Supplementary Information

Interplay between H_2O and CO_2 coadsorption and space-charge on Y-doped $BaZrO_3$ surfaces

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1. Computational details

This section gives a detailed description of the numerical solution scheme for the thermodynamic framework describing the system. The code was developed by the authors using the finite element method for the space-charge layers and implemented in C++. In the manuscript, the energy of the space-charge layer was defined in Eq. 9:

$$E_{\mathrm{sc}} = \int_0^l \left(\sum_i c_i \left(\Delta E_i^{\mathrm{f}} + q_i \phi \right) + \frac{1}{2} \varepsilon \varepsilon_0 \left(\frac{d\phi}{dx} \right)^2 \right) dx$$

The energy terms for the adsorbates and surface defects were defined in Eqs. 2, 4, 5, 6, 10, amounting to:

$$E_{\mathrm{surface}} = E_{\mathrm{CO_2}}^{\mathrm{ads}} + E_{\mathrm{H_2O}}^{\mathrm{ads}} + E_{\mathrm{H_2O-CO_2}}^{\mathrm{int}} + E_{\mathrm{OH_O^\bullet}}^{\mathrm{exc}} + E_{V_{\mathrm{O}}^{\bullet\bullet}}^{\mathrm{seg}} - TS_{\mathrm{config}}$$

The unknown variables were the equilibrium concentrations of surface defects and adsorbates, $\Theta_{\mathrm{CO_2}}$, $\Theta_{\mathrm{OH_O^\bullet}}$ and $\Theta_{\mathrm{OH'_{ad}}}$ and $\Theta_{V_{\mathrm{O}}^{\bullet\bullet}}$, and the surface potential, ϕ_0. The correct solution was defined according to minimization of the total energy of the system, $E_{\mathrm{tot}} = E_{\mathrm{sc}} + E_{\mathrm{surface}}$. The solution scheme for a given temperature and pressure was as follows:

(1) Give an initial guess of ϕ_0.
(2) Solve Poisson's equation (Eq. 7, 8) for the given ϕ_0 using the finite difference method. The result provides a spatial profile of electrostatic potential, $\phi(x)$, and defect concentrations, $c_j(x)$. The total charge of the space charge layer is then obtained according to $Q_{\mathrm{sc}} = \int_0^l q_j c_j \, dx$.

(3) Search for $\Theta_{\mathrm{CO_2}}$, $\Theta_{\mathrm{OH_O^{\bullet}}}$, $\Theta_{\mathrm{OH'_{ad}}}$ and $\Theta_{V_O^{\bullet\bullet}}$ that minimize E_{surface} by the nonlinear conjugate gradient method. Only three variables are independent due to the global charge neutrality constraint in Eq. 11.

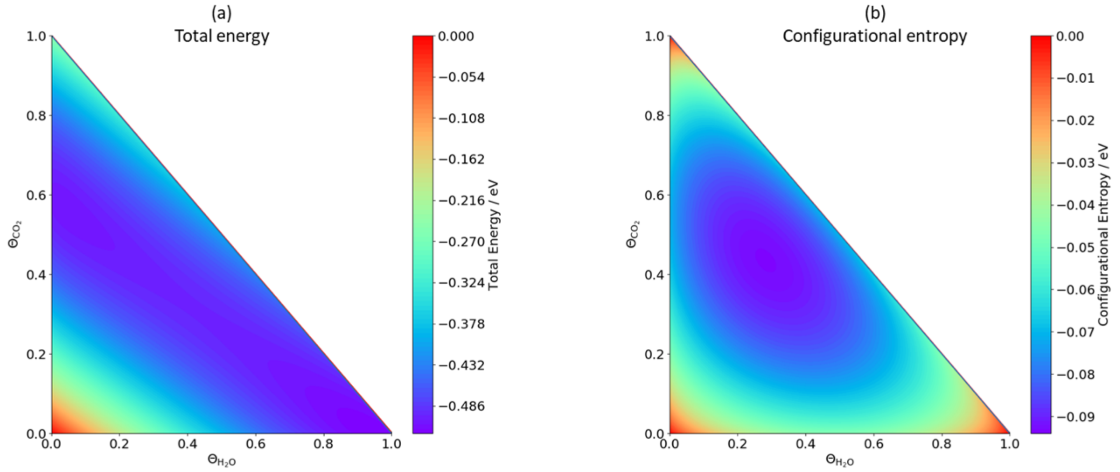
(4) The entire system is solved and E_{tot} is obtained for the given ϕ_0.

