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Why Does the Performance of Nitrogen-Doped Carbon Electrocatalysts Decrease in Acidic Conditions?

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Abstract: Nitrogen-doped carbon has emerged as a promising low-cost and durable alternative to platinum catalysts for the oxygen reduction reaction (ORR) in fuel cells. However, its catalytic activity decreases significantly in acidic electrolytes, limiting the practical applications. Here, we report the degradation mechanisms of nitrogen-doped carbon catalysts, focusing on the acid-base equilibrium of pyridinic nitrogen (pyri-N), which serves the primary active site. We found that the electrochemical hydrogenation of pyri-N to pyri-NH, coupled with oxygen adsorption, is a critical process. While this reaction occurs at higher potentials in basic electrolytes, it shifts to lower potentials in acidic environments due to the protonation and stabilization of pyri-N. These results demonstrate that the decrease of the catalytic activity in acidic electrolytes is tied to the basicity of pyri-N. By controlling the basicity of pyri-N, specifically its pK_a , a guideline for enhancing the ORR and other electrode reactions has been established.

Introduction

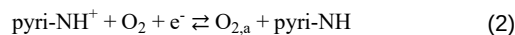
Catalysts made entirely of carbon and nitrogen have emerged as highly promising electrode materials for a carbon-neutral society, thanks to their abundant resources and exceptional structural stability. As humanity transitions away from fossil fuels, the adoption of artificial fuels like hydrogen, ammonia, and methanol as energy carriers is widely anticipated. In this future, fuel cells that efficiently and effectively convert these carriers into electricity and heat will play an essential role. To enable the widespread adoption of fuel cells in a hydrogen-based society, the development of highly durable alternatives to platinum (Pt) catalysts is both urgent and critical, given the anticipated depletion of Pt in the near future. Currently, fuel cells with practical performance require the use of high-performance Pt in the oxygen

reduction reaction (ORR) catalyst of the cathode electrode. However, the high cost and limited reserves of Pt necessitate the urgent development of alternative cathode catalysts to lower the price of fuel cells and promote their widespread adoption globally. Carbon- and oxide-based catalysts have also been studied,^[1–3] however, carbon-based catalysts have demonstrated superior activity and durability under practical conditions. Furthermore, among carbon-based catalysts, metal-doped carbon catalysts^[4–9] and metal-free nitrogen-doped carbon catalysts^[10–13] are the most common type of the catalysts. While metal-doped carbon catalysts exhibit high activity, they encounter significant challenges with dissolution and compositional changes in the fuel cell operating environment. In contrast, nitrogen-doped carbon catalysts possess the critically important property of high durability. However, a major drawback is that their high catalytic activity in alkaline electrolytes is not replicated in acidic electrolytes.^[10,14–16] The contribution of counter anions and the shift from 4-electron reduction to 2+2-electron reduction have been proposed as potential causes of the decreased activity; however, no direct evidence, such as spectroscopic data or other supporting factors, has been presented.^[17,18] Although it has been suggested that adsorption of proton inhibits the adsorption of oxygen molecules, leading to the degradation of the activity, no experimental identification of the elementary steps or evidence-based discussions based on such processes have been conducted.^[17,19–21]

To spectroscopically elucidate the mechanism of this reduced activity, we have shown that the active site is composed of pyridinic nitrogen (pyri-N)^[22] and have used model catalysts to elucidate the reaction mechanism of pyri-N in acidic electrolytes.^[23] The pyri-N is protonated by acid-base equilibrium in acidic electrolytes, as shown in Equation (1), and exists as protonated pyri-N (pyri-NH⁺).



Next, as shown in Equation (2), the adsorption of oxygen molecules on adjacent carbon atoms proceeds coupled with the hydrogenation of pyri-N (pyri-NH) by electron transfer^[23].



The important point in this equation is that the electrons added by the formation of pyri-NH enter the π^* orbital of the carbon structure, where they have unpaired electrons that interact with the oxygen molecule, thereby promoting the reaction. The Gibbs free energy gain in Equation (2) is greater compared to the gain in the absence of an oxygen molecule, owing to the adsorption energy of the oxygen molecule.^[23]

