treated as mobile species that can redistribute within the space-charge region at distance $x$ from the surface according to

$$c_i(x) = n_i \frac{\exp(\Delta E_i + q_i \phi(x))}{1 + \sum_{j} \exp(\Delta E_j + q_j \phi(x))}$$

(8)

where $i$ denotes defect species that share the same site as $c_i$. The dopant species, $\text{Y}_\text{Zr}$, were considered immobile with a fixed concentration of 0.2. The total energy of the space-charge layer was represented as

$$E_{\text{sc}} = \int_0^l \left( \sum_i c_i \left( \Delta E_i + q_i \phi \right) + \frac{1}{2} e \phi_0 \left( \frac{d \phi}{dx} \right)^2 \right) dx$$

(9)

where $\Delta E_i$ is the formation energy of each defect species and the space-charge layer extends a distance $l$ into the bulk. The configurational entropy of all the surface species was calculated considering shared sites for CO$_2$, OH$_\text{o}$, and $V_{\text{O}}$

$$S_{\text{config}} = -k \left[ \Theta_{\text{CO}_2} \ln \Theta_{\text{CO}_2} + \Theta_{\text{OH}_\text{o}} \ln \Theta_{\text{OH}_\text{o}} + \Theta_{\text{OH}_\text{o}} \ln \Theta_{\text{OH}_\text{o}} + \Theta_{\text{OH}_\text{o}} \ln \Theta_{\text{OH}_\text{o}} + \Theta_{\text{OH}_\text{o}} \ln \Theta_{\text{OH}_\text{o}} \right]$$

(10)

The above set of equations form a thermodynamic framework describing the total energy of the system, including the adsorption layer, segregation layer and subsurface space-charge layer. The system was solved for each environmental condition (temperature and partial pressures) by variation of $\phi_0$ to minimize the total energy of the system, and thus obtain the equilibrium concentrations of surface defects and adsorbates, $\Theta_{\text{CO}_2}$, $\Theta_{\text{OH}_\text{o}}$, $\Theta_{\text{OH}_\text{o}}$, and $\Theta_{\text{CO}_2}$, the surface potential $\phi_0$, as well as the subsurface concentration profiles in a self-consistent way. The constraint for the energy minimization was the global charge neutrality condition

$$\sum_i q_i \Theta_i + \int_0^l q_i c_i dx = 0$$

(11)

where $\Theta_i$ denotes charged adsorbates and surface defects, and $c_i$ denotes defects in the subsurface space-charge region. Details on the implementation of the thermodynamic model and numerical solution scheme is provided in the ESI (Section 1†).

3. Results

Fig. 1 shows relaxed structures of dissociatively adsorbed H$_2$O on the BaO-terminated BaZrO$_3$ (0 0 1) surface at coverages from 0.11 to 1 monolayer. The H$_2$O adsorbate was found to be most stable with surface hydroxide, denoted OH$_\text{ad}$, bridged between two barium, and surface protons, OH$_\text{o}$, directed towards the oxide ion of OH$_\text{ad}$ (Fig. 1a). The lowest energy configurations consisted of evenly spaced adsorbates at half coverage (Fig. 1b) and alternating rows with different symmetry at full coverage (Fig. 1c).

The interaction between H$_2$O and CO$_2$ adsorbates was evaluated for total surface coverages of 0.5 and 1. With respect to structural interactions, no significant changes were observed due to coadsorption of H$_2$O and CO$_2$ in the case of half coverage (Fig. 2a). On the other hand, a molecular H$_2$O adsorbate formed by association between OH$_\text{ad}$ and OH$_\text{o}$ on the fully covered surface as shown in Fig. 2b.

The energetics of H$_2$O and CO$_2$ adsorption that comprise the main input from the first-principles calculations to the thermodynamic model are summarized in Table 2. The adsorption energy of H$_2$O ranged from $-1.4$ to $-1.1$ eV for coverages of 0.11 to 1, respectively. These values are similar albeit somewhat less exothermic than previously reported values of $-1.5$ to $-1.3$ eV for half and full coverage, respectively.$^{19}$ Calculations for the ZrO$_2$-terminated surface exhibited similar energies for dissociative adsorption of H$_2$O in range of $-1.1$ to $-1.4$ eV.$^{17,20}$ The adsorption energy of CO$_2$ was more exothermic than that of H$_2$O at low coverage, $-2.20$ eV at $\Theta_{\text{CO}_2} = 0.06$. However, stronger adsorbate interactions resulted in a slightly lower adsorption energy for CO$_2$ than for H$_2$O at full coverage.$^{22}$ The zero-point energy contribution to the adsorption enthalpy was quite small for both H$_2$O and CO$_2$, which can be ascribed to the rather similar bond relationships for the adsorbed species and gaseous molecules.