(5) Repeat the procedure from step 1 and iterate over a range of ϕ_0 to minimize the total energy of the system.

2. Surface coverage without space-charge

The H_2O and CO_2 coverage as a function of temperature was reported without considering space-charge layers in **Error! Reference source not found.**. In this section, we provide a detailed analysis of the energy terms involved in this model. Without the possibility of space-charge formation, $\mathrm{OH_O^{\bullet}}$ and $\mathrm{OH'_{ad}}$ must be paired to achieve charge neutrality. Thus, there exist only two variables for the system, $\Theta_{\mathrm{H_2O}}$ and $\Theta_{\mathrm{CO_2}}$. The total energy of the system can be described as $E^{\mathrm{tot}} = E^{\mathrm{ads}}_{\mathrm{H_2O}} + E^{\mathrm{ads}}_{\mathrm{CO_2}} + E^{\mathrm{int}}_{\mathrm{H_2O-CO_2}} + S_{\mathrm{config}}$.

Fig. S1 shows contour maps of the energy terms in the two-dimensional space of $\Theta_{\mathrm{H_2O}}$ and $\Theta_{\mathrm{CO_2}}$. The equilibrium coverage is obtained by minimizing the total energy and we can look closer into the three energy terms contributing to the total energy. The configurational energy term is symmetric for $\Theta_{\mathrm{H_2O}}$ and $\Theta_{\mathrm{CO_2}}$ and prefers equal coverage of the two species. However, the magnitude and variation of S_{config} is within 0.1 eV over the entire coverage range, which is the smallest among the three contributions. The adsorption and interaction energy terms predominate in deciding the equilibrium coverage. The lowest energy is obtained on the line of $\Theta_{\mathrm{H_2O}} + \Theta_{\mathrm{CO_2}} = 1$, with a slightly higher share for H_2O due to its more exothermic adsorption energy. This will be the predicted equilibrium coverage if the interaction energy is neglected. However, the quite substantial interaction energy of 1.72 eV between CO_2 and H_2O adsorbates results in a large energy penalty for similar levels of $\Theta_{\mathrm{H_2O}}$ and $\Theta_{\mathrm{CO_2}}$ (Table 2). Looking at Fig. S1d, we see that the interaction term drives the system towards zero coverage of one of the species, resulting in the adsorption isotherm in **Error! Reference source not found.**a.



