Favorable Role of the Metal–Support Perimeter Region in Electrochemical NH₃ Synthesis: A Density Functional Theory Study on Ru/BaCeO₃

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ABSTRACT: The catalytic electrochemical synthesis of NH₃ on Ru/BaCeO₃ was investigated using density functional theory. The competition between NH₃ formation and the hydrogen evolution reaction (HER) is a key for a high NH₃ formation rate. Our calculations show that H adsorbs more strongly than N₂ at the Ru particle moiety, while the adsorption of N₂ is stronger than the H adsorption at the Ru/BaCeO₃ perimeter, a model for the triple-phase boundary that is proposed to be an active site by experimental studies. This indicates that, while the HER is more favorable at the Ru particle moiety, it should be suppressed at the Ru/BaCeO₃ perimeter. We also calculated the Gibbs free energy changes along the NH₃ formation and found that the N₂H formation, the NHNNH₂ formation, and the NH₃ formation steps have a relatively large Gibbs energy change. Therefore, these are possible candidates for the potential-determining step. The calculated equilibrium potential (U = −0.70 V, vs RHE) is in reasonable agreement with experiments. We also evaluated the reaction energy (ΔE) and the activation barrier (Eₐ) of the N₂H formation at several sites. ΔE and Eₐ were high at the Ru particle moiety (ΔE = 1.18 eV and Eₐ = 1.38 eV) but became low (ΔE = 0.32 eV and Eₐ = 1.31 eV) at the Ru/BaCeO₃ perimeter. These provide the atomic-scale mechanism how the proton conduction in BaCeO₃ assists the electrochemical NH₃ synthesis.

1. INTRODUCTION

Recently, ammonia (NH₃) has attracted considerable attention as a hydrogen (H₂) energy carrier for several reasons. First, NH₃ is much easier to liquefy and transport than H₂. Second, NH₃ has a higher volumetric H₂ density (120.3 kg·H₂·m⁻³) than liquid H₂ (70.9 kg·H₂·m⁻³) or toluene/methylcyclohexane (47.1 kg·H₂·m⁻³).¹ Despite these advantages of NH₃, as a H₂ carrier, the Haber–Bosch process² remains the main synthetic route for producing NH₃ from N₂. However, the main hydrogen source for this process is currently the hydrogen gas formed from natural gas. This requires large amounts of energy; thus the NH₃ formation without using hydrogen from natural gas is highly desirable. For this purpose, electrochemical NH₃ synthesis is a promising approach because it utilizes H₂O as a hydrogen source.³ Electrochemical NH₃ synthesis could be a key technology for a carbon-neutral society.

One promising approach for electrochemical NH₃ synthesis is to employ a fuel cell with a solid electrolyte. Many studies have reported using a solid electrolyte for NH₃ synthesis at the gas–solid interface.⁴,⁵ This device consists of an anode, a cathode, and a solid electrolyte. The anode and cathode reactions are

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (1)
\]

and

\[
\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3 \quad (2)
\]

respectively, and the net reaction is

\[
\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \frac{3}{2}\text{O}_2 \quad (3)
\]

Water dissociation on the anode generates protons, which are transported to the cathode through the solid electrolyte and combine with electrons and N₂ there to produce NH₃. The NH₃ formation at the cathode is known to determine the overall reaction rate and yield, and extensive efforts have been devoted to finding effective catalysts for the cathode reaction. For example, several research groups have investigated metal systems such as Ru and Ni. Ru is well known as a suitable catalyst for NH₃ synthesis because it exhibits a high NH₃ formation rate.⁶ However, the electrochemical NH₃ formation rates reported are still low, such as 3.0 × 10⁻¹³ mol·s⁻¹·cm⁻² on Ru/MgO, as observed by Skodra and Stoukides.⁷

To further enhance the NH₃ formation rate for practical purposes, a detailed understanding of the reaction mechanism is necessary. Several mechanistic studies based on kinetic

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measurements or theoretical calculations have been performed.\(^3\) Currently, there are two widely accepted pathways for NH\(_3\) synthesis: the dissociative mechanism (in which \(N-N\) bond dissociation occurs first) and the associative mechanism (in which NH\(_x\) (\(x = 1-3\)) species form before N-N bond dissociation).\(^8\)-\(^11\) The Haber–Bosch process is considered to occur through the dissociative mechanism, while many researchers believe that electrochemical NH\(_3\) synthesis occurs through an associative mechanism because of its milder reaction conditions.\(^12\)-\(^15\) Another important mechanism is the Mars–van Krevelen mechanism, in which lattice N atoms are used for NH\(_3\) formation; several research groups have investigated electrochemical NH\(_3\) synthesis via this mechanism using a metal nitride cathode.\(^3\)-\(^5\)