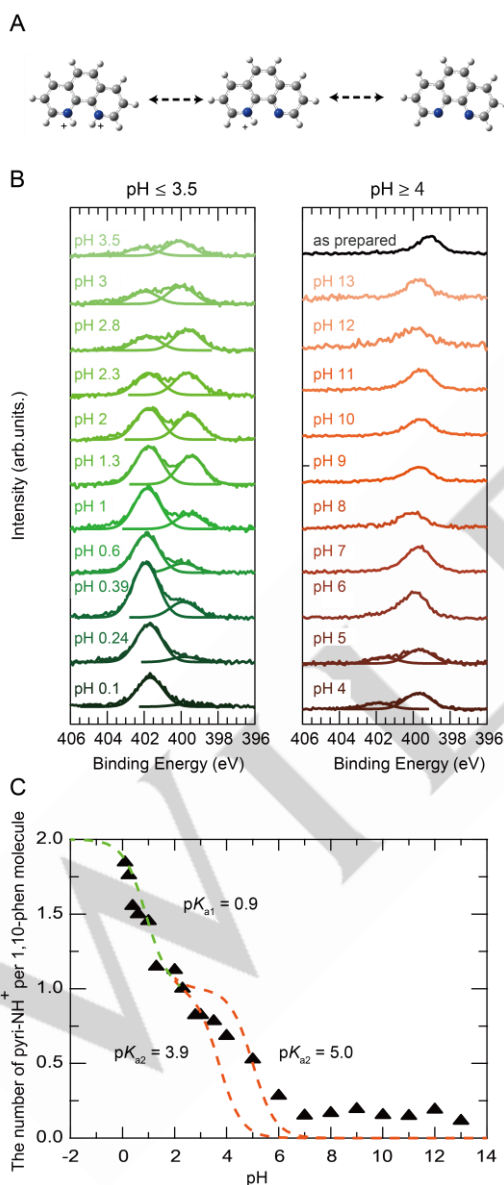
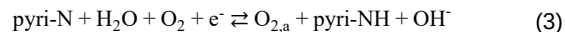


Figure 1. Acid-base equilibrium of pyridinic nitrogen in the model catalyst | (A): Schematic representation of the acid-base equilibrium of the 1,10-phen. (B) N 1s spectra obtained after immersing the 1,10-phen/CB model catalyst in electrolytes with pH ranging from 0.1 to 13. (C) Plot showing the proportion of pyri-NH⁺ relative to the total pyri-N as a function of pH.

According to the acid-base equilibrium, pyri-N exists as pyri-NH⁺ in acidic electrolytes and as pyri-N in basic electrolytes. Therefore, in basic electrolytes, pyri-N may react directly with H₂O to form pyri-NH, as shown in Equation (3), in contrast to Equation (2).



In Equation (2), pyri-NH⁺ is lower in energy and more stable than the bare state (pyri-N). Consequently, the Gibbs free energy change in Equation (2) is expected to be smaller than that in Equation (3). This means that the redox potential will be lower. In other words, when the pH is around pK_a for pyri-N, the redox potentials of Equations (2) and (3) are the same because the ratio of pyri-NH⁺ to pyri-N is 1:1. As the pH decreases and pyri-NH⁺ becomes more stable, the redox potential of Equation (2) is lowered.

The objective of this study is to elucidate the deactivation mechanism of nitrogen-doped carbon catalysts with pyri-N as the active site for the ORR in acidic media, with a focus on the base properties of pyri-N. We hypothesize that Equation (3) proceeds in basic electrolytes and that the difference in redox potential from Equation (2) is the cause of the pH-dependent variation in activity. As a result, the protonation of pyri-N may lower the redox potential of Equation (2), leading to the degradation of the activity of nitrogen-doped carbon in acidic electrolytes. To verify this, we employed a model catalyst with a homogeneous pyri-N structure and investigated the acid-base equilibrium of pyri-N and the formation potential of pyri-NH by X-ray photoelectron spectroscopy.

Results and Discussion

Quantification of Protonation States of Pyri-N in the Model Catalyst at Each pH

First, the chemical states of pyri-N in the model catalyst were investigated in both acidic and basic electrolytes, and the results are presented in Figure 1. The model catalyst was 1,10-phenanthroline (1,10-phen), a pyri-N-containing aromatic molecule, adsorbed on a carbon black (CB) support.^[23,24] The pK_a in the 1,10-phen/CB model catalyst was first measured using X-ray photoelectron spectroscopy (XPS). As shown in Figure 1A, 1,10-phen has two pK_a because it has two pyri-N. The lower pK_a is designated as pK_{a1} and the other as pK_{a2}. For 1,10-phen dispersed in aqueous solution, pK_{a1} = 1.29 and pK_{a2} = 4.93.^[25] After immersing 1,10-phen/CB in aqueous solutions of different pH, N 1s spectra were measured, and pK_a was determined from the peak area ratio of pyri-N and pyri-NH⁺. Figure 1B shows the N 1s spectra measured after immersing the model catalyst in various pH electrolytes. Peaks attributed to pyri-N and pyri-NH⁺ appeared at 399.5 eV above pH 6 and at 401.5 eV below pH 5, respectively.^[26] The binding energy of pyri-N at 399.5 eV, which is higher than the 399.0 eV observed in the as-prepared model catalyst, may be attributed to the formation of hydrogen bonds between water molecules and pyri-N upon immersion in the electrolytes (Figure S1).^[27,28]