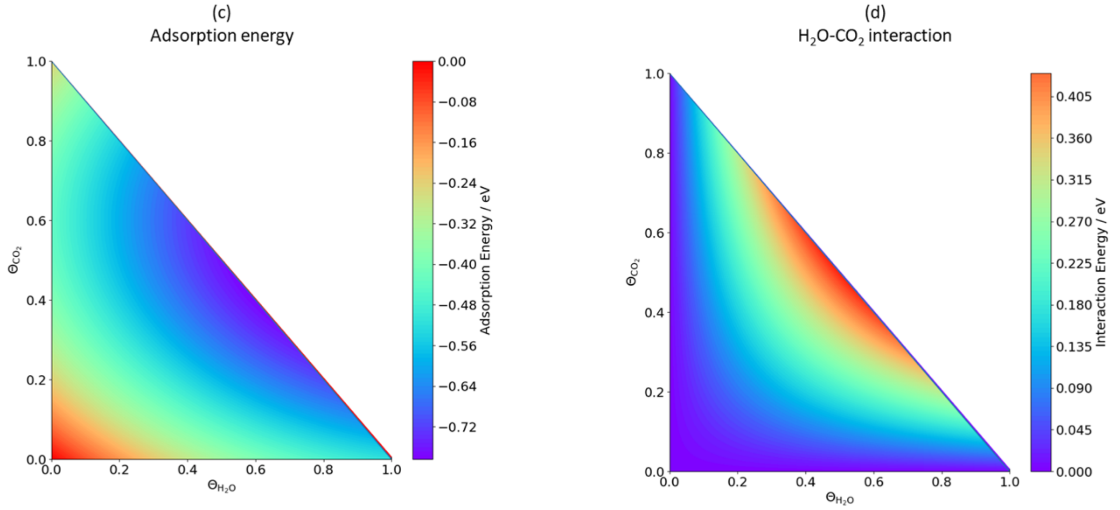


Figure S1: Two-dimensional contour maps with varying H_2O and CO_2 coverage for (a) total energy, (b) configurational entropy, (c) adsorption energy and (d) H_2O-CO_2 interaction energy at 773 K and 1 bar H_2O, 1 bar CO_2.

3. Subsurface space-charge

Figure S2 **Error! Reference source not found.** shows the concentration and potential profiles obtained with the Mott-Schottky and Gouy-Chapman approximations which correspond to a constant and equilibrated Y-acceptor profile, respectively. Under the Gouy-Chapman approximation, the surface concentration of $\mathrm{OH}_\mathrm{O}^\bullet$ was higher due to the increased charge compensation by $\mathrm{Y}_\mathrm{Zr}^\prime$ accumulated in the space-charge (Figure S2b). The resulting space-charge potential of 0.22 V was also slightly higher than under the Mott-Schottky approximation (0.19 V). The segregation profile of $\mathrm{Y}_\mathrm{Zr}^\prime$ will depend on the fabrication procedure and thermal history of the BZY material and can be expected to lie in between the Mott-Schottky and Gouy-Chapman approximations.

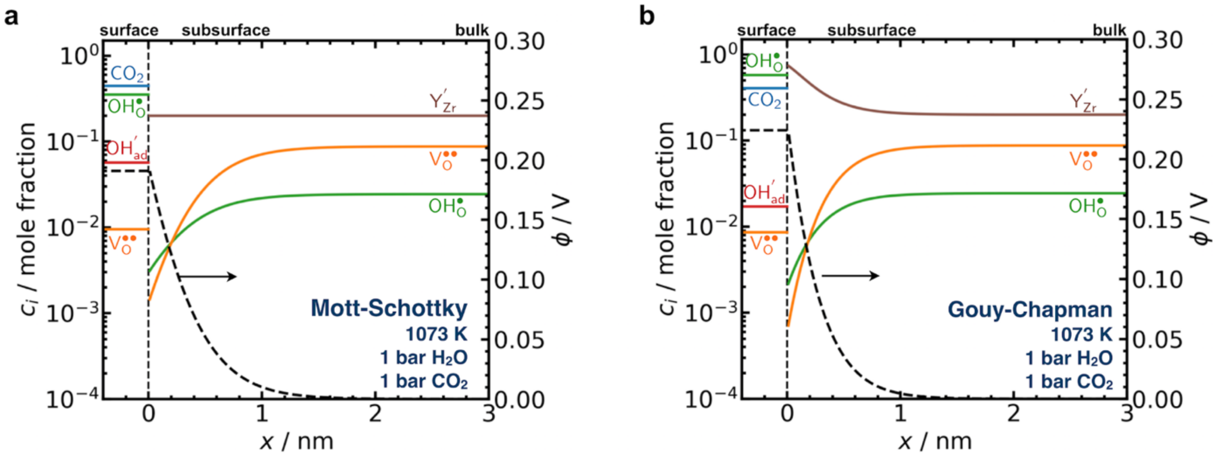


Figure S2: Surface potential and concentration profile of defects and adsorbates from the surface layer on $BaZrO_3$ (0 0 1) (x = 0 nm) into bulk with a fixed Y-acceptor profile (a) and a fully equilibrated Y-profile (b) at 1073 K and 1 bar CO_2 and 1 bar H_2O.