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Atomic structure observations and reaction dynamics simulations on triple phase boundaries in solid-oxide fuel cells

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The triple phase boundary (TPB) of metal, oxide, and gas phases in the anode of solid oxide fuel cells plays an important role in determining their performance. Here we explore the TPB structures from two aspects: atomic-resolution microscopy observation and reaction dynamics simulation. Experimentally, two distinct structures are found with different contact angles of metal/oxide interfaces, metal surfaces, and pore opening sizes, which have not previously been adopted in simulations. Reaction dynamics simulations are performed using realistic models for the hydrogen oxidation reaction (HOR) at the TPB, based on extensive development of reactive force field parameters. As a result, the activity of different structures towards HOR is clarified, and a higher activity is obtained on the TPB with smaller pore opening size. Three HOR pathways are identified: two types of hydrogen diffusion processes, and one type of oxygen migration process which is a new pathway.

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Among several types of fuel cells, the solid oxide fuel cell (SOFC) has the highest efficiency and could utilize various fuels¹. The anode materials in SOFC are typically based on porous composites of Ni with oxides such as yttria-stabilized zirconia (YSZ) or doped ceria^{1,2}. Linking the complex porous structure to the cell performance is a critical issue for the development of SOFC. Realistic three-dimensional (3D) microstructures were obtained after the introduction of focused ion beam-scanning electron microscopy (FIB-SEM) technique to the field of SOFC^{3–6}. Meanwhile, numerical modeling of porous electrode characteristics has been extended from two-dimensional^{7,8} to 3D with the development of simulation methods, such as the lattice Boltzmann method^{8,9} and phase-field method¹⁰. Microscopically, the most important location related to the SOFC performance is the triple phase boundary (TPB), where the fuels are electrochemically oxidized¹¹. The TPB structure and its local chemical environment determine the thermodynamics and kinetics of the electrochemical reaction.

Numerous works have been conducted to understand the local activity and reaction mechanism at the TPB. Patterned anodes were fabricated as ideal models to allow easy evaluation of the relationship between the TPB length and electrochemical characteristics^{12–15} and to develop kinetic modeling methods^{14–19}. However, both the experimental characteristics and modeling results show large variation among different reports^{20,21}. For example, the current densities normalized by TPB length²¹ obtained by Bieberle et al.¹³ and Yao et al.¹⁵ are about three orders of magnitude higher compared to those by Mizusaki et al.¹² while different rate-determining steps were reported, respectively, in those works including either H₂ adsorption/desorption on Ni surface or removal of O^{2–} from the YSZ surface¹³, charge transfer reactions coupled with H₂O-related process¹⁵, and Ni surface hydrogen oxidation¹². First-principles calculations were also applied to the TPB, nevertheless the deduced mechanism and estimated energy barriers differ significantly even when using similar structural models^{22–26}. Recently, Liu et al.²¹ analyzed those deviations and pointed out the significant importance of elementary processes directly related to TPB at the atomic level. This encouraged us to trace the elementary reaction mechanism at TPB more carefully. Meanwhile, a reactive force field (ReaxFF) method has been developed to model the Ni/YSZ/pore TPB and deduce the hydrogen oxidation mechanism²⁷. However, the Ni surface amorphization and Ni decohesion from YSZ are observed at 1250 K, which, we believe, may be due to a lack in the model stability or parameter reliability.

The TPB strongly affects the properties (including electrocatalysis) of various supported metal catalysts. Owing to their small sizes and easier handlings for observation, the atomic structures of TPB in nano-catalysts, such as Ni/MgAl₂O₄²⁸, Pd/CeO₂²⁹, Pt/SnO₂³⁰, and Au/γ-Fe₂O₃³¹ have been determined using transmission electron microscopy (TEM) or scanning TEM (STEM). In contrast, Ni/YSZ cermet in conventional SOFC is a bulk composite material whose particle size ranges from the submicrometer to micrometer. Its complex microstructure is challenging for the TEM specimen preparation³². Thus there has been no report on the atomic structure of TPBs in a practical cell, while significant experimental attention has been paid to the interfacial structures of Ni/YSZ^{33–37}.

Considering the above-mentioned problems and difficulties in the atomic-scale researches on the TPB of SOFC, herein we report our experimental observations of realistic atomic TPB structures. In addition, we develop ReaxFF for TPB. Based on the obtained results, we computationally deduce the reaction mechanism therein. Two atomic structures of TPB, different from the models used in previous theoretical calculations, are introduced in this work. Overall, our reactive molecular dynamics (MD) simulations

show that the hydrogen oxidation reaction (HOR) mechanism is notably influenced by the TPB models. Additionally, we find that the HOR can proceed through a newly discovered reaction pathway.

Results

TPB structure observation. In this work, the Ni/YSZ anode was fabricated through conventional processes³⁸. For the microscopy observation, the pores in Ni/YSZ were infiltrated with epoxy resin. The TEM specimens were extracted from the resin-embedded bulk sample by the lift-out technique using an FIB-SEM and thinned by gallium ion beam with a final voltage as low as 3 kV. In order to remove the damaged layers and the redeposition on the surfaces as much as possible, post-FIB processing was conducted using an Ar ion-milling machine with low voltages from 900 to 600 V³⁹. Even after such mild procedure, some TPB areas were damaged by the ion beam because the sputtering rate of resin was higher than that of the anode materials.