The interaction energy between the coadsorbates, $E_{\text{int}}^{\text{H$_2$O-CO$_2$}}$, was found to be quite similar to the average interaction energy of the individual adsorbates from the coverage dependent adsorption enthalpies. For instance, the average increase in interaction energy from half to full coverage was 0.39 eV for adsorption of H$_2$O or CO$_2$, and 0.43 eV in the case of coadsorption. It should be noted that the stabilizing interaction...
between CO2,ad and OH,0 only refers to excess OH,0 since the interaction between OH,0 and OH,ad is included in the H2O adsorption energy.

Fig. 3 shows the contributions to the overall energy of the BaZr0.8Y0.2O3 system at equilibrium coverages as a function of temperature in Fig. 4 including a subsurface space-charge with a corresponding potential. Under 1 bar H2O and 400 ppm CO2, the surface is predominated by protons partly charge compensated by hydroxide, i.e., dissociatively adsorbed H2O and excess OH,0 segregated from the bulk (Fig. 4a). The surface attains a positive charge over the whole temperature range with a potential of up to about 0.3 V mainly due to excess OH,0. The surface remained free of CO2,ad despite the strong adsorption enthalpy of CO2 due to the unfavorable EintH2O–CO2 interaction term (Table 2). This behavior is shown graphically in contour maps of the contributions to the energy of the charge-neutral system spanning the complete ranges of ΘH2O and ΘCO2 in Fig. S1 (ESI, Section 2†).

By reducing the H2O pressure to 0.01 bar, ΘCO2 predominates up to 800 K and remains significant to even higher temperatures (Fig. 4b). Protons become the predominant surface species above 800 K, but the coverage of OH,ad is considerably lower which leads to a surface potential of up to 0.26 V at 500 K. At equal H2O and CO2 pressures of 1 bar, the surface is predominated by carbonate species up to about 1300 K (Fig. 4c).
Fig. 4d shows a similar trend with 0.1 bar H$_2$O where CO$_{2,ad}$ remains the predominant species over the whole temperature range.

Fig. 5 shows coverage isotherms at 1073 K as function of $p_{CO_2}$ and $p_{H_2O}$ under 1 bar CO$_2$ and H$_2$O, respectively. Under these conditions, the coverage of CO$_2$ is negligible below 0.01 bar CO$_2$ (Fig. 5a). From Fig. 5b it becomes apparent that the space-charge potential to a large extent follows the segregation of OH$^0_{ad}$ with a significant contribution above 1 bar H$_2$O at this temperature. The potential increases with $p_{H_2O}$ up to a pressure of 1 bar where OH$^0_{ad}$ increasingly charge compensates the surface protons. Notably, the coverage of OH$^0_{ad}$ exhibits an inverse relationship with that of CO$_2$ as the coverage of OH$^0_{ad}$ surpasses $\Theta_{CO_2}$ at around 0.5 bar H$_2$O (Fig. 5b). This behavior can be explained by the unfavorable interaction between CO$_2$ and OH$^0_{ad}$ (Eq. (4)).

Fig. 6 shows the concerted changes of the surface concentrations and the subsurface space-charge regions under 0.01 bar H$_2$O and 400 ppm CO$_2$ at 573–1473 K. The depletion of protons and oxygen vacancies in the subsurface space-charge region becomes less prominent as the potential is reduced from 0.25 V (Fig. 6a) to 0.11 V (Fig. 6d). While the bulk becomes increasingly dehydrated above 573 K, segregated surface protons predominate the surface even at 1473 K due to the favorable proton segregation energy (Table 1). It has previously been shown that inclusion of a Y-segregation profile significantly affects the space-charge properties of BZY surfaces and interfaces. In the present case, equilibration of Y$_{Zr}$ to the potential profile, i.e., Gouy-Chapman approximation, lead to a slight increase in the potential while the surface proton concentration increased significantly at 1073 K in 1 bar H$_2$O and 1 bar CO$_2$ (Fig. S2, ESI Section 3†).

Fig. 4 Surface coverages of adsorbates and defects (protons, oxygen vacancies, hydroxide and carbonate species) as well as free surface sites (top) and the corresponding space-charge potential (bottom) on BaZr$_{0.8}$Y$_{0.2}$O$_3$ (0 0 1) as function of temperature under 1 bar H$_2$O, 400 ppm CO$_2$ (a), 0.01 bar H$_2$O, 400 ppm CO$_2$ (b) and 1 bar CO$_2$, 1 bar H$_2$O (c) and 0.1 bar H$_2$O, 1 bar CO$_2$ (d).

Fig. 5 Surface coverages of adsorbates, defects and free surface sites, and the corresponding space-charge potential on BaZr$_{0.8}$Y$_{0.2}$O$_3$ (0 0 1) at 1073 K as function of partial pressure of CO$_2$ (a) and H$_2$O (b) under 1 bar H$_2$O and CO$_2$, respectively.
4. Discussion