Another key factor in the electrochemical NH\(_3\) synthesis is its competition with the hydrogen evolution reaction (HER).\(^3\)-\(^5\) This reaction is expressed as

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\]

(4)

H adsorption on the catalyst surface or active site competes with \(N_2\) adsorption, and when a negative potential is applied, the HER becomes easier than NH\(_3\) formation. This is unfavorable for the NH\(_3\) formation because the active sites and the electronic current are consumed by the HER. Some catalyst systems with high \(N_2\) dissociation rates (e.g., Ru and Ni) suffer from low NH\(_3\) formation rates because of the HER; several groups previously analyzed the competition of the HER and NH\(_3\) formation and have shown that overcoming the HER is necessary condition to have a high NH\(_3\) formation rate.\(^12\)-\(^15\)

As stated above, many mechanistic insights into electrochemical NH\(_3\) synthesis have been obtained. However, several important features remain uninvestigated, such as the metal–support interaction, which is known to play an important role in catalysis.\(^16\) Indeed, the triple-phase boundary (TPB) is considered to be the active site for electrochemical NH\(_3\) synthesis in the gas phase.\(^17\) Therefore, identifying the detailed mechanism at the TPB is of particular importance. One of the authors of the present study found that, in the Ru/BaCeO\(_3\) system, a smaller Ru particle size is favorable for electrochemical NH\(_3\) synthesis because of the increased Ru/BaCeO\(_3\) perimeter region, which has an NH\(_3\) formation rate of \(1.1 \times 10^{-11}\) mol·s\(^{-1}\)·cm\(^{-2}\).\(^17\) Recently, we proposed the formation of an effective double layer during NH\(_3\) electrosynthesis with Fe/BaCeO\(_3\), which can be considered as an extension of the TPB active site model.\(^18\) Several researchers have investigated the metal–support interaction in the electrochemical reaction and noted some similarities between this interaction and the electrochemical promotion effect.\(^19\) An understanding of the complex relationship between these two factors is important for enhancing the electrochemical catalysis process. However, there is still much to be learned on this issue.

In this study, we theoretically investigated electrochemical NH\(_3\) synthesis using a Ru/BaCeO\(_3\) system. To the best of our knowledge, this is the first computational analysis of the metal–support interaction during electrochemical NH\(_3\) synthesis. Our focus was the effect of the metal–support interaction on the mechanistic details, especially on the competition between NH\(_3\) formation and the HER and the energetics of NH\(_3\) formation. First-principles density functional theory (DFT) calculations were employed to provide a reliable description of the thermodynamic and kinetic properties. We first examined the competitive adsorption of H and \(N_2\) on the Ru surface to identify the available active sites for NH\(_3\) synthesis. Then, we investigated NH\(_3\) formation by considering the free energy profiles under an applied electric potential. Based on the energetic profile of H and \(N_2\) adsorption on the active sites, the availability of the sites, that is, competition between the HER and the NH\(_3\) formation is discussed. The calculated free energy profile is compared with experimental results. Finally, we evaluated the activation barrier \(E_a\) of the \(N_2\)H formation step, identified as one of the key steps of electrochemical NH\(_3\) formation from the analysis of the free energy profile.

2. METHOD

2.1. Reaction Model. For electrochemical NH\(_3\) synthesis, two pathways have been discussed, namely, the dissociative and associative mechanisms.\(^10\),\(^11\),\(^20\) With Ru catalysts, it is widely accepted that the dissociative mechanism mainly occurs at stepped surfaces.\(^5\),\(^21\) However, the associative mechanism is more plausible for the current purpose from the following reasons: (1) considering the structure of the perimeter moiety, stepped surfaces are unlikely to be formed at the Ru/BaCeO\(_3\) perimeter, and (2) NH\(_3\) formation at the Ru/BaCeO\(_3\) perimeter occurs under proton-rich conditions because a proton is always supplied through BaCeO\(_3\). Note that the NH\(_3\) formation on Ru nanoparticles (i.e., nonperimeter sites) can be modeled using a conventional Ru slab model. As such models have been extensively studied, we did not repeat the calculations.\(^11\),\(^12\)