Before showing the observed structures of TPB, we defined three angle parameters for the TPB. As shown in Supplementary Fig. 1, θ_{Ni} , the so-called contact angle in metal/ceramic material, is the dihedral angle between the Ni/pore and Ni/YSZ boundaries taking ceramic as the substrate. θ_{YSZ} and θ_{pore} are defined in a similar way. Owing to the poor wettability between metallic Ni and ceramic YSZ, θ_{Ni} was evaluated by Nelson et al. to be in the range of 140°–155°, based on 3D reconstruction⁴⁰. Large values of θ_{Ni} were also observed in our sample (Supplementary Fig. 2). The value of θ_{YSZ} falls into two main cases if we restrict the spatial scale to several nanometers around the TPB. One is when YSZ acts as a flat substrate to the Ni particle ($\theta_{\text{YSZ}} = 180^\circ$, Supplementary Fig. 1a), which corresponds to a small pore opening size (θ_{pore}) and is the dominant case in Supplementary Fig. 2. If the above-mentioned statistical values of θ_{Ni} are adopted⁴⁰, θ_{pore} should be in the range of 25°–40°. In the other case, YSZ does not extend in a straight way from the Ni/YSZ interface to the TPB area, and θ_{YSZ} is much smaller than 180° (Supplementary Fig. 1b), thereby a big pore opening size (θ_{pore}) is obtained with a value usually exceeding 90° as pointed out by red arrows in Supplementary Fig. 2. Hereafter, these two TPB structures will be referred to as TPB-1 and TPB-2 types, respectively.

TPB-1 has a small θ_{pore} , and one such example is indicated by the yellow arrow in Supplementary Fig. 2. The TEM observation was conducted in two directions of YSZ: the [013] and [001] zone axes, which have an included angle of 18.4°. The corresponding orientation relationships between Ni and YSZ are Ni[123]//YSZ[013] (Supplementary Fig. 3) and Ni[110]//YSZ[001] (Supplementary Fig. 4), respectively. The abrupt Ni/YSZ and resin/YSZ interfaces were maintained after rotation (Fig. 1a, b), which indicates that they were always parallel to the observation directions. However, the Ni/resin interface (Ni surface) shows an apparent slope (marked by an arrow in Fig. 1a), which becomes abrupt in Fig. 1b. This phenomenon indicates that only the latter observation direction was parallel to the Ni surface. The contact angle between Ni and YSZ (θ_{Ni}) was measured from Fig. 1b to be 145°, which is in good agreement with the previously reported values⁴⁰. Herein, θ_{pore} equals the supplementary angle of θ_{Ni} , namely 35°.

The high-resolution TEM (HRTEM) image at the YSZ[013] zone axis is shown in Fig. 1c. The YSZ(200) plane is exposed to the gas phase and in contact with the Ni(111) plane. Along the Ni/YSZ interface, small steps could be detected that appeared blurred owing to the lattice overlap, as shown in Supplementary Fig. 5. The “steps” are where the Ni and YSZ are not perfectly parallel along the TEM observation direction or in the image plane. They are believed to be a part of the interfacial migration process that has been previously observed in NiO/YSZ⁴¹ and Ni/

Fig. 1 Atomic structure of triple phase boundary-1. **a** Low-magnification transmission electron microscopy (TEM) image at YSZ[013] zone axis. The arrow in **a** points out the slope feature of Ni surface in this observation direction. **b** Low-magnification high-angle annular dark-field-scanning TEM (HAADF-STEM) image at YSZ[001] zone axis. The dash arc in **b** stands for the contact angle (θ_{Ni}). **c** High-resolution TEM image at YSZ[013] zone axis. The arrow in **c** denotes a pore after electron beam damage of the resin. **d** HAADF-STEM image at YSZ[001] zone axis. The arrow in **d** points to a thin layer of NiO on the Ni surface. Scale bars in **a**, **b**: 50 nm; in **c**, **d**: 1 nm

YSZ⁴² as well as other metal–ceramic systems such as Ag/ZnO⁴³ and Cu/MgO⁴⁴. During the baking and reduction processes of NiO/YSZ, the interfacial layers of both Ni(O) and YSZ are expected to migrate due to many factors, such as thermal expansion, lattice shrinkage during reduction, lattice misfit, oxygen bonds change, etc. The migration of Ni, O, and Zr(Y) should proceed toward thermodynamic equilibrium. The interfacial distance between the contacting Ni and YSZ layers was measured to be 0.238 nm from the HRTEM image after background filtering (Supplementary Fig. 5). This value is intermediate to the lattice distances of Ni(111) and YSZ(200) planes and close to the reported value of 0.244 nm for a metal–metal (Ni–Zr) featured interconnection³³ that was observed in a Ni/YSZ specimen having the same orientation as

