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Interplay between H₂O and CO₂ coadsorption and space-charge on Y-doped BaZrO₃ surfaces†

Jonathan M. Polfus, †‡a,b Jing Yang †‡b and Bilge Yildiz*bc

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 concentrations of chemisorbed H₂O and CO₂ as well as surface protons and oxygen vacancies were calculated for Y-doped BaZrO₃ 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 $-1.44 + 0.34\theta_{H₂O}$ eV and $-2.25 + 1.21\theta_{CO₂}$ eV for chemisorption of H₂O and CO₂, respectively. The interaction between the adsorbates was found to follow $1.72\theta_{H₂O}\theta_{CO₂}$ eV. The coverage of surface protons was above 0.3 up to 1000 K under most considered conditions (0.01–1 bar H₂O, 4 x 10⁻⁴–1 bar CO₂) due to a favorable interaction with both surface hydroxide and CO₂ 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,†‡ electrolysis cells,⁵,⁶ and electrochemical catalytic membrane reactors for steam-methane reforming⁷ and dehydrogenation processes.⁸,⁹ Most of these devices operate at temperatures from about 350 to 800 °C in H₂O and CO₂ containing atmospheres and the equilibrium surface chemistry can be expected to be significantly affected by the operating environment.¹⁰,¹¹ 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. recently demonstrated significantly enhanced CO₂ and H₂O exchange kinetics on oxide ion conducting perovskites and fluorites, as well as enhanced oxygen exchange rates in the presence of H₂O or CO₂ in addition to O₂ on electronically conducting Sr-doped LaMnO₃.¹²,¹³ Duan et al.¹⁴ recently reported excellent performance and durability of BaZrO₃-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 BaZrO₃ (BZY) readily dissolves protons from water vapor by hydration of oxygen vacancies.¹⁵ Both the BaO and ZrO₂ terminations of the preferred (0 0 1) surface exhibit strong affinity for H₂O and dissociative adsorption predominates according to computational studies.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°_ad respectively in Kröger–Vink notation, are central in the formation of space-charge layers at the surface.¹⁸,¹⁹ 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 CO₂ has recently been shown to be particularly exothermic for the (0 0 1) surfaces by chemisorption of carbonate species, CO₃²⁻. The calculated surface coverage as functions of temperature and $P_{CO₂}$ showed that a full carbonate overlayer was stable under ambient 400 ppm CO₂ up to 400 K and that significant coverage could be retained up to 2000 K
under 1 bar CO\textsubscript{2}. While the overall chemical stability of bulk BaZrO\textsubscript{3} towards CO\textsubscript{2} has been demonstrated\textsuperscript{22,23}, recent studies have shown surface reactivity with CO\textsubscript{2} to form BaCO\textsubscript{3} by accommodating Ba-deficiency in the subsurface region\textsuperscript{23}. Considering the strong adsorption of both H\textsubscript{2}O and CO\textsubscript{2}, 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 H\textsubscript{2}O and CO\textsubscript{2} 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\textsuperscript{24-26}. The plane-wave cut-off energy was 500 eV and the \textit{k}-point sampling was equivalent to 8 x 8 x 8 for the cubic BaZrO\textsubscript{3} 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 x 2 and 3 x 3 expanded slabs (up to 243 atoms), and coadsorbate interaction was evaluated for equal coverages of 0.25 and 0.5 on 2 x 2 slabs, \textit{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, \Delta \text{E}_{\text{ads}}^{\text{int}}\text{ds}, was calculated as the total energy differences of the adsorption reactions. The equilibrium constant of the adsorption reactions was given by

\begin{equation}
K = \exp\left(\frac{-\Delta H_{\text{ads}}^{\text{int}}}{kT}\right)\exp\left(\frac{\Delta S_{\text{ads}}^{\text{int}}}{T}\right)
\end{equation}

where \Delta H_{\text{ads}}^{\text{int}} = \Delta E_{\text{ads}}^{\text{int}}(\Theta_i) + \Delta \text{ZPE}. Bulk parameters including a nominal Y-dopant concentration and surface segregation energies used for the thermodynamic model are listed in Table 1.