In addition to differences in the order of N–H bond formation and \(N_2\) dissociation, there are two possibilities for the H addition to \(N\) or \(N_2\): the Tafel mechanism and the Heyrovsky mechanism. In the former, the N–H bond is

Figure 1. Schematic reaction mechanisms for associative NH\(_3\) synthesis via distal and alternating pathways. The shaded area denotes the Ru surface. The alternating pathway has two further possibilities shown by the black and light gray arrows.
formed between N and H atoms both adsorbed on the metal surface, while in the latter, the added H comes from a medium such as a gas, solvent, or solid electrolyte. Skúlason et al. compared these two mechanisms and concluded that the Heyrovsky mechanism is favorable in terms of the reaction energy.12 Based on this, we considered the associative Heyrovsky mechanism, which involves the following elementary steps (the active site is denoted by an asterisk (*)):

\[
\begin{align*}
N_2 + & \rightarrow N_2^* \quad (5) \\
N_2^* + 6(H^+ + e^-) & \rightarrow N_2H^8^* + 5(H^+ + e^-) \quad (6) \\
N_2H^8^* + 5(H^+ + e^-) & \rightarrow N_2H_2^{8^*} + 4(H^+ + e^-) \quad (7) \\
N_2H_2^{8^*} + 4(H^+ + e^-) & \rightarrow N_2^* + NH_3 + 3(H^+ + e^-) \quad (8) \\
N_2^* + 3(H^+ + e^-) & \rightarrow NH_4^* + 2(H^+ + e^-) \quad (9) \\
NH_4^* + 2(H^+ + e^-) & \rightarrow NH_3^* + (H^+ + e^-) \quad (10) \\
NH_3^* + (H^+ + e^-) & \rightarrow NH_2^* \quad (11) \\
NH_2^* & \rightarrow NH_3^* \quad (12)
\end{align*}
\]

For the associative Heyrovsky mechanism, Li et al. proposed two possible pathways depending on the position of H addition to the N₂H intermediate.22 These pathways are denoted as the alternating and distal pathways in Figure 1.

The Gibbs free energy change for NH₃ electrolys thesis was analyzed using the approach proposed by Nørskov et al.12,23 It was calculated as follows:

\[
\Delta G(U) = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S - n_eU
\]

where \(\Delta E_{\text{DFT}}\) is the reaction energy calculated using DFT; \(\Delta E_{\text{ZPE}}\) and \(\Delta S\) are the changes in the zero-point energy (ZPE) and entropy along the reaction step, respectively. \(U\) is the externally applied electric potential that shifts the Gibbs energy of the reaction intermediate by \(-n_eU\) (\(n = \) number of electrons involved). The ZPE and the entropies of gaseous molecules (\(N_2, H_2,\) and \(NH_3\)) were obtained from experimental data and are listed in Table S1.24 To calculate the chemical potential of the proton–electron pair (\(H^+ + e^-\)), we employed the computational hydrogen electrode model.23 In this model, the Gibbs energy \(G(H^+ + e^-)\) is equivalent to half of the Gibbs energy of gaseous hydrogen (1/2\(G(H_2)\)) under standard conditions (pH = 0, 298.15 K, 1 atm) with no external potential.

2.2. Computational Details. We employed the DFT + U method (DFT plus Hubbard-U parameter) for all DFT calculations.25 The Perdew–Burke–Ernzerhof functional was used for the exchange-correlation functional.26 The effective Hubbard-U parameter, that is, \(U - J\) was set to 6.0 eV, which was used for the Ce 4f electrons as in a previous DFT + U study on BaCeO₃.27 We examined the dependence of the results on the Hubbard-U parameter by using the \(N_2\) adsorption energy on Ru/BaCeO₃ as a benchmark (Figure S1). When the \(U\) parameter was varied within 0.0–8.0 eV, the \(N_2\) adsorption energy ranged from 0.47 to 0.51 eV. This indicates that the \(U\) parameter has only weak effects on the Gibbs free energy profiles.