TPB-1 and prepared by the reduction/ion milling procedures similar to those adopted in the present study. Namely, the oxygen tends to be lost from the Ni/YSZ interface in TPB-1, and we attribute this to the NiO reduction process rather than the ion damage during FIB preparation. The final voltage adopted by us in FIB is 3 kV, which will cause a damage depth of around 5 nm if the milled material is silicon⁴⁵. Furthermore, we adopted low voltage post-polishing by using Ar ion during the cooling with liquid nitrogen. This process removed most of the damaged layers on the specimen surfaces, especially the non-resin areas. All those procedures resulted in a damaged layer of merely <3 nm, judging from the Ni or YSZ surfaces in Fig. 1 and Supplementary Fig. 6. The specimen is estimated to have a thickness of about 70 nm near the Ni surface (resin) according to the geometrical parameters of the slope in Fig. 1a and the known angles. Therefore, the thin damaged layer on the surface will not change the whole structure of the specimen. Actually, O loss from the Ni/YSZ interface is not surprising because the anode was reduced under a 2% humidified hydrogen environment. Reportedly, O–Ni and Zr–Ni bonds are energetically favorable³⁵ and the O content at the interface may change with its partial pressure in the gas³⁶. Thus the O content at the Ni/YSZ interface in TPB-1 is expected to be augmented with increasing oxygen partial pressure in the atmosphere.

When the YSZ zone axis is changed to [001], the Ni surface can be indexed to (220) as shown in Fig. 1d. Actually, the dihedral angle between Ni(220) and Ni(111) planes in a single crystal is 35°, which is identical to θ_{pore} and confirms that the Ni surface facing the pore is the Ni(220) plane. Partial oxidation was found on the Ni surface (as pointed out by an arrow in Fig. 1d) but not at the TPB. Because of the damaged layers and thickness difference between the grain edges and bulk, the STEM contrast was weakened. We also found another region of interest with the same orientation and configuration as the one shown in Fig. 1d. In fact, its HRTEM image (Supplementary Fig. 6) exhibits the ion damage on the surfaces more clearly and supports the facet index. Therefore, we obtained the atomic structure near TPB, showing the Ni(220) and YSZ(200) surfaces to the pore at an interfacial orientation of Ni[110]/YSZ[001] and Ni(111)/YSZ(200). The same oriented interfacial structure was observed in the Ni/YSZ samples prepared by directionally solidified eutectics³³ and molecular beam epitaxy³⁴. This is, in fact, one of the most stable interfaces found in Ni/YSZ cermet³⁷.

Clear TEM images on TPB-2 were obtained from a specimen shown in Fig. 2 and Supplementary Fig. 7 with different magnifications. Apparently, this TPB has a larger θ_{pore} than that in TPB-1. An HRTEM image (Fig. 2b) was taken at the Ni[112] zone axis. It was found that YSZ is close to the [001] zone axis, which can be seen more clearly from the diffraction patterns in Supplementary Fig. 7. The Ni(111) and YSZ(020) planes exposed to the resin (pore) and YSZ(200) planes act as one of the contact surfaces at the Ni/YSZ interface. θ_{Ni} and θ_{pore} were measured to be 167° and 103° from the dihedral angles between Ni(111) and YSZ(200) and between Ni(111) and YSZ(020), respectively. Hence, θ_{pore} in TPB-2 is about two times larger than that in TPB-1. The Ni(220) planes display a dihedral angle of 76.8° to the Ni/YSZ interface. These planes show a lattice misfit of merely 0.4%, relative to the YSZ(020) plane, when taking into consideration that two layers of Ni(220) planes match with one layer of YSZ(020) plane. Such a good match would stabilize the interface, although the contact surface of Ni phase was estimated to be a high-index (957) plane. Previously, we have reported other high-index interfaces that ubiquitously exist in the conventional Ni/YSZ anode³⁷. Later in this study, we will compare the structures of TPB-2 and TPB-1 in terms of their HOR activity.

Fig. 2 Atomic structure of triple phase boundary-2. **a** Low-magnification transmission electron microscopy (TEM) image. **b** High-resolution TEM image at Ni[112] zone axis. Scale bars in **a**, **b**: 100 and 1 nm, respectively

Fig. 3 Interaction energies and angle-energy curves. **a** H-O-H angle energy as a function of angle (θ). **b** YSZ(111) (Y-site)-H₂ interaction energy. **c** Ni(220)-H₂ interaction energy. **d** Ni(111)-YSZ(111) interaction energy. **b-d** are plotted as a function of distance (r). The interaction energy and angle energy are expressed as relative to the equilibrium structure, through single-point energy calculations by changing (r) and (θ). The insets show the models that are used for the energy calculation. Balls represent hydrogen (H), oxygen (O), zirconium (Zr), yttrium (Y), and nickel (Ni) atoms. YSZ(111) slab with 3-layer Zr/Y and 6-layer O is used in **b** and the entire structure is shown in **d**