Figure 1C plots the number of pyri-NH⁺ molecules, which corresponds to a single molecule of 1,10-phen, as a function of pH based on the ratio of the N 1s peak area. The dotted lines in the figure represent simulation curves indicating behavior at pK_{a1} of 0.9 and pK_{a2} of 3.9, as well as at pK_{a1} of 0.9 and pK_{a2} of 5.0. The results of the fitting with this simulation curve were evaluated as $pK_{a1} = 0.9$, $pK_{a2} = 3.9\sim 5.0$. These values are close to but slightly smaller than the pK_a values for the isolated 1,10-phen molecule. This difference can be attributed to the hydrophobic effect of CB surface on which 1,10-phen is loaded. Figure 1C shows that between pH 2 and 5, one proton is coordinated to 1,10-phen, and below pH 2, a second proton is coordinated. Therefore, it is important to note that the chemical state of pyri-N is already different when this model catalyst is immersed in acidic and basic electrolytes.

Activity and Selectivity of the Model Catalyst for ORR by pH

Next, we examined the change in activity of the 1,10-phen/CB model catalyst for the ORR due to acid-base equilibrium. Figures 2A and S2 show the pH dependence of the linear sweep voltammogram (LSV). As a comparison, the LSV of Pt/Carbon (Pt/C) catalyst is also plotted in the figure. These figures clearly show the degradation of the activity in the acidic region. Figure 2B shows the onset potential (-0.1 mA/cm^2 potential) obtained from Figure 2A plotted against pH. In Figure 2B, the onset potential was almost constant at pH 1–5, and the onset potential showed a slope of 59 mV/pH at pH 5–13. In other words, the elementary process that determines the onset potential changes from around pH 5. This change, in conjunction with the results in Figure 1, may be related to the state of the nitrogen, pyri-NH⁺ and pyri-N, in the electrolytes prior to the reaction. The degradation of the activity of 10-phen/CB in the acidic region is not due to nitrogen leaching, poisoning by impurities, or adsorption of counter anions. When ORR measurements with different counter anions were performed under acidic electrolytes, no change in onset potential was observed (Figure S4). This means that the degradation of the activity in acidic electrolytes is not due to the adsorption of counter anions. In addition, since no significant change in the amount of pyri-N was observed before and after immersion in the acidic electrolyte (Figure S5, S6), the degradation of the activity is not attributed to the leaching of pyri-N. No impurities such as Cl and Br were confirmed by XPS, indicating that the effect of impurities on the degradation of the activity is negligible.

Variation in Pyri-NH Formation Potential with Changes in pH

Furthermore, we investigated the difference in reaction pathways between acidic (pH 1) and basic electrolytes (pH 13). We focused on whether the direct 4-electron reduction or 2+2-electron reduction proceeds. For the analysis, the Nabae method^[29,30] was employed to examine the dependence of H₂O₂ production on the amount of catalyst in the ORR, distinguishing between direct 4-electron reduction current density (i_1^0), H₂O₂ production current density (i_2^0), and H₂O₂ reduction current density (i_3^0) (Supplementary texts). Figures 2C and 2D show the total disk