We performed geometry optimization by fixing the lower two-thirds of the BaCeO₃ structure. The Ru moiety and the adsorbates were fully relaxed. Figure 2 displays details of the Ru/BaCeO₃ unit cell model, which contained 284 atoms, with 13 atomic layers of BaCeO₃ and 4 of Ru. No spatial symmetry was imposed in the calculations. To evaluate the ZPE, a vibrational analysis was performed using a finite difference of 0.015 Å and allowing only the adsorbate molecules to move. Unit cell optimization was performed for the Ru/BaCeO₃ system (without an adsorbate), and the optimized unit cell parameters were used for the subsequent calculations. For the surface energy calculations, another unit cell optimization was performed. For a selected case, we performed a molecular dynamics (MD) simulation with an NVT ensemble to search for a stable adsorbate structure. A Nose–Hoover thermostat was used there, the temperature was controlled at 500 K, and the simulation was carried out for 1 ps with a time step of 1 fs.

The core electrons were represented using the projector-augmented wave method.28 The valence electrons were expanded by the plane wave basis set up to a cutoff energy (\(E_{\text{cutoff}}\)) of 400 eV. The electron occupation near the Fermi level was determined using the first-order Methfessel–Paxton scheme with \(\sigma = 0.1\). The convergence criteria for the electronic state and geometry optimization calculations were set to 1.0 × 10⁻⁵ and 0.03 eV Å⁻¹ in energy and force, respectively. Transition state (TS) search was done with the climbing image nudged elastic band (CINEB) and the dimer methods.29 The vibrational analysis of the TSs confirmed that they were the first-order saddle point in the potential energy surface. Reciprocal space integration was performed with the k-point placed using the Monkhorst–Pack scheme. The k-point mesh was set to 3 × 3 × 1 for the surface calculations and to 9 × 9 × 9 for the bulk material calculations. Gamma-point sampling (1 × 1 × 1) was used in the MD and CINEB calculations. A vacuum layer of ~20 Å was introduced between the slabs. Bader charge analysis was used to investigate the electronic properties.30 Dipole correction in the z-direction was applied in all calculations except when calculating the bulk material and isolated molecules. All DFT calculations were performed using the Vienna ab initio simulation package version 5.4.31
3. RESULTS AND DISCUSSION

3.1. Determination of the Most Stable Surface Termination. Herein, we employed perovskite BaCeO$_3$ as the proton-conducting electrolyte. Although a previous experimental study used yttrium-doped BaCeO$_3$ as the electrolyte, the doping level was moderate (BaCe$_{0.9}$Y$_{0.1}$O$_3$) and was therefore not expected to change the reaction mechanism of NH$_3$ synthesis. The orthorhombic unit cell structure of BaCeO$_3$ was obtained from the Inorganic Crystal Structure Database (ICSD ID = 188637). First, we need to identify the most stable surface of BaCeO$_3$ among several candidates, because the surface should be exposed during electrochemical NH$_3$ synthesis. Previously, Shishkin and Ziegler employed the DFT method to compare the stabilities of the (100), (110), and (111) surfaces of BaCeO$_3$ and found (100) to be the most stable. Based on their result, we considered the (100) surface of BaCeO$_3$ in this study.

We used a $2 \times 2 \times 2$ supercell to model the BaCeO$_3$ surface. The surface energy ($E_{surf}$) was evaluated as follows:

$$E_{surf} = \frac{1}{2A} \left[ E_{slab} - \left\{ N \cdot E_{bulk} + \sum_{X} \mu_{X} (n_{X,slab} - n_{X,bulk}) \right\} \right]$$

(14)

where $A$ is the surface area calculated from the optimized unit cell, $E_{slab}$ is the total energy of the slab, $E_{bulk}$ is the total energy of bulk BaCeO$_3$, $N = n_{Ba,slab}/n_{Ba,bulk}$ is the number of BaCeO$_3$ unit cells, and $n_{X,slab}$ and $n_{X,bulk}$ are the numbers of atom X in the slab and bulk models, respectively. $\mu_{X}$ is the chemical potential of atom X. The chemical potential of an oxygen atom ($\mu_{O}$) is calculated from

$$\mu_{O} = E_{O} + \frac{1}{2} \text{BDE}_{O_{2}} - \text{ZPE}$$

(15)

where $E_{O}$ is the total energy of O atom, and BDE$_{O_{2}}$ and ZPE are the bond dissociation energy and zero-point energy of O$_2$, respectively. We employed the experimentally measured values of BDE$_{O_{2}} = 4.89$ eV and ZPE = 0.10 eV. For the total energy calculation of O atom, DFT calculations were performed using B3LYP as the exchange-correlation functional.