Force field development. In order to perform reliable calculation for the Ni/YSZ/H₂ systems, we optimized the parameters adopted in the previously published ReaxFF descriptions of Ni and YSZ^{27,46,47}. POTFIT⁴⁸ code, combined with LAMMPS⁴⁹, was used to determine the new ReaxFF parameters for H-O-H, YSZ-H₂, Ni-H₂, Ni-H, Ni-YSZ, and O-O interactions, together with 24 additional energy values corresponding to the intermediate energy profiles of the HOR at TPB. The parameters were optimized to fit an extensive set of interaction energies in the Ni/YSZ/H₂ systems, and the fitting results are shown in Fig. 3 and Supplementary Figs. 8–12. Figure 3a shows that the H-O-H equilibrium angle of the published ReaxFF has a deviation of about 4° compared with that of the first-principles results, whereas our developed ReaxFF shows only 1°. For the published ReaxFF, the energy of

nondissociative adsorption of H₂ on YSZ(Y-site) is overestimated by 64% in comparison with the first-principles data (Fig. 3b), whereas the overestimation obtained with our developed ReaxFF is reduced to 33%. Also, it is shown in Fig. 3c that the discrepancy of 0.6 Å obtained for the equilibrium Ni-H₂ distance using the published ReaxFF has been eliminated with our ReaxFF. As shown in Fig. 3d, the magnitude of the interaction energy of Ni-YSZ interface at the equilibrium distance is underestimated by 86% with the published ReaxFF, while the underestimation is only 9% by using our ReaxFF. In summary, our developed ReaxFF parameters can reproduce the results of the first-principle calculations with much higher accuracy than the published ReaxFF²⁷. More details on the way we evaluate the deviations between ReaxFF simulations and first-principles calculations can be found in Supplementary Notes 1,

while the higher accuracy of the developed ReaxFF can be further proved by the comparison data in Table 1 and Supplementary Tables 1–11. In addition, the interactions of H-O-H, YSZ-H₂, Ni-H₂, Ni-H, Ni-YSZ, and O-O are described in Supplementary Notes 2–6 and the energies for the HOR are described in Supplementary Note 7.

TPB modeling and TEM image simulation. Based on the observed images, the initial atomic models were built in Material Studio by taking into account the actual lattice distances and crystal orientations. In an effort to validate the initial models, the QSTEM⁵⁰ software was used to simulate the TEM images by the multislice method. The observed and simulated images as well as the model for TPB-1 are shown in Fig. 4a, b, d. For TPB-1, there was a good agreement between the simulated (Fig. 4b) and observed (Fig. 4a) images, except for the possible thinning and damage of Ni and YSZ surfaces in Fig. 4a. To clarify the interfacial distance between Ni and YSZ, we superimposed the model on the experimental image in Fig. 4c. In the experimental image, it was difficult to determine the exact TPB region. Therefore, we constructed two more models by increasing the number of Ni layers toward the gas phase, resulting in different interfacial distances of 1.9, 1.8, and 1.7 Å between Ni and O at the TPB region, hereafter referred to, respectively, as model-1 (Fig. 4 and Supplementary Fig. 13a), model-2 (Supplementary Fig. 13b), and

model-3 (Supplementary Fig. 13c). The model of TPB-2 will be illustrated in a later section.

Reaction dynamics. Before simulating the reaction dynamics, we optimized the structures of TPB-1 by adding hydrogen (H) atoms at randomly selected atop sites of Ni surfaces. To investigate the hydrogen oxidation process, we prepared the model with adsorbed H assuming that the adsorption is sufficiently fast and is in equilibrium. The surface coverage of H is predicted to be 7%, which is the maximum coverage under the conditions of 1073 K and 1 atm with 100% H₂ following the reported calculation method⁵¹. After the optimization, H atom on the Ni(220) surface is found to be at the long bridge site.

For model-1, a single pathway was observed during the simulation as shown in Fig. 5a. In particular, H moved on the Ni (220) surface to react with O at the TPB site, resulting in the formation of OH (see the series of snapshots in Supplementary Fig. 14). This pathway is noted herein as HOR-I, which was reported by Vogler et al.¹⁸ using kinetic modeling and defined as an H spillover process. Subsequently, in their density functional theory (DFT) calculations Shishikin et al.²², Cucinotta et al.²³, and Liu et al.²⁶ concluded that the H spillover process is the most favorable pathway. Liu et al. also found that the reaction barrier of this process varies from 0.46 to 0.57 eV depending on the local structures of TPB sites. This process was also identified by employing ReaxFF-MD simulations²⁷. For our simulation, a total of 3 OH species were formed after 700 ps. One of them moved to the YSZ surface near TPB with the distances of 2.7 and 2.1 Å from the nearest Ni and Zr atoms, respectively. The other two OH species gradually moved toward the Ni(220) surface sites, which was specified as the OH spillover or back-transfer in the kinetic study by Goodwin et al.¹⁹. In contrast, the OH spillover process was not favorable according to the above-mentioned DFT calculations^{22,23,26}, while it was not perceived in the ReaxFF-MD simulations²⁷.

Two other HOR pathways were observed on model-2 during the simulation. One pathway is dominated by H atom incorporation into the interstitial site of the Ni lattice and diffusion to the interface between Ni and YSZ. In this case, H eventually combines with O at the Ni/YSZ interface to form OH.