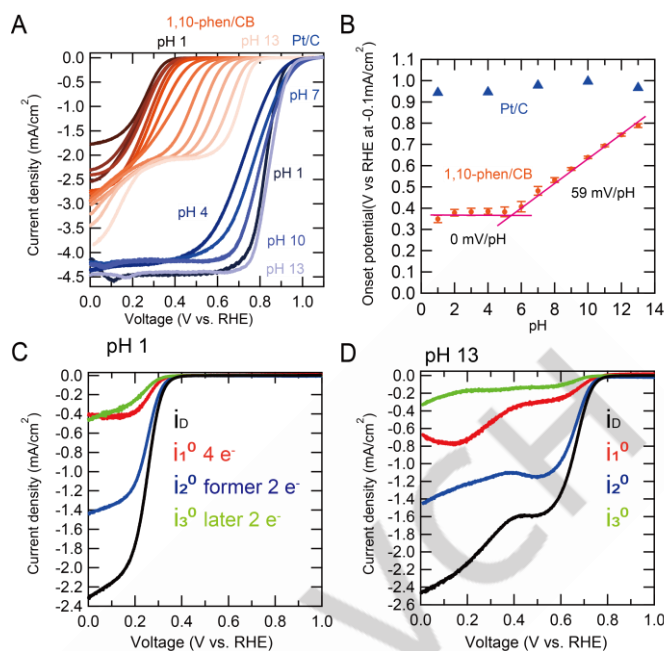


Figure 2. Activity and reaction pathway of the model catalyst at various pH | (A) LSV of the ORR for Pt/C and 1,10-phen/CB. (B) Onset potentials (-0.1 mA/cm^2 potential) for Pt/C and 1,10-phen/CB. (C), (D) Contributions of the current densities for the i_1^0 , i_2^0 , and i_3^0 to the i_D by the 1,10-phen/CB model catalyst at pH 1 and pH 13.

current density (i_D), i_1^0 , i_2^0 , and i_3^0 , at pH 1 and pH 13, respectively. pH 1 shows that i_D accounts for approximately 60 % of the i_2^0 in the first stage, and i_3^0 and i_1^0 account for approximately 20 %. Since i_1^0 is primarily derived from the CB support (Figure S7A), little 4-electron reduction occurs at 1,10-phen/CB. Therefore, it is considered that 2-electron and 2+2-electron reductions predominate, leading to the formation of H₂O₂ and H₂O through the H₂O₂ intermediate. The formation of H₂O₂ via a 2-electron reduction, without further reduction to H₂O, corresponds to $i_2^0 - i_3^0$, while the formation of H₂O via the H₂O₂ intermediate corresponds to $2i_3^0$. Consequently, the ratio of $i_2^0 - i_3^0 : 2i_3^0 = 5:4$ suggests that the formation of H₂O₂ and H₂O occurs to a similar extent. Next, the results for pH 13 (Figure 2D) showed that the i_2^0 accounted for approximately 80 % of the i_D at around 0.8 V of the onset potential; excluding the effect of the CB support (Figure S7B), H₂O₂ formation was the dominant process. When the applied voltage fell below 0.6 V vs. RHE, i_2^0 became a constant value and i_1^0 began to flow. This means that 4-electron reduction began to proceed in the low-potential region. Note that the redox potential for H₂O₂ reduction is 1.78 V vs. RHE, and for 2+2-electron reduction, the onset potential is determined by H₂O₂ formation in the first half. Thus, at both pH 1 and 13, the onset potential is determined by the redox potential of H₂O₂ production. In other words, the difference in onset potentials in acidic and basic electrolytes in Figure 2B is not due to the difference in reaction pathways but to the difference in redox potentials of the elementary processes leading to H₂O₂ formation. Nabae et al. have reported that, under acidic conditions, nitrogen-doped carbon catalysts follow the Nabae methods, in which the 2-electron reduction pathway is dominant with a minor contribution from the 2+2-electron pathway, while the 4-electron reduction does not proceed.^[31] In contrast, at pH 13, the 2-electron reduction proceeds at high potentials, and the 4-electron