The chemical potentials of Ce and Ba were evaluated as

$$\mu_{Ce} = E_{CeO_{2}} - 2 \mu_{O}$$

(16)

$$\mu_{Ba} = E_{BaO} - \mu_{O}$$

(17)

where the references for Ce and Ba were bulk CeO$_2$ and BaO, respectively. The total energies ($E_{CeO_{2}}$ and $E_{BaO}$) were evaluated using DFT. The initial structures of CeO$_2$ and BaO were obtained from the ICSD (ID = 88759 and 616005, respectively). The calculated chemical potentials of H, O, Ce, and Ba are listed in Table S2. Using these quantities, we calculated the surface energies with four different terminations: CeO$_2$ termination, CeO$_2$–O termination, BaO termination, and BaO–O termination (see Figure S2 for their surface structures). According to the calculated $E_{surf}$ values in Table 1, BaO termination is the most stable. Based on this result, we constructed the Ru/BaCeO$_3$ model to represent the Ru/BaCeO$_3$ perimeter. We placed a Ru rod consisting of 80 atoms on this surface. The resultant structure is shown in Figure 2. This model is used in the NH$_3$ synthesis at the Ru/BaCeO$_3$ perimeter, which will be discussed in the following sections.

3.2. Competitive Adsorption of H and N$_2$. As discussed in Introduction, one reason for a low NH$_3$ formation rate is competition with the HER. In this subsection, we investigated the adsorption of H and N$_2$ on Ru/BaCeO$_3$. We consider the adsorption of H and N$_2$ to occur on the several sites on the Ru rod (top, edge, side) and the Ru/BaCeO$_3$ perimeter sites. The top part of the Ru rod has a surface structure similar to that of Ru(0001); therefore, we assume that this part has a reactivity similar to that of the Ru surface or nanoparticles. Figure 3 summarizes Gibbs free energies of H and N$_2$ adsorption ($\Delta G_{ad}$), together with the optimized geometries. First, we discuss N$_2$ and H adsorption on the top part of the Ru rod. At this location, N$_2$ undergoes atop adsorption, while H adsorption is exergonic at both the fcc and hcp threefold hollow sites. Notably, N$_2$ adsorption on the top part is weak, as indicated by the positive $\Delta G_{ad}$ value (0.08 eV); this is in agreement with the previously reported tendency on Ru(0001). On the other hand, H adsorption is strong ($\Delta G_{ad} = -0.36$ eV) on the Ru particle, suppressing NH$_3$ formation at these locations through serious H poisoning. A similar tendency was observed for H and N$_2$ adsorption on the upper edge part. Among the Ru edge or side part of the rod, the H adsorption is most strong at the edge site with bridge type adsorption ($\Delta G_{ad} = -0.59$ eV). The H adsorption on this site is stronger than the H adsorption on the Ru top part. N$_2$ adsorption here is much weaker than the H adsorption ($\Delta G_{ad} = -0.29$ eV), although still stronger than that at the Ru top part.

Next, we consider N$_2$ and H adsorption on the Ru/BaCeO$_3$ perimeter. Here, H adsorption is the strongest at the bridge site (bridge(A) in Figure 3), as its $\Delta G_{ad}$ is $-0.79$ eV; it is much stronger than that on the Ru top or edge parts. The strongest N$_2$ adsorption on Ru/BaCeO$_3$ occurs at the atop(A) site with side-on adsorption mode, as its $\Delta G_{ad}$ is $-1.02$ eV. In this configuration, two Ru atoms at the perimeter are used, where each N atom binds different Ru atoms as shown in the top view (Figure 3). This adsorption mode is close to the enzymatic configuration (N$^*$–N$^*$), which is seen in the N$_2$ adsorption on the enzyme nitrogenase. Another mode of N$_2$ adsorption, atop adsorption, is also strong as its $\Delta G_{ad}$ is $-0.64$ eV. This is also much stronger than the N$_2$ adsorption on the Ru top and edge parts.

Thus, these results show that the N$_2$ adsorption at the Ru/BaCeO$_3$ perimeter is stronger than the H adsorption, which differs from the scenario at the Ru top or edge parts. To examine the stability of this N$_2$ adsorption site, we performed an MD simulation at $T = 500$ K up to 1 ps (see Figure S3 for the energy and geometry changes along the MD trajectory). Our MD calculation showed that N$_2$ is always adsorbed on the Ru/BaCeO$_3$ perimeter region. Thus, we can conclude that this site binds N$_2$ with considerable strength.