ReaxFF	MAD ^a	MSD ^b	STD ^c
Published (eV)	0.59	1.00	0.81
This work (eV)	0.18	0.17	0.37

Each deviation was calculated by the collections of 24 HOR energies and the interaction energies of H-O-H, YSZ (three sites)-H₂, Ni-H₂, Ni-H, Ni-YSZ, and O-O ReaxFF reactive force field

^aMean absolute deviation (MAD) = $\frac{\sum |E_{\text{ReaxFF}} - E_{\text{FP}}|}{n}$

^bMean square deviation (MSD) = $\frac{\sum (E_{\text{ReaxFF}} - E_{\text{FP}})^2}{n}$

^cStandard deviation (STD) = $\sqrt{\frac{\sum ((E_{\text{ReaxFF}} - E_{\text{FP}}) - (MAD))^2}{n}}$

where E_{FP} and E_{ReaxFF} are the energies obtained from first-principles calculations and ReaxFF simulations, respectively, and n is the number of data points

Fig. 4 Model structures of triple phase boundary-1. **a** Experimental image. **b** Simulated image by using the QSTEM software. **c** Atomistic model imposed on the experimental image. **d** Atomistic model containing Ni (1770 atoms) and YSZ (Zr₁₀₀Y₂₀₀O₂₅₀₀, 8 mol% of yttria)

Fig. 5 Reaction dynamics simulations for triple phase boundary-1. **a** Hydrogen oxidation reaction (HOR)-I pathway. **b** HOR-II pathway. The trajectory of hydrogen (H) starts from the arrow, and the circle denotes the final position where OH species is formed after a simulation period of 700 ps. The local environment near the formed OH species is presented in the magnified image, which is linked to the circle by dotted lines. **c** HOR-III pathway. A trajectory of oxygen (O) starts from the arrow, and the circle denotes the final position where OH species is formed after a simulation period of 700 ps. The local environment near the formed OH species is presented in the magnified image, which is linked to the circle by dotted lines. Trajectories are shown along the Ni[110] and YSZ[001] directions

This pathway was labeled as HOR-II (Fig. 5b), which has been discussed theoretically by Weng et al.⁵². They concluded that a barrier of 0.89 eV needs to be overcome for H diffusion through the Ni bulk, while the surface diffusion barrier is only 0.1 eV. Nevertheless, experiments have proved the enhanced H diffusion and absorption in Ni lattice at high temperatures^{53,54}. Another pathway, which is referred to as HOR-III, is associated with O atom migration from YSZ to the Ni(220) surface through the Ni bulk to react with H on Ni surface to form OH. A trajectory of O together with the snapshot of the formed OH is shown in Fig. 5c. A series of snapshots with time for HOR-II and HOR-III are provided in Supplementary Fig. 14. To validate the determined ReaxFF parameters for O migration into the Ni bulk, we calculated the NiO formation energy to be -0.8 eV, which is in reasonable agreement with the first-principles calculation result (-1.0 eV)⁵⁵. Besides, we did not observe O migration into the Ni bulk during optimization (see Supplementary Fig. 15). This result supports the fact that O migration in Ni can occur at certain two-

Table 2 Normalized average production of OH

TPB-1 ($\text{\AA}^{-1}$)			TPB-2 ($\text{\AA}^{-1}$)
Model-1	Model-2	Model-3	0.0035
0.0075	0.0041	0.0029	
TPB triple phase boundary			

phase interfaces like TPB-1 under high temperature (see Supplementary Fig. 16). Experimentally, O migration through the Ni bulk had been reported for Ce-Zr oxide-supported Ni catalyst⁵⁶.

For model-3, two OH species are formed. One of them is formed through the HOR-III pathway and remains on the Ni surface site. The other OH, formed via HOR-I, is found to be 2.88 and 2.0 Å away from the nearest Ni and Zr, respectively.

In short, we observed three pathways for the formation of OH in HOR after the above simulations on TPB-1, namely, HOR-I (H diffusion on Ni surface toward TPB), HOR-II (H diffusion through Ni bulk to Ni/YSZ interface), and HOR-III (O migration from YSZ to Ni surface through bulk transfer).

For TPB-2 (Fig. 2b), the YSZ phase was not at the exact [001] zone axis. However, we adopted an ideal YSZ[001] model to represent the observed TPB structure for simplicity, and the model is presented in Supplementary Fig. 17. It should be noted that, owing to the high index (957) of the Ni surface, it is not worthy to increase the number of YSZ(020) layers toward the gas phase, as it may lead to improper contact between them at the TPB region. Therefore, we constructed only one model instead. After optimization, the H atom was located at the fcc site of Ni (111) surface. In this simulation, a single OH is formed through the HOR-I pathway. A trajectory of H is also shown in Supplementary Fig. 17. Note that the OH remains at TPB, having distances of 1.7 and 2.3 Å from the nearest Ni and Zr, respectively. The other two pathways (HOR-II and HOR-III) may also occur, because O and H migration into the Ni bulk is detected (Supplementary Fig. 18), indicating the relatively low activity of HOR through those processes compared to TPB-1.