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

| Parameter            | Value   |
|----------------------|---------|
| Y-dopant/mol%        | 20      |
| Lattice constant/Å   | 4.214 (DFT) |
| \(\varepsilon\)      | 75 (exp)\textsuperscript{27} |
| \(\Delta H_{\text{hydration}}\)/eV | \(-0.97 \text{ (exp)}\textsuperscript{1}\) |
| \(\Delta S_{\text{hydration}}\)/eV K\textsuperscript{-1} | \(-1.1 \times 10\textsuperscript{-3}\) (exp)\textsuperscript{1}\) |
| \(\Delta E_{\text{ads}}^{\text{int}}\)/eV | \(-0.96\) (DFT)\textsuperscript{19}\) |
| \(\Delta E_{\text{ads}}^{\text{int}}\)/eV | \(-0.42\) (DFT)\textsuperscript{19}\) |

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.\textsuperscript{28} 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 H\textsubscript{2}O adsorbates, CO\textsubscript{2} adsorbates and an interaction term. The energy of the H\textsubscript{2}O/CO\textsubscript{2} adsorption layer without interadsorbate interactions was calculated by

\begin{equation}
E_{\text{ads}} = \Theta_i(\Delta H_{\text{ads}}^{\text{int}} - T\Delta S_{\text{ads}}^{\text{int}} - \Delta \mu_i)
\end{equation}

where \(\Delta \mu_i = kT \ln(p/p^0)\) 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 H\textsubscript{2}O and CO\textsubscript{2} was obtained from the difference in adsorption energy of the coadsorbates and the individual adsorbates (see Table 2), and described as

\begin{equation}
E_{\text{int}}^{\text{H}2\text{O}-\text{CO}2} = 1.72 \Theta_{\text{H}2\text{O}} \Theta_{\text{CO}2}
\end{equation}

when the surface was considered to be neutral, \(\Phi\), \(\Theta_{\text{H}2\text{O}}\), denoting paired surface proton and hydroxide species, OH\textsubscript{ad} and OH\textsubscript{ad}, respectively. For charged surfaces, the concentration of excess surface protons segregated from bulk was defined as \(\Theta_{\text{OH}^+} = \Theta_{\text{OH}^+} - \Theta_{\text{OH}^+}\), when \(\Theta_{\text{OH}^+} > \Theta_{\text{OH}^+}\), and zero otherwise. The \(E_{\text{int}}^{\text{H}2\text{O}-\text{CO}2}\) interaction energy was then described as

Table 2: Energetics for dissociative adsorption of H\textsubscript{2}O and chemisorption of CO\textsubscript{2} on pristine BaO-terminated BaZrO\textsubscript{3} (0 0 1) and parameters describing the interaction between surface species. The coverage dependent adsorption energies were obtained from linear fits with \(R^2 = 0.999\) for CO\textsubscript{2} and \(R^2 = 0.997\) for H\textsubscript{2}O. The linear fit of \(E_{\text{int}}^{\text{H}2\text{O}-\text{CO}2}\) according to eqn (3) showed \(R^2 = 0.999\)

| Species | H\textsubscript{2}O | CO\textsubscript{2} |
|---------|-----------------|-----------------|
| \(\Delta \text{E}_{\text{ads}}\)/eV | \(-1.44 + 0.34 \Theta_{\text{H}2\text{O}}\) | \(-2.52 + 1.21 \Theta_{\text{CO}2}\) |
| \(\Delta \text{ZPE}\)/eV | 0.991 | 0.117 |
| \(\Delta \text{S}_{\text{ads}}\)/eV K\textsuperscript{-1} | \(-6.37 \times 10\textsuperscript{-4}\) | \(-8.78 \times 10\textsuperscript{-4}\) |
| \(\Delta E_{\text{ads}}^{\text{int}}\)/eV | 1.72 \(\Theta_{\text{H}2\text{O}} \Theta_{\text{CO}2}\) |
| \(\Delta E_{\text{ads}}^{\text{int}}\)/eV | \(-0.31\) eV (ref. 21) |

Table 2. Further details can be found in our previous work on the same system.\textsuperscript{20,21}
The total energy of the system, and thus obtain the equilibrium concentrations of surface defects and adsorbates, \( \Theta_{\text{CO}_2}, \Theta_{\text{OH}_0^\text{-}}, \Theta_{\text{OH}_0^\text{ad}}, \) and \( \Theta_{\text{OH}_0^\text{ad}} \), 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

\[
\sum_{i} n_i \Theta_i + \int_{0}^{\phi} q_i c_i \, dx = 0
\]