To analyze the electronic properties of the Ru/BaCeO$_3$ system, we carried out Bader charge analysis. The calculated charges of the Ru rod are summarized in Figure S4. The results show that the Ru atoms in the Ru/BaCeO$_3$ perimeter region are more negatively charged ($\sim -0.2$ e) than those in other parts of the Ru rod. This could lead to stronger adsorption of H and N$_2$ on the perimeter sites due to the possibility of

Table 1. Surface Energies ($E_{surf}$) of BaCeO$_3$(100) Surfaces with Different Terminations, as Calculated Using DFT

|     | CeO$_2$ | CeO$_2$–O | BaO | BaO–O
|-----|---------|-----------|-----|------|
| energy (J m$^{-2}$) | 1.38    | 4.75      | 1.03| 4.34 |

Table S2.
stronger electrostatic interactions or back-donation to $\text{N}_2^\pi$ orbitals. This interaction is expected to enhance $\text{N}_2$ adsorption on the perimeter site, which is a unique feature not found in the Ru top or edge parts. This result strongly indicates that $\text{H}_2$ and $\text{N}_2$ adsorption is promoted on the TPB compared with that at other parts of the catalyst surface.

3.3. Gibbs Energy Changes during $\text{NH}_3$ Formation.

Next, we investigated the Gibbs energy changes during $\text{NH}_3$ formation. Because the previous section concluded that $\text{N}_2$ most strongly interacts with the Ru/BaCeO$_3$ perimeter site, we consider it the active site for $\text{NH}_3$ formation. Figure 4 summarizes the Gibbs energy changes during $\text{NH}_3$ formation on Ru/BaCeO$_3$, considering both the distal and alternating pathways of $\text{NH}_3$ formation. The alternating pathway also includes two possible routes, namely $\text{NHH}_2^*$ to $\text{NH}^*$ via $\text{NH}_3$ formation and desorption, or $\text{NHH}_2^*$ to $\text{NH}_2\text{NH}_2^*$ formation. Therefore, we can propose three pathways for the $\text{NH}_3$ formation, that is, (i) the distal pathway, (ii-a) the alternating pathway without $\text{NH}_2\text{NH}_2^*$ formation, and (ii-b) the alternating pathway with $\text{NH}_2\text{NH}_2^*$ formation. These pathways are shown in Figure 4b, where the inset images show the optimized structures.

Based on our calculation, the elementary reactions with large $\Delta G$ values are $\text{N}_2\text{H}^*$ formation from $\text{N}_2^*$ ($\Delta G = 0.67$ eV), $\text{NHH}_2^*$ formation from $\text{NHH}_\text{N}\text{H}^*$ in path (ii-a) ($\Delta G = 0.66$ eV), and $\text{NH}_2^*$ formation from $\text{NH}_\text{N}\text{H}^*$ ($\Delta G = 0.70$ eV). Therefore, these are possible candidates for the potential-determining step (PDS, i.e., the elementary step that requires the largest $\Delta G$). Because the $\text{N}_2\text{H}^*$ formation and $\text{NH}_2^*$ formation appear in all the paths, it is difficult to conclude...
whether the distal or alternating pathway is favorable. However, we could exclude the (ii-b) pathway because the NH$_2$NH$_2^*$ state is more thermodynamically unfavorable than the NH$_2$ state. Note that the last reaction step, that is, the NH$_2^*$ desorption process is endergonic in Figure 4, but this process becomes exergonic by 0.57 eV at $T = 500$ °C, which corresponds to the experimental reaction temperature. Therefore, the NH$_2^*$ desorption does not hinder the NH$_2$ formation.

The theoretical overpotential can be calculated from this $\Delta G$ value by applying an external potential $U$ to make $\Delta G = 0$ for the PDS. Figure 4 also shows the Gibbs energy changes under $U = -0.70$ V (vs RHE), which corresponds to the $\Delta G$ of NH$_3^*$ formation from NH$_2^*$. One of the present authors reported in the experimental work that NH$_3$ electrolysynthesis can be initiated by applying a potential of approximately $-0.3$ V. Thus, the present calculation exhibits semiquantitative agreement with the experimental result, although it moderately overestimates the overpotential. Our calculated overpotential value is similar to that reported by Back and Jung ($-0.68$ V), who considered a Ru step as the active site. Therefore, the Ru/BaCeO$_3$ perimeter site is not likely to reduce the overpotential for NH$_3$ synthesis.