In order to clarify the impact of the TPB structures as well as the different reaction pathways, we repeated all calculations six more times by changing the H positions on the Ni surface. The resulting time-averaged number of OH normalized by the TPB length is summarized in Table 2. It is calculated as $(\sum N_{\text{OH}} dt/t)/l$, where N_{OH} is the number of OH while dt , t , and l indicate the time step between frames, the total simulation time, and TPB length, respectively. The TPB lengths of TPB-1 and TPB-2 are 27.167 and 27.170 Å, respectively, which are almost the same. From TPB-1, the OH formations through the HOR-I pathway were found as nine, four, and five times during the simulations using model-1, model-2, and model-3, respectively. In addition, only one OH formation through the HOR-II pathway was observed in simulations using either model-1 or model-3, while model-2 exhibited three OH formations. Finally, the HOR-III pathway was not detected in model-1, whereas simulations using model-2 and model-3 displayed OH formation through the HOR-III pathway once and twice, respectively. By contrast, the TPB-2 simulations showed four and one OH formations via the HOR-I and HOR-III pathways, respectively. Therefore, our simulations indicate that TPB-1 was more active than TPB-2 and that the activity at TPB-1 was influenced by the different interfacial distances between Ni and O. The HOR-I pathway seems to be the easiest pathway regardless of the models, and this agrees well with many studies using DFT calculations^{22,23,26}.

Apart from the HOR pathways observed in this study, an O spillover process, namely O migration from YSZ to Ni surface leading to the formation of OH, was previously reported by using kinetic modeling method^{16,57,58}. Later, this process was examined by Ammal et al.²⁴ through DFT calculations and found to dominate over the H migration pathway. Fu et al. also investigated the O spillover process, coexisting with the H spillover process²⁵. From our dynamics simulations, it can be concluded that the number of O migration was limited: for TPB-1 (model-1) four O atoms migrate, while only one O atom migrates during the simulation using TPB-2. Liu et al. also pointed out the importance of this process for the higher activity based on a kinetic study²¹. Therefore, it is indicated that the TPB-1 structure is favorable compared to TPB-2, while the relatively slow kinetics does not lead to the formation of OH species.

Finally, we did not observe H₂O formation during the simulations. This may be due to the rate-limiting step of the OH + H reaction, as well as the limited number of H atoms, the consumption of H atoms because of OH formation, or limited simulation time. DFT calculations^{22,23,26}, ReaxFF-MD²⁷, and kinetic modeling¹⁸ have concluded that H₂O is formed near the TPB for HOR-I, while Goodwin et al. reported H₂O formation on the Ni surface site¹⁹. In this study, MD simulations indicated that all pathways are possible for H₂O formation.

Discussion

The motivation of this work is to understand the TPB on an atomic scale and simulate the HOR process on realistic models. First, we fabricated a conventional Ni/YSZ half-cell, and then we prepared high-quality TEM specimens through an FIB lift-out technique and moderate post-polishing. Finally, the TPB structures were observed by TEM and STEM, through which the visualization of the real atomic structure of TPB to the best of our knowledge is realized for the first time. Herein we demonstrated the existence of two TPB structures (TPB-1 and TPB-2), which are different from the structures assumed in the reported simulations. In TPB-1, Ni and YSZ formed a stable interface with an orientation of Ni[110]/YSZ[001] and Ni(111)/YSZ(200), and the Ni(220) and YSZ(200) surfaces were open to the pore. Near TPB-2, the Ni/YSZ interface was Ni(957)/YSZ(200) while Ni(111) and YSZ(020) were exposed to the pore. In these two structures, the angle (θ_{pore}) between the Ni and YSZ surfaces was very different, being 35° and 103°, respectively.

After constructing models based on these realistic structures, we carried out ReaxFF simulations. In order to obtain reliable simulation data, we began with extensive development of ReaxFF parameters for Ni/YSZ/H₂ systems to clarify the HOR at TPB. Compared to the results of first-principles calculations, our developed ReaxFF parameters produced much smaller average energy deviations that are only about one third of those obtained from published ReaxFF parameters as shown in Table 1.

Using our own ReaxFF parameters and realistic models, three pathways for OH formation in HOR were observed during the reaction dynamics simulations: HOR-I (H diffusion on Ni surface toward TPB), HOR-II (H diffusion through Ni bulk to Ni/YSZ interface), and a new pathway HOR-III (O migration from YSZ to Ni surface through bulk transfer). Besides, the migration process of H and O was influenced by the TPB structures. The TPB-1 type structure was also found to be more active compared to TPB-2. Moreover, it was predicted that H₂O may form at distinct sites on account of the OH back-transfer process. Our simulation results on the three models of TPB-1 and one model of TPB-2 indicate that the HOR pathway depends on many factors around the TPB, and it could be tuned by adjusting the local

atomic structures. This finding agrees well with a recent study of dopant effect on HOR pathway, which changes with different cation dopants on ZrO₂⁵⁹. In addition, there are many more reports on surface pathways like HOR-I than on the bulk pathways including HOR-II and HOR-III observed in our simulation. Therefore, we propose that more studies should be carried out both theoretically and experimentally on the bulk pathways.