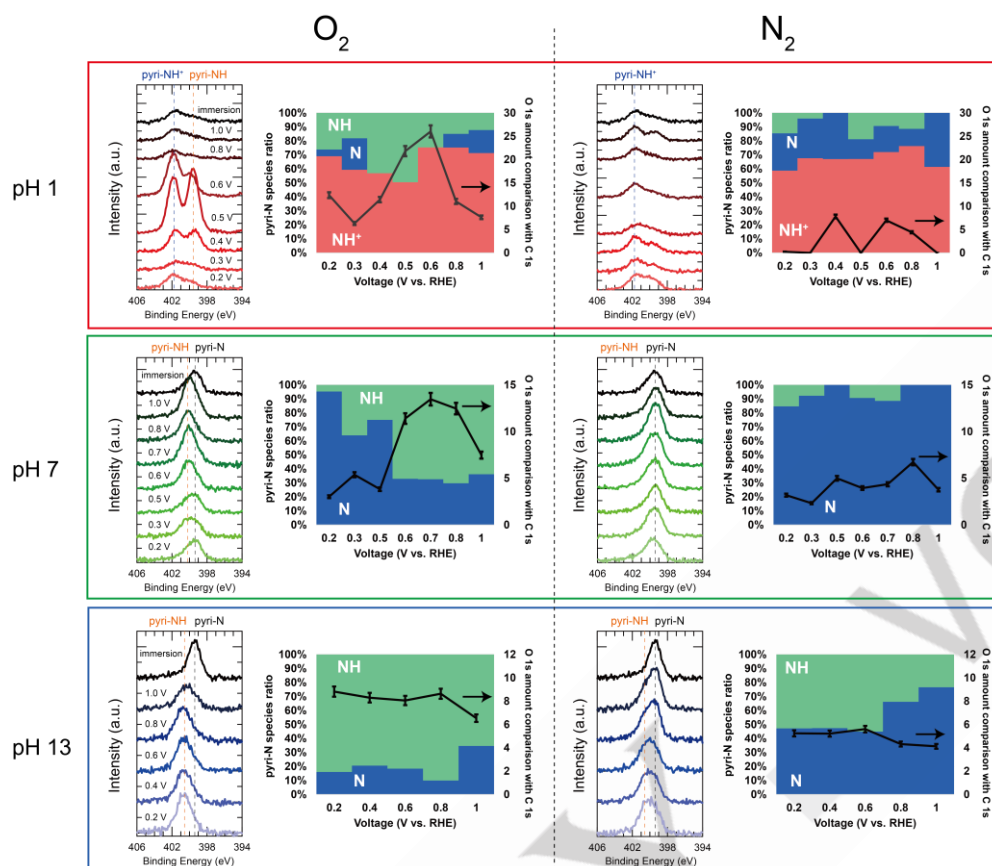


Figure 3. Evaluation of the hydrogenation potential of pyri-N | N 1s spectra measured ex-situ after applying potential to the 1,10-phen/CB. The plots show the proportions of pyri-N, pyri-NH⁺, and pyri-NH relative to total pyri-N, as well as the O 1s peak intensity normalized to the C 1s signal, as a function of applied potential.

reduction becomes dominant at lower potentials. Sakaushi et al. also demonstrated that nitrogen-doped carbon catalysts with a high content of pyri-N tend to follow a reaction pathway close to the 2-electron reduction.^[32] These results align perfectly with our observations that the model catalyst follows nearly 4-electron reduction pathway at low potentials in pH 13, and that the 2-electron reduction pathway predominates at pH 1 and at high potentials in pH 13. These findings emphasize the role of pyri-N as the active site that determines the reaction pathway in nitrogen-doped carbon catalysts.

As mentioned earlier, the formation behavior of pyri-NH coupled with adsorption of oxygen molecules, which is the focus of this study, was investigated in acidic and basic electrolytes. The formation behavior of pyri-NH was measured by ex-situ XPS after applying a potential of 0.2–1.0 V in the presence of O_2 and N_2 . Figure 3 shows the N 1s spectrum, and Figure S8 shows the C 1s and O 1s spectra. In the N 1s spectrum, the peaks at 399.5 eV and 401.5 eV correspond to pyri-N and pyri-NH⁺, respectively, and the peaks at 400.2–400.6 eV correspond to pyri-NH.^[22,23] The peak areas of pyri-N, pyri-NH⁺, and pyri-NH as a percentage of the total peak area of the spectrum and the peak area of O 1s normalized by C 1s are plotted together in Figure 3. When the electrolyte was saturated with O_2 at pH 1, only pyri-NH⁺ was observed above 0.7 V, whereas below 0.6 V, the formation of pyri-NH began. Additionally, the formation of pyri-NH was accompanied by an increase in the O 1s peak area. In contrast,