In summary, the calculated Gibbs energy profiles have shown that (i) the PDS of the electrochemical NH$_3$ synthesis is the NH$_2^*$ formation step (NH$_2^* + H^+ + e^- \rightarrow$ NH$_3^*$), while the NH$_2$H$_2^*$ formation step (NH$_2^* + H^+ + e^- \rightarrow$ NH$_2$H$_2^*$) has a similar $\Delta G$ value; thus these two are the possible candidate for the PDS, (ii) NH$_3$ synthesis can occur at the Ru/BaCeO$_3$ perimeter site upon applying a weak external potential, and this site is less vulnerable to H poisoning than the Ru top part is. Because we used the Ru/BaCeO$_3$ perimeter site to model the TPB of the solid electrolyte, the DFT results indicate that the presence of the TPB is favorable for NH$_3$ formation compared with the HER, from the thermodynamic viewpoint. In the next section, we further investigate the effect of the Ru/BaCeO$_3$ perimeter on the kinetics of NH$_3$ formation.

3.4. Reaction Path for the N$_2$H Formation Process. The Gibbs energy analysis in the previous section has shown that N$_2$H formation is a key step in the NH$_3$ electrolysis, because it is involved in both distal and alternating pathways and has relatively large $\Delta G$. Therefore, the kinetic parameters such as activation energy ($E_a$) or reaction energy ($\Delta E$) for this process would be a governing factor for the NH$_3$ formation rate. In this section, we analyze how the Ru/BaCeO$_3$ boundary affects these parameters of the N$_2$H formation. We investigated three pathways for N$_2$H formation: (I) at the Ru particle edge site, (II) in the Ru/BaCeO$_3$ boundary region, between the N$_2$ molecule and H atom, both adsorbed on the Ru perimeter sites, and (III) in the Ru/BaCeO$_3$ boundary region, between the N$_2$ molecule adsorbed on the Ru perimeter site and the H atom occupied the octahedral site in BaCeO$_3$. The calculated path III because BaCeO$_3$ is the proton-conducting solid electrolyte, thus the proton supply to the BaCeO$_3$ surface is possible; the optimized structures for the reactants, TSSs, and product states for the three pathways are shown in Figure 5, together with the corresponding $\Delta E$ and $E_a$ values. All the TSSs are confirmed to have one imaginary frequency; see Table S3 for the calculated vibrational frequencies.

Figure 5 shows that N$_2$H formation via pathway I has $E_a = 1.38$ eV and is highly endothermic ($\Delta E = 1.18$ eV). Thus, when N$_2$ is adsorbed on the Ru edge site, N$_2$H formation is quite slow. In addition, our adsorption energy calculation (in Section 3.2) shows that the H atom adsorsbs more strongly than N$_2$ at the edge site. Therefore, the active site is predominantly covered with H atoms (and thus more of the HER occurs), and N$_2$H formation at the Ru particle is unfavorable.

Next, we consider the pathway II. As shown in Section 3.2, the adsorption energies of N$_2$ and H at the Ru perimeter site are comparable; thus N$_2$H formation from this site is highly probable. However, our calculations show that the reaction requires a relatively large $E_a (1.60$ eV) and $\Delta E (1.09$ eV). Note that the calculated N$_2$H formation Gibbs energy was 0.67 eV, where the coadsorption of N$_2$ and H was not accounted. The $\Delta E$ value of the pathway II includes the coadsorption effect, and this indicates that the adsorption of H considerably stabilizes the reactant state for N$_2$H formation. As a result, $\Delta E$ becomes larger than that in Figure 4. These results indicate that N$_2$H formation at the Ru perimeter site is slow, even when N$_2$ is strongly adsorbed on the Ru perimeter site.