Finally, we would like to correlate our results to the anode performance and durability enhancement from three points of view. First, we found that HOR-1 pathway (H diffusion on Ni surface toward TPB) seems to be the easiest one regardless of TPB structures. Hence, the performance can be enhanced by increasing the TPB length^{3,6}. This is actually a well-known fact and can be realized experimentally by adjusting the Ni/YSZ ratio, Ni grain refinement, Ni infiltration, and so on as long as the mechanical robustness is well maintained. Second, we observed a new pathway (HOR-III) that proceeds via the diffusion of O in the bulk Ni. During this process, Ni may be partially oxidized, especially under high fuel utilization conditions, which will lead to performance degradation and mechanical disruption. Therefore, care must be taken to ensure mild operation parameters. Dopants could also be added into Ni/YSZ cermet to suppress the Ni oxidation⁶⁰. Third, we concluded that TPB-1 type has higher activity toward HOR than TPB-2 type. The TPB-1 type was also more often observed in our TEM analysis, and it represents Ni standing on a flat YSZ substrate at TPB with very stable interface. Hence, the performance and durability are supposed to be improved if more TPBs of TPB-1 type exist, which could be achieved by reducing the particle size ratio of Ni(O)/YSZ⁶¹ and enhancing the thermal treatment under the condition of avoiding excessive Ni coarsening. However, those motions should be considered globally because the anode performance is a comprehensive output of various factors.

Methods

Cell preparation. A YSZ (8 mol% yttria stabilized zirconia) electrolyte-supported half-cell was fabricated in a conventional way. First, NiO and YSZ with a weight ratio of 55:45 were ball-milled in ethanol. After drying the ethanol, the NiO/YSZ powder was grinded with 8 wt.% ethyl cellulose and α -terpineol solvent to make the slurry, which was then screen-printed onto the YSZ electrolyte support (thickness = 1 mm). The half cell was sintered at 1400 °C for 3 h. Finally, the reduction of NiO was carried out in humid H₂ (2% H₂O) at 800 °C for 2 h.

TEM specimen preparation and atomic structure observation. The pores of the porous electrode were first infiltrated by epoxy resin under vacuum in a CitoVac (Struers) system, so that the bulk cell could be readily handled in the next step. TEM specimen lift-out was performed using an FIB-SEM (HITACHI MI4000L) instrument. The specimen polishing was performed while the FIB voltage decreased from 30 to 3 kV. To remove the damaged/amorphous layers on the two sides of the specimen as much as possible, final polishing was carried out in an Ar ion milling machine (NanoMill Model 1040, Fischione) with a cold stage (−165 °C) at voltages between 0.6 and 1 kV. Structure observation at different scales was performed with JEOL JEM3200FSK (TEM and STEM modes, 300 kV) and JEOL JEM-ARM200F (TEM and STEM modes, 200 kV). Both machines were equipped with energy-dispersive X-ray spectroscopy detectors for elemental analysis.

TEM image simulation. STEM image simulations were performed using the QSTEM software (V2.22)⁵⁰ based on the multislice method with the experimental parameters used in the JEOL ARM200F. The following electron beam parameters were employed: acceleration voltage = 200 kV, chromatic aberration C_C = 1.6 mm, spherical aberration C_S = 0.0011 mm, fifth-order spherical aberration C_5 = 1.756 mm, convergence angle α = 24 mrad, and high-angle annular dark-field-STEM detector acceptance semi-angle of 90–370 mrad. During the microscope operation, the two-fold astigmatism and focus were continuously adjusted by the user and can be identified manually from the live imaging and fast Fourier transforms of the live image. However, in the simulations the two-fold astigmatism and high-order aberrations were neglected.

Force field theory. The ReaxFF⁶² is based on the concept of bond order (BO), which is calculated according to the following equation:

$$\begin{aligned} \text{BO}_{ij}^{\sigma} &= \text{BO}_{ij}^{\sigma} + \text{BO}_{ij}^{\pi} + \text{BO}_{ij}^{\pi\pi} \\ &= \exp\left[p_{\text{bo}1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{p_{\text{bo}2}}\right] + \exp\left[p_{\text{bo}3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{p_{\text{bo}4}}\right] \\ &\quad + \exp\left[p_{\text{bo}5}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{\text{bo}6}}\right], \end{aligned} \quad (1)$$

where r_0^{σ} , r_0^{π} , and $r_0^{\pi\pi}$ are respectively the single, double, and triple bonds as a function of interatomic distances r_{ij} . $p_{\text{bo}1}$, $p_{\text{bo}2}$, $p_{\text{bo}3}$, $p_{\text{bo}4}$, $p_{\text{bo}5}$, and $p_{\text{bo}6}$ are parameters of the ReaxFF.