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 \( \text{H}_2\text{O} \) on the \( \text{BaO}\)-terminated \( \text{BaZrO}_3 \) \((0 \ 0 \ 1)\) surface at coverages from 0.11 to 1 monolayer. The \( \text{H}_2\text{O} \) adsorbate was found to be most stable with surface hydroxide, denoted \( \text{OH}_0^\text{-} \), bridged between two barium, and surface protons, \( \text{OH}_0^\text{ad} \), directed towards the oxide ion of \( \text{OH}_0^\text{ad} \) (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 \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) 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 \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) in the case of half coverage (Fig. 2a). On the other hand, a molecular \( \text{H}_2\text{O} \) adsorbate formed by association between \( \text{OH}_0^\text{ad} \) and \( \text{OH}_0^\text{-} \) on the fully covered surface as shown in Fig. 2b.

The energetics of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) adsorption that comprise the main input from the first-principles calculations to the thermodynamic model are summarized in Table 2. The adsorption energy of \( \text{H}_2\text{O} \) 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.\(^{18}\) Calculations for the \( \text{ZrO}_2\)-terminated surface exhibited similar energies for dissociative adsorption of \( \text{H}_2\text{O} \) in range of \(-1.1 \) to \(-1.4 \) eV.\(^{17,20}\) The adsorption energy of \( \text{CO}_2 \) was more exothermic than that of \( \text{H}_2\text{O} \) 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 \( \text{CO}_2 \) than for \( \text{H}_2\text{O} \) at full coverage.\(^{23}\) The zero-point energy contribution to the adsorption enthalpy was quite small for both \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), which can be ascribed to the rather similar bond relationships for the adsorbed species and gaseous molecules.

The interaction energy between the coadsorbates, \( E_{\text{int, CO}_2} \), 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 \( \text{H}_2\text{O} \) or \( \text{CO}_2 \), and 0.43 eV in the case of coadsorption. It should be noted that the stabilizing interaction

\[
E_{\text{H}_2\text{O}, \text{CO}_2} = 1.72\Theta_{\text{OH}_0^\text{-}}\Theta_{\text{CO}_2} - 0.31\Theta_{\text{OH}_0^\text{ad}}\Theta_{\text{CO}_2}
\]
between CO$_2$$_{ad}$ and OH$^{-}$, $E^{\text{int}}_{H^+\text{-CO}_2}$, only refers to excess OH$^{-}$ since the interaction between OH$^{-}$ and OH$^{-}_{ad}$ is included in the H$_2$O adsorption energy.

Fig. 3 shows the contributions to the overall energy of the BaZr$_{0.8}$Y$_{0.2}$O$_3$ system at equilibrium coverages as a function of temperature at ambient conditions, i.e., 0.01 bar H$_2$O and 400 ppm CO$_2$. The strong adsorption enthalpy of CO$_2$ predominates the stabilization of the system at temperatures below 800 K. Formation of the space-charge layer driven mainly by the segregation of protons also exhibits a significant contribution in this temperature range. Notably, the adsorption of H$_2$O is almost negligible despite the strongly exothermic adsorption of H$_2$O (see Table 2). This can be understood from the comparatively large interaction energy between H$_2$O and CO$_2$, $\Delta E^{\text{int}}_{H_2O\text{-CO}_2}$, combined with the favorable coupling between CO$_2$$_{ad}$ and OH$^{-}$ ($E^{\text{int}}_{H^+\text{-CO}_2}$). The configurational entropy plays an increasingly important role as temperature increases due to the lower coverage and larger number of configurations of the surface species.

The calculated equilibrium coverages of adsorbates and defects are shown as a function of temperature in Fig. 4 including a subsurface space-charge with a corresponding potential. Under 1 bar H$_2$O and 400 ppm CO$_2$, the surface is predominated by protons partly charge compensated by hydroxide, i.e., dissociatively adsorbed H$_2$O and excess OH$^{-}$ 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$^{-}$. The surface remained free of CO$_2$$_{ad}$ despite the strong adsorption enthalpy of CO$_2$ due to the unfavorable $E^{\text{int}}_{H_2O\text{-CO}_2}$ 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 $\Theta_{H_2O}$ and $\Theta_{CO_2}$ (ESI, Section 2†).

By reducing the H$_2$O pressure to 0.01 bar, $\Theta_{CO_2}$ 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 H$_2$O and CO$_2$ pressures of 1 bar, the surface is predominated by carbonate species up to about 1300 K (Fig. 4c).

