# Importance of oxygen spillover for fuel oxidation on Ni/YSZ anodes in solid oxide fuel cells

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### ABSTRACT

Using the first principle simulations and Monte Carlo method, the optimal structure of triple-phase boundaries (TPB) of the Ni/Yttria-Stabilized Zirconia (YSZ) anode in solid oxide fuel cells (SOFCs) is determined. Based on the new TPB microstructures we reveal different reactions pathways for H<sub>2</sub> and CO oxidations. In contrast to what was believed in previous theoretical studies, we find that the O spillover from YSZ to Ni plays a vital role in electrochemical reactions. The H<sub>2</sub> oxidation reaction can proceed very rapidly, by means of both the H and O spillovers, whereas the CO oxidation can only proceed through the O spillover pathway. Further understanding on the roles of defects and dopants allows us to explain the puzzling experimental observations and to predict the way to improve the catalytic performance of SOFCs.

### I. Model and Computation method

Here we address the details of Monte Carlo (MC) methods in this work: For the  $Ni_{46}/YSZ(111)$  adsorption system, an interface between the large cluster  $Ni_{46}(111)$  and YSZ(111) is constructed in our model. Obviously various possible matching patterns at the joint of two sections should be taken into account, and each of matching

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patterns corresponds to one adsorption configuration, which leads to one special triple-phase boundary (TPB) structure. In MC method, we can use a set of conformational parameters to depict the different matching patterns. The following sketch map can help us understand how the Monte Carlo works.



Various possible interface configurations can be get by the translation along X, Y, Z axis and the rotation of one surface (for example, Surface 1) in the X-Y plane as shown in the sketch map. In this figure the meanings of symbol H, X, Y and  $\Theta$  are listed respectively.

H: The distance between two surfaces constructing the interface;

X: The x coordinate of the center of Surface 1,  $\Delta X$  is used to depict the relative moving of Surface 1 along X-axis;

Y: The y coordinate of the center of Surface 1,  $\Delta Y$  is used to depict the relative moving of Surface 1 along Y-axis;

 $\Theta$ : The angle is used to depict the relative rotation of Surface 1 around the center O'(x, y) in the X-Y plane.

The sequence of random variables (H, X, Y,  $\Theta$ ) constructs a conformational parameter space with four dimensions, and a possible configuration of interface or TPB corresponds to a random point in this four dimensional sample space. In the program the operations of the translation and rotation are carried out by the following transformations of coordinates:

Translations along X, Y, Z axis:

$$\hat{T}x_{\mu} = x_{\mu} + \Delta x \qquad \mu = 1, 2, 3$$

Where the  $x_i$  (x, y z) are the coordinates of one atom in Ni cluster.  $\Delta x_i$  respects the change due to the translation operation.

Rotation in the X-Y plane:

$$\hat{R}^{(O')}\begin{bmatrix}x'\\y'\end{bmatrix} = \begin{bmatrix}\frac{\sin(\alpha-\theta)}{\sin\alpha} & \sin(\alpha-\theta)\cot\alpha - \cos(\alpha-\theta)\\\\\frac{\sin\theta}{\sin\alpha} & \cos\theta + \cot\alpha\sin\theta\end{bmatrix}\begin{bmatrix}x'\\y'\end{bmatrix}$$

Where the O' is the center of the Ni cluster in the X-Y plane, x' and y' are the relative coordinates of any Ni atom to O'.  $\alpha$  is the angle between two basis vectors. For the most simple rectangular coordinate system,  $\alpha$  is equal to 90°, and the matrix is reduced to the usual rotation transformation in two dimensional space. But for (111) surface of the crystal with face-centered cubic structure,  $\alpha$  is equal to 120°, corresponding to an oblique coordinate system, which is just the case in the present work.  $\theta$  represents the rotation angle of the cluster in the X-Y plane, which is regarded as a conformational parameter and corresponds to one random variable.