The total system energy consists of several partial energy terms that depend on the BOs, such as the bond energy (E_{bond}) which in ReaxFF is given as:

$$E_{\text{bond}} = -D_e^{\sigma}\text{BO}_{ij}^{\sigma}\exp\left[p_{\text{be}1}\left(1 - (\text{BO}_{ij}^{\sigma})^{p_{\text{be}2}}\right)\right] - D_e^{\pi}\text{BO}_{ij}^{\pi} - D_e^{\pi\pi}\text{BO}_{ij}^{\pi\pi}, \quad (2)$$

where D_e is the dissociation energy for each bond type. $p_{\text{be}1}$ and $p_{\text{be}2}$ are parameters of the ReaxFF.

Besides E_{bond} , other contributors to the total energy include: the lone pair electrons, under- and over-coordination terms, valence angle energy, torsion energy terms, as well as van der Waals (vdW) and Coulomb interactions, which do not depend on the BOs. Details of the force field can be found elsewhere^{62,63}. For the interactions of H-O-H, YSZ-H₂, Ni-H₂, Ni-H, Ni-YSZ, and O-O, we developed a new set of ReaxFF for the atomic, bonding, off-diagonal (used to describe BO and vdW pair interactions)⁴⁶, and angle parameters. All these parameters are included in Supplementary Data 1.

Quantum mechanical calculations. In order to fit the ReaxFF parameters, QM calculations were performed using the first-principles DFT method implemented in the VASP code^{64,65}. The exchange–correlation interactions were described by the Perdew–Burke–Ernzerhof functional. Spin-polarized calculations were applied throughout. To describe the electron–ion interactions, the projector augmented wave method was adopted. The cutoff energy of the plane wave basis set was 400 eV. The electronic tolerance for a self-consistent loop and the energy tolerance for the ionic relaxation were 1×10^{-6} and 1×10^{-5} eV/atom, respectively. The nudged elastic band calculation has been described elsewhere²¹.

Fitting procedure. To fit the ReaxFF potential, we utilized the algorithm described in POTFIT⁴⁸. The target function for minimization is based on the deviation between the calculated ReaxFF values and DFT reference values with the following equation:

$$Z(\alpha) = w_e \sum_{i=1}^n u_k \left(E_{\text{ReaxFF},i}(\alpha) - E_{\text{FP},i} \right)^2 + w_s Z_s + Z_F, \quad (3)$$

where n is the number of configuration structures, $E_{\text{FP},i}$ is the reference values (such as energies) from first-principles DFT calculation, $E_{\text{ReaxFF},i}(\alpha)$ is the calculated ReaxFF values on the i th structure after parametrization by α ; w_e and u_k are the global and individual structural weights for the energy; and Z_s , Z_F , and w_s indicate the stress, the force, and the global weights for the stress, respectively. In our fitting, $w_s Z_s$ was neglected. For Ni/YSZ/H₂ systems, we have fitted 69 parameters to improve the H-O-H, YSZ-H₂, Ni-H₂, Ni-H, Ni-YSZ, and O-O interaction energies plus 24 energies for the HOR.

MD and mechanics simulations. First, models were built by using the lattice distances observed in the experiment (see Fig. 4). Then they were allowed to change due to the lattice expansion of Ni and YSZ in the course of isobaric–isothermal simulation at a temperature of 1073 K and a pressure of 1 atm. The main reaction dynamics was calculated under the canonical ensemble corresponding to the constant volume and temperature condition. The temperature and pressure were controlled with the Nose–Hoover thermostat⁶⁶ and barostat⁶⁷, respectively.

The lattice parameters of two heterogeneous phases usually cannot perfectly match. Therefore, to obtain a well-matched Ni/YSZ interface, we expanded or compressed (for TPB-1 and TPB-2, respectively) the softer nickel crystal according to the misfit as calculated in Eq. (4):

$$\text{Misfit} = \frac{m * a_{\text{Ni}} - n * a_{\text{YSZ}}}{n * a_{\text{YSZ}}} \quad (4)$$

where n and m are the number of unit cells for YSZ and Ni, respectively, and a is the plane lattice parameter. The misfit was minimized down to 3%. We used periodic boundary conditions to simulate an infinite horizontal surface. Because the simulation box length along the z axis was long, the periodicity in the z direction was virtually removed. We ran the MD trajectory for 700 ps. To optimize the TPB structures, we employed the FIRE method⁶⁸. All MD and energy minimization calculations were carried out with USER-REAXC package⁶⁹ as implemented in the LAMMPS code⁴⁹.

Data availability

The data that support the findings of this study are available within the paper and its Supplementary Information and Data. Other relevant data are available from the corresponding authors upon reasonable request.

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Author contributions

S.-S.L. prepared the sample and carried out the microscope operation. L.C.S. performed the parameterization of ReaxFF, computational simulations, and modeling. A.I. (currently on leave of absence from the Institute for Metals Superplasticity Problems of RAS, Khalturin St. 39, Ufa, 450001, Russia) assisted the technical set-up of POTFIT, and T.I. aided the simulations. T.Y. assisted the TEM operation and QSTEM simulation. Y.U., S. M., and M.K. conceived and supervised the project. S.-S.L. and L.C.S. composed the manuscript and prepared the figures. All the authors discussed the results, commented, and revised the manuscript.

Additional information

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