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**Fig. 1** Dissociatively adsorbed H$_2$O at coverages of (a) 0.11, (b) 0.5 and (c) 1 monolayer of the surface oxide ion sites on BaZrO$_3$ (0 0 1).

**Fig. 2** Coadsorption of H$_2$O and CO$_2$ on BaZrO$_3$ (0 0 1) at total coverages of (a) 0.5 and (b) 1 monolayer.

**Fig. 3** Contributions from gas adsorption, space-charge, surface interactions and configurational entropy to the overall energy of the system at equilibrium coverages on BaZr$_{0.8}$Y$_{0.2}$O$_3$ (0 0 1) per unit cell.
Fig. 4d shows a similar trend with 0.1 bar H₂O where CO₂_ad remains the predominant species over the whole temperature range.

Fig. 5 shows coverage isotherms at 1073 K as function of p\textsubscript{H₂O} and p\textsubscript{CO₂} under 1 bar CO₂ and H₂O, respectively. Under these conditions, the coverage of CO₂ is negligible below 0.01 bar CO₂ (Fig. 5a). From Fig. 5b it becomes apparent that the space-charge potential to a large extent follows the segregation of OH\textsubscript{ad} with a significant contribution above 1 bar H₂O at this temperature. The potential increases with p\textsubscript{H₂O} up to a pressure of 1 bar where OH\textsubscript{ad} increasingly charge compensates the surface protons. Notably, the coverage of OH\textsubscript{ad} exhibits an inverse relationship with that of CO₂ as the coverage of OH\textsubscript{ad} surpasses Q\textsubscript{CO₂} at around 0.5 bar H₂O (Fig. 5b). This behavior can be explained by the unfavorable interaction between CO₂ and OH\textsubscript{ad} (Eq. (4)).

Fig. 6 shows the concerted changes of the surface concentrations and the subsurface space-charge regions under 0.01 bar H₂O and 400 ppm CO₂ 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 (Figure 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 may significantly affect the space-charge properties of BZY surfaces and interfaces. In the present case, equilibration of Y\textsubscript{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 H₂O and 1 bar CO₂ (Fig. S2, ESI Section 3†).
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$^\cdot$/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$^\cdot$/C$_{15}$O partly charge compensated by OH$^\cdot$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$^\cdot$/C$_{15}$O was allowed due to segregation from bulk), a surface potential of 0.68 V was obtained due to a OH$_2$ 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$_{ad}$-CO$_2$$_{ad}$ = 0 eV. In this case, $\Theta$H$_2$O 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. However, Kwon et al. obtained a lower interaction energy between chemisorbed H₂O and CO₂ on BaO (0 0 1) even for a total coverage of 0.5. The apparent difference in $E_{\text{H₂O-CO₂}}$ may be associated with a lower basicity of the BaO-terminated BaZrO₃ surface due to the presence of zirconium, which reduces the capacity for charge transfer to the adsorbates upon chemisorption.

It is interesting to note that the calculated coverage of the OH$_{\text{ad}}$ adsorbate increases with temperature under some conditions (e.g., Fig. 7c), which can seem counterintuitive due to the negative entropy of adsorption. Such behavior of OH$_{\text{ad}}$ 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. However, the calculated space-charge potential becomes less positive at higher temperatures in the present work, and the increased OH$_{\text{ad}}$ coverage may instead be associated with the rather strong adsorbate interactions which become lower as Θ$_{\text{CO₂}}$ decreases.

In terms of the functional properties of Y-doped BaZrO₃ as a proton conducting electrolyte, the present result show that the surface exhibits a high coverage of protons in the form of OH$^-$ under all the considered conditions. The presence of H₂O prevents the formation of a carbonate overlayer which is assumed to be detrimental to both performance and stability. Similar results were recently observed for SrO-terminated SrTiO₃ based on DFT calculations and in situ FTIR analysis, although a relatively less exothermic chemisorption of CO₂ led to generally lower coverages of CO₂. The favorable interaction between surface OH$_{\text{ad}}$ and CO₂$_{\text{ad}}$ (Δ$E_{\text{H₂O-CO₂}}$) 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 BaZrO₃ surface with respect to formation of Ba(OH)$_2$ and BaCO₃, as well as coke deposition.