when the electrolyte was saturated with N_2 , no pyri-NH formation was detected. These observations suggest that Equation (2) is taking place, where the formation of pyri-NH is coupled to the adsorption of oxygen molecules. It should be noted here that the N 1s peak intensity at 1.0 V is smaller than those at 0.4–0.6 V observed in our previous results.^[23] This result does not imply that the actual amount of nitrogen has changed. This is a photoemission issue in ex-situ XPS measurements, likely due to photoemission interference from water molecules hydrating the pyri-NH⁺ species. At 1.0 V, pyri-N is protonated to form pyri-NH⁺, a cationic species that coordinates with water molecules, leading to increased hydration and a consequent decrease in the N 1s photoelectron intensity. In contrast, at 0.4–0.6 V, pyri-N is converted to neutral pyri-NH, which exhibits reduced hydration, resulting in an increase in the N 1s photoelectron intensity. At pH 7 and 13, pyri-N was present as bare pyri-N when the model catalyst was immersed in the electrolytes. In electrolytes saturated with O_2 at both pH 7 and 13, the formation of pyri-NH was already observed upon applying 1.0 V, along with a corresponding increase in the O 1s peak area. On the other hand, in the electrolyte saturated with N_2 at pH 13, pyri-NH was formed at 0.6 V, and no increase in the O 1s peak was observed at that time. These results indicate that the formation of pyri-NH proceeded even in the absence of O_2 , as shown in Equation (4). However, the reaction described in Equation (3), involving O_2 adsorption, led to an increase in the potential for pyri-NH

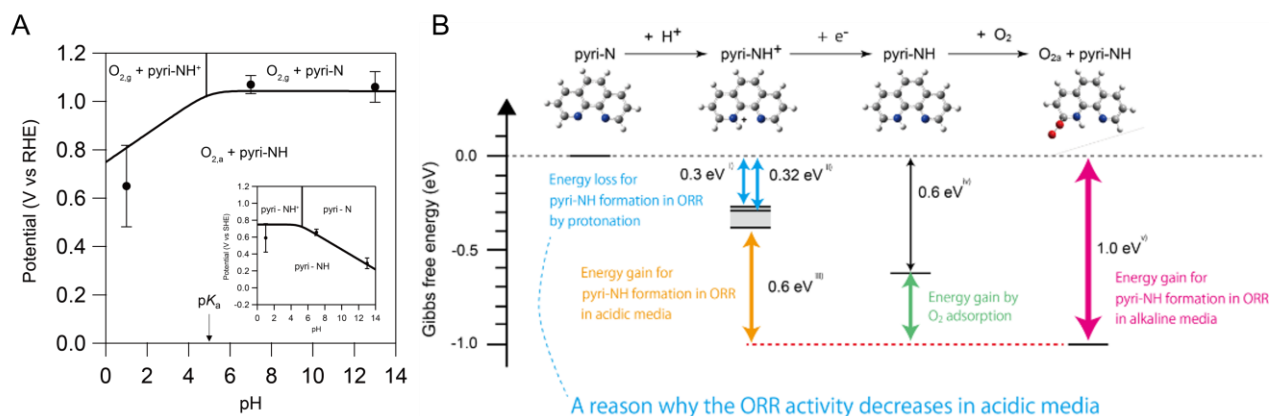
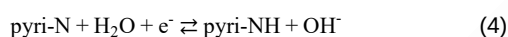
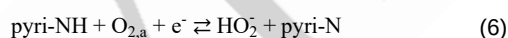
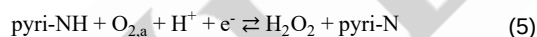


Figure 4. (A) Pourbaix diagram in RHE standard showing the possible stable phases of nitrogen species of 1,10-phenanthroline on CB in the presence of O_2 . The insert graph is SHE standard. (B) Summary of experimental results and factors contributing to degraded activity in acidic electrolytes | Gibbs energy diagram. i) Proton adsorption energy of 0.3 eV calculated from the pK_a measurement in Figure 1. ii) Proton adsorption energy of 0.32 eV obtained from DFT calculations. iii) From pyri-NH formation potential of 0.6 V in O_2 saturation in pH 1 iv) From pyri-NH formation potential of 0.6 V in N_2 saturation in pH 13 in Figure 3. v) From pyri-NH formation potential of 1.0 V in O_2 saturation in pH 13 in Figure 3.

formation. Therefore, the results presented in Figure 3 clearly demonstrate that the difference between acidic and basic electrolytes is reflected in the formation potential of pyri-NH and the adsorption of oxygen.



It is also worth noting that, in the presence of O_2 at pH 1 and 7, as the potential was further decreased and the reaction accelerated, the formed pyri-NH decreased again, accompanied by a reduction in the O 1s peak area. This suggests that at steady state, the hydrogen of pyri-NH is consumed in the reaction. Given that a 2-electron or 2+2-electron reduction is occurring, it is likely that the reactions described in Equations (5) and (6) have taken place in acidic and basic electrolytes, where the formed pyri-NH reacts with O_2 to produce H_2O_2 or HO_2^- , respectively. These equations are crucial for illustrating the role of pyri-N in the hydrogenation of O_2 . That is, the hydrogen from pyri