Another possibility for N$_2$H formation at the Ru/BaCeO$_3$ boundary region is pathway III, that is, N$_2$H formation between N$_2$ at the Ru perimeter and the H atom from BaCeO$_3$. Although several positions of the H atom are possible in BaCeO$_3$, we selected the octahedral site of Figure 5 as it is closest to the surface. Figure 5 shows that pathway III has lower $E_a (1.31$ eV) and $\Delta E (0.32$ eV) values compared with pathways I and II. Because the product state of N$_2$H formation is the same as that of pathway II, N$_2$H formation at the Ru/BaCeO$_3$ boundary region is more favorable when it occurs between N$_2$ molecule on the Ru perimeter and H atom conducted from BaCeO$_3$. This computational result indicates that the proton-conducting support materials such as BaCeO$_3$ are kinetically favorable because they open a new pathway that accelerates the formation of N$_2$H.
4. CONCLUSIONS

Electrochemical NH₃ synthesis using a solid electrolyte is a promising approach for environmentally friendly NH₃ production. Previous experimental investigations of electrochemical NH₃ synthesis in the Ru/BaCeO₃ demonstrated the Ru/BaCeO₃ perimeter region (or three-phase boundary) to be the active site. In the present study, we used DFT calculations of a Ru rod model supported by BaCeO₃ to investigate electrochemical NH₃ synthesis and clarify the contribution of the metal—support interaction. First, after considering the BaCeO₃(100) surface with four different terminations, the surface with the Ba termination was determined to be the most stable as it had the lowest surface energy.

We then compared the adsorption of H and N₂ at several sites in the Ru/BaCeO₃ system, because this is a key factor influencing the two competitive reactions, that is, NH₃ formation and the HER. Because our calculated Gibbs energy of adsorption (ΔGₐd) shows that H adsorbed more strongly than N₂ at the top part of the Ru particle, the HER is considered more favorable at that site, which corroborates previous reports. In contrast, N₂ has stronger adsorption (ΔGₐd = -1.02 eV) than the H atom (ΔGₐd = -0.79 eV) at the Ru/BaCeO₃ perimeter site. This suggests the weaker hydrogen poisoning on the Ru/BaCeO₃ perimeter site, which is favorable for the NH₃ formation.

Assuming the Ru/BaCeO₃ perimeter as the active site, we also calculated the Gibbs free energy changes along NH₃ formation; the associative mechanism (N₂H₃ formation prior to N–N dissociation) was assumed. Our results indicate that the PDS for NH₃ formation is either the NH₃* formation step (ΔG = 0.70 eV) or the N₂H* formation step (ΔG = 0.67 eV). Accordingly, the theoretical equilibrium potential is U = -0.70 V, which is in reasonable agreement with the experimental value. This value is similar to the previously reported value for the pure Ru model. Considering these DFT results, the Ru/BaCeO₃ perimeter site is favorable for the electrochemical NH₃ synthesis because the HER is inhibited there and not because of the decrease in the overpotential of the NH₃ formation. We also located the TS for the potential-determining N₂H formation step. Our calculated activation barriers showed that N₂H formation in the Ru/BaCeO₃ boundary region is favorable, especially when N₂ at the Ru perimeter site reacts with an H atom from BaCeO₃. Thus, a faster rate for N₂H formation is expected in the Ru/BaCeO₃ perimeter region.

This investigation is the first to confirm theoretically that electrochemical NH₃ synthesis is favorable at the TPB. The proton-conducting nature of BaCeO₃ is beneficial for the NH₃ formation because (i) it supplies the N₂ activation site that has some resistance to the hydrogen poisoning, (ii) it assists the N₂H formation by lowering the activation barrier, and (iii) it helps the supply of the reactant species (H atom in the present case). We consider that such a metal—support interaction might be a clue for increasing the NH₃ formation rate. Our theoretical analysis strongly implies that enlarging this area is beneficial for electrochemical NH₃ synthesis, from the above reasons. Based on this idea, detailed catalyst designs at the interface could enhance the reaction rate of electrochemical NH₃ synthesis.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01222.

Table S1: Thermal corrections and ZPEs taken from experimental values, Table S2: Calculated chemical potentials for Ce, Ba, and O, Table S3: Vibrational frequencies for the TS geometries in Figure S5, Figure S1: Effect of the U parameter in the DFT + U scheme on N₂ adsorption energy (in eV) in the Ru/BaCeO₃ system, Figure S2: Optimized structures of BaCeO₃(100) surfaces with four different terminations, Figure S3: Energy and geometry changes along the MD trajectory for N₂ binding on the Ru/BaCeO₃ perimeter site, and Figure S4: Bader charges of the Ru rod in the Ru/BaCeO₃ model (PDF)

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Notes
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