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 H₂O chemisorption on Y-doped BaZrO₃, the calculated H₂O coverage was quite low due to the more exothermic CO₂ chemisorption and unfavorable interaction between H₂O and CO₂ 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 CO₂ adsorbates. The calculated coverages were found to be significantly affected by the interactions between surface species, in particular between surface protons and CO₂. 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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References

1. K. D. Kreuer, S. Adams, W. Münch, A. Fuchs, U. Klock and J. Maier, Proton Conducting Alkaline Earth Zirconates and Titanates for High Drain Electrochemical Applications, Solid State Ionics, 2001, 145(1–4), 295–306.
2. Y. Yamazaki, R. Hernandez-Sanchez and S. M. Haile, High Total Proton Conductivity in Large-Grained Yttrium-Doped Barium Zirconate, Chem. Mater., 2009, 21(13), 2755–2762.
3. C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almannsouri and R. O’Hayre, Readily Processed Protonic Ceramic Fuel Cells with High Performance at Low Temperatures, Science, 2015, 349(6254), 1321–1326.
4. S. Choi, C. J. Kucharczyk, Y. Liang, X. Zhang, I. Takeuchi, H.-I. Ji and S. M. Haile, Exceptional Power Density and Stability at Intermediate Temperatures in Protonic Ceramic Fuel Cells, Nat. Energy, 2018, 3, 202–210.
5. L. Bi, S. P. Shafi and E. Traversa, Y-Doped BaZrO₃ as a Chemically Stable Electrolyte for Proton-Conducting Solid Oxide Electrolysis Cells (SOECs), J. Mater. Chem. A, 2015, 3, 5815–5819.
6. R. Strandbakke, E. Vøllestad, S. A. Robinson, M.-L. Fontaine and T. Norby, BaO₀.₆GdO₀.₄LaO₀.₄CoO₃₋₀.₆ Infiltrated in Porous BaZrO₀.₇CeO₀.₃Y₀.₃O₃ Backbones as Electrode Material for Proton Ceramic Electronicyltes, J. Electrochem. Soc., 2017, 164(4), F196–F202.
7. H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martínez, D. Beeaff, S. H. Morejudo, P. K. Vestre, T. Norby, R. Haugsrud, J. M. Serra and C. Kjølseth, Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss, Nat. Energy, 2017, 2, 923–931.
8. S. Hamakawa, T. Hibino and H. Iwahara, Electrochemical Methane Coupling Using Protonic Conductors, J. Electrochem. Soc., 1993, 140(2), 459–462.
9. S. H. Morejudo, R. Zanon, S. Escolastico, I. Yuste-Tirados, H. Malerød-Fjeld, P. K. Vestre, W. G. Coors, A. Martinez, T. Norby, J. M. Serra, et al., Direct Conversion of Methane to Aromatics in a Catalytic Co-Ionic Membrane Reactor, Science, 2016, 353(6299), 563–566.
10 Z. A. Feng, C. Balaji Gopal, X. Ye, Z. Guan, B. Jeong, E. Crumlin and W. C. Chueh, Origin of Overpotential-Dependent Surface Dipole at CeO$_2$/Gas Interface during Electrochemical Oxygen Insertion Reactions, *Chem. Mater.*, 2016, 28(17), 6233–6242.

11 A. K. Opitz, A. Nenning, C. Rameshan, M. Kubicek, T. Götsch, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, B. Klötzer, *et al.*, The Surface Chemistry of Perovskite-Type Electrodes during High Temperature CO$_2$ Electrolysis Investigated by Operando Photoelectron Spectroscopy, *ACS Appl. Mater. Interfaces*, 2017, 9(11), 35847–35860.

12 Y.-L. Huang, C. Pellegrinelli, A. Geller, S.-C. Liou, A. Jarry, L. Wang, Y. Yu, H. Bluhm, E. J. Crumlin, K. J. Gaskell, *et al.*, Direct Observation of Enhanced Water and Carbon Dioxide Reactivity on Multivalent Metal Oxides and Their Composites, *Energy Environ. Sci.*, 2017, 919–923.

13 Y.-L. Huang, C. Pellegrinelli and E. D. Wachsman, Oxygen Dissociation Kinetics of Concurrent Heterogeneous Reactions on Metal Oxides, *ACS Catal.*, 2017, 7(9), 5766–5772.

14 C. Duan, R. J. Kee, H. Zhu, C. Karakaya, Y. Chen, S. Ricote, A. Jarry, E. J. Crumlin, D. Hook, R. Braun, *et al.*, Highly Durable, Coking and Sulfur Tolerant, Fuel-Flexible Protonic Ceramic Fuel Cells, *Nature*, 2018, 557(7704), 217–222.