The present results show that interactions between coadsorbates, charged surface species and sub-surface space-charge formation can play a predominant role in the calculated surface coverages. The effect of not taking into account all aspects of the surface equilibria and space-charge formation is therefore evaluated next. Fig. 7 shows the calculated coverages at 1 bar H$_2$O and 1 bar CO$_2$ compared with coverages obtained without considering space-charge formation and without taking into account competitive adsorption of CO$_2$. Without space-charge, the calculated surface coverage was dominated by chemisorbed H$_2$O since excess OH$^-$/C$_{15}$O was not included in this model (Fig. 7a). On the other hand, in the absence of competitive CO$_2$ coadsorption, the surface was saturated by OH$^-$/C$_{15}$O partly charge compensated by OH$^0$/ad (Fig. 7b). It is clear that these shortcomings of not taking into account space-charge or coadsorption significantly affect the calculated surface coverages in comparison to the results obtained with the complete model in Fig. 7c. By only considering space-charge formation in the absence of H$_2$O and CO$_2$ adsorbates (while OH$^-$ was allowed due to segregation from bulk), a surface potential of 0.68 V was obtained due to a OH$^-$ coverage of 0.66. Thus, it is clear that adsorption of uncharged gas species can also significantly affect the space-charge properties because of inter-adsorbate interactions and surface site limitations.

It was confirmed that the predominance of H$_2$O$_{ad}$ over CO$_2$$_{ad}$ obtained in Fig. 4a and 7a did not occur when removing the interaction between H$_2$O$_{ad}$ and CO$_2$$_{ad}$, i.e., $E_{int}$H$_2$O-CO$_2$ = 0 eV. In this case, $\Theta_{H_2O}$ and $\Theta_{CO_2}$ were similar as expected due to their comparable adsorption energetics as well as the increased configurational entropy associated with coadsorption. These coverages were similar to those obtained by Tutuianu et al. for the structurally equivalent BaO (0 0 1) surface without
interactions between coadsorbates or surface defects.\textsuperscript{30} However, Kwon \textit{et al.} obtained a low interaction energy between chemisorbed H\textsubscript{2}O and CO\textsubscript{2} on BaO (0 0 1) even for a total coverage of 0.5.\textsuperscript{31} The apparent difference in $E_{\text{int}}^\text{H\textsubscript{2}O-CO\textsubscript{2}}$ may be associated with a lower basicity of the BaO-terminated BaZrO\textsubscript{3} surface due to the presence of zirconium, which reduces the capacity for charge transfer to the adsorbates upon chemisorption.\textsuperscript{32}

It is interesting to note that the calculated coverage of the OH\textsubscript{ad} adsorbate increases with temperature under some conditions (\textit{e.g.}, Fig. 7c), which can seem counter intuitive due to the negative entropy of adsorption. Such behavior of OH\textsubscript{ad} has been predicted previously for BZY surfaces based on an increasingly positive space-charge potential at higher temperatures which thereby stabilized the negatively charged adsorbate.\textsuperscript{33} However, the calculated space-charge potential becomes less positive at higher temperatures in the present work, and the increased OH\textsubscript{ad} coverage may instead be associated with the rather strong adsorbate interactions which become lower as $\Theta_{\text{CO}_2}$ decreases.

In terms of the functional properties of Y-doped BaZrO\textsubscript{3} as a proton conducting electrolyte, the present result show that the surface exhibits a high coverage of protons in the form of OH\textsubscript{ad} under all the considered conditions. The presence of H\textsubscript{2}O prevents the formation of a carbonate overlayer which is assumed to be detrimental to both performance and stability.\textsuperscript{21,23} Similar results were recently obtained for SrO-terminated SrTiO\textsubscript{3} based on DFT calculations and \textit{in situ} FTIR analysis, although a relatively less exothermic chemisorption of CO\textsubscript{2} led to generally lower coverages of CO\textsubscript{2}.\textsuperscript{32} The favorable interaction between surface OH\textsubscript{ad} and CO\textsubscript{2}\textsubscript{ad} ($\Delta E_{\text{int}}^{\text{H\textsubscript{2}O-CO\textsubscript{2}}}$) implies that there will be relatively large concentrations of protons available for incorporation into the electrolyte also in carbonate rich areas of the surface. The strong coadsorption may also correspond to an increased stability of the Y-doped BaZrO\textsubscript{3} surface with respect to formation of Ba(OH)\textsubscript{2} and BaCO\textsubscript{3}, as well as coke deposition.\textsuperscript{14}

5. Conclusion

The present work demonstrates quantitatively the crucial role of adsorbate interactions and space-charge formation simultaneously in determining the equilibrium surface chemistry of oxides in the presence of multiple gas components. Despite the favorable H\textsubscript{2}O chemisorption on Y-doped BaZrO\textsubscript{3}, the calculated H\textsubscript{2}O coverage was quite low due to the more exothermic CO\textsubscript{2} chemisorption and unfavorable interaction between H\textsubscript{2}O and CO\textsubscript{2} adsorbates. However, the coverage of surface protons was found to be considerable up to 1500 K under most conditions due to a favorable interaction with both hydroxide and CO\textsubscript{2} adsorbates. The calculated coverages were found to be significantly affected by the interactions between surface species, in particular between surface protons and CO\textsubscript{2}. Competitive adsorption and space-charge formation were also determined to play major roles in the obtained coverages and concentration of defects.

Conflicts of interest

There are no conflicts to declare.

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