For each matching pattern determined by ones set of conformational parameters, the number of O-Ni bond at the interface can be calculated. One can determine whether an O-Ni bond is formed by judging whether the distances of Ni atoms and surface O atoms are close to standard O-Ni bond length. Thus, we use the classical Monte Carlo method to screen out the Ni/YSZ adsorption configurations that have large number of O-Ni bonds. For example, we can leave out the structures with less O-Ni bonds and only take those with at least a certain number (N<sub>cutoff</sub>) of O-Ni bonds, where N<sub>cutoff</sub> is a parameter allows to be set at any integer. In this work we consider the configurations with the maximum number of bonds. The interfacial O-Ni bond lengths between Ni(111) and YSZ (111) are set to 2.0  $Å^{1, 2}$  , and the maximum allowable deviation is 0.2 Å in our bonding criterions. In the previous image simulations of high-resolution transmission electron microscopy (HRTEM)<sup>3</sup>, the interlayer distances (H) between the Ni and YSZ were set to be 1.95 Å for the Oterminated YSZ(111) model. Here the H values are sampled in the range from 1.85 to 2.05. The interfacial matching is estimated according to the number of O-Ni bonds. One other thing to note is the calculation for the distance of two atoms in the oblique coordinate system. To this end, we need introduce the metric tensor. In the X-Y plane, the metric tensor is:

$$g^{\mu\nu} = \begin{bmatrix} 1 & \cos \alpha \\ \cos \alpha & 1 \end{bmatrix} \quad \mu, \nu = 1, 2$$

 $\alpha$  is the angle between two basis vectors in X-Y plane. The square of distance is:

$$d^{2} = g^{\mu\nu}\Delta x_{\mu}\Delta x_{\nu} = \Delta x_{1}^{2} + \Delta x_{2}^{2} + 2\Delta x_{1}\Delta x_{2}\cos\alpha$$

where the Einstein summation convention is used. If Z axis is perpendicular to the X-Y plane, the metric tensor in 3D space is:

$$g^{ij} = \begin{bmatrix} 1 & \cos \alpha & 0 \\ \cos \alpha & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad i, j = 1, 2, 3$$

And the square of the distance is:

$$d^{2} = g^{ij} \Delta x_{i} \Delta x_{j} = \Delta x_{1}^{2} + \Delta x_{2}^{2} + \Delta x_{3}^{2} + 2\Delta x_{1} \Delta x_{2} \cos \alpha$$

For the YSZ (111) surface,  $\alpha$  is equal to 120°.

By random sampling to the matching patterns, the adsorption configurations with the maximum bonding numbers can be got according the mentioned criterions. It should be noted that the adsorption structure that satisfy the requirements is usually more than one. However it is found that these configurations can be divided into two categories as shown in the following figures: (a) the Ni atoms at the cluster edges arrange along the <110> orientations on the substrate; (b) the Ni atoms at the cluster edges edges do not arrange along the <110> orientations.



Now we employ the DFT calculations to relax the five representative configurations for category (a) and (b), respectively (ten systems in all are reached in our case), and get the values of adsorption energy for each configurations. Finally, it is found that the adsorption energies of the category (a) are generally lower than those of category (b) by about 2~4 eV, suggesting that Ni atoms at the cluster edges tend to arrange along the <110> orientations on the substrate. Therefore we focus on the adsorption configurations of category (a). If the equivalence of some configurations is considered further, a small number of stable configurations are obtained. In our simulations five nonequivalent adsorption configurations with a high degree of accuracy. The triple-phase boundaries (TPBs) in these systems belong to two types [denoted as type-I and type-II], as have been discussed in detail in the manuscript. In the present work three adsorption structures are studied. The best configuration referred in the text is just the adsorption system with the lowest adsorption energy among these systems. This configuration is assumed to the most stable adsorption structures.

#### II. Additional calculations



Fig. S1 The energy profile along the H spillover from the Ni part to the interface O atom with a hydroxyl formed in the Ni/YSZ(111) system. The left and right inset is the initial and final states, respectively.



Fig. S2 The initial and final state of the O spillover process in the Ni/YSZ(111) system with an interface O vacancy, which is signed by the yellow transparent ball. These two pictures display the initial and final state of the blue dashed curve in Fig. 2.



Fig. S3 The initial and final state of the O spillover process in the Ni doped Ni/YSZ(111) system. These two pictures display the initial and final state of the blue thin curve in Fig. 2. Here the Ni diffusion into YSZ at the interface is taken into account with a dopant Ni replaced an O atom near the TPB.



Fig. S4 The sketch of energy profile for CO spillover from Ni part to YSZ. The black horizontal lines represent the initial, intermediate and final states, respectively, and red horizontal lines represent the supposed transition states. The minimum energy barriers are determined from the reaction heat.



Fig. S5

Fig. S5 The stable adsorption site of H and CO next to the interface. CO can not be adsorbed at the hollow site A due to the repulsion between CO and the active interface O, while the H atom can be adsorbed at the A site due to its small size.

## Reference

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