15 K. D. Kreuer, Aspects of the Formation and Mobility of Protonic Charge Carriers and the Stability of Perovskite-Type Oxides, *Solid State Ionics*, 1999, 125(1), 285–302.

16 A. V. Bandura, R. A. Evarestov and D. D. Kuruch, Hybrid HF-DFT Modeling of Monolayer Water Adsorption on (001) Surface of Cubic BaHFO$_3$ and BaZrO$_3$ Crystals, *Surf. Sci.*, 2010, 604(19–20), 1591–1597.

17 R. A. Evarestov and A. V. Bandura, LCAO Calculation of Water Adsorption on [001] Surface of Y-Doped BaZrO$_3$, *Solid State Ionics*, 2011, 188(1), 25–30.

18 F. A. Kröger and H. J. Vink, Relations between the Concentrations of Imperfections in Crystalline Solids, *Solid State Phys.*, 1956, 3(C), 307–435.

19 J.-S. Kim, J.-H. Yang, B.-K. Kim and Y.-C. Kim, Proton Conduction at BaO-Terminated (001) BaZrO$_3$ Surface Using Density Functional Theory, *Solid State Ionics*, 2015, 275, 19–22.

20 J. M. Polfus, T. S. Björheim, T. Norby and R. Bredeesen, Surface Defect Chemistry of Y-Substituted and Hydrated BaZrO$_3$ with Subsurface Space-Charge Regions, *J. Mater. Chem. A*, 2016, 4, 7437–7444.

21 J. M. Polfus, B. Yildiz, H. L. Tuller and R. Bredeessen, Adsorption of CO$_2$ and Facile Carbonate Formation on BaZrO$_3$ Surfaces, *J. Phys. Chem. C*, 2018, 122(1), 307–314.

22 K. H. Ryu and S. M. Haile, Chemical Stability and Proton Conductivity of Doped BaCeO$_3$-BaZrO$_3$ Solid Solutions, *Solid State Ionics*, 1999, 125(1), 355–367.

23 R. Sažinas, C. Bernuy-López, M.-A. Einarsrud and T. Grande, Effect of CO$_2$ Exposure on the Chemical Stability and Mechanical Properties of BaZrO$_3$-Ceramics, *J. Am. Ceram. Soc.*, 2016, 99(11), 3685–3695.

24 P. E. Blöchl, Projector Augmented-Wave Method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, 50(24), 17953–17979.

25 J. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, 77(18), 3865–3868.

26 G. Kresse and D. Joubert, From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, 59(3), 1758–1775.

27 S. Ricote, N. Bonanos, A. Manerbio, N. P. Sullivan and W. G. Coors, Effects of the Fabrication Process on the Grain-Boundary Resistance in BaZr$_{0.9}$Y$_{0.1}$O$_{3-δ}$. *J. Mater. Chem. A*, 2014, 2(38), 16107–16115.

28 D. S. A. Mebane, Variational Approach to Surface Cation Segregation in Mixed Conducting Perovskites, *Comput. Mater. Sci.*, 2014, 103, 231–236.

29 J. M. Polfus, T. Norby and R. Bredeesen, Proton Segregation and Space-Charge at the BaZrO$_3$ (0 0 1)/MgO (0 0 1) Heterointerface, *Solid State Ionics*, 2016, 297, 77–81.

30 M. Tutuianu, O. R. Inderwildi, W. G. Bessler and J. Warnatz, Competitive Adsorption of NO, NO$_2$, CO$_2$, and H$_2$O on BaO(100): A Quantum Chemical Study, *J. Phys. Chem. B*, 2006, 110(35), 17484–17492.

31 S.-C. Kwon, W.-R. Lee, H.-N. Lee, J.-H. Kim and H.-L. Lee, Competitive Adsorption of CO$_2$ and H$_2$O Molecules on the BaO (100) Surface: A First-Principle Study, *Bull. Korean Chem. Soc.*, 2011, 32(3), 988–992.

32 A. Staykov, S. Fukumori, K. Yoshizawa, K. Sato, T. Ishihara and J. Kilner, Interaction of SrO-Terminated SrTiO$_3$ Surface with Oxygen, Carbon Dioxide, and Water, *J. Mater. Chem. A*, 2018, 6, 22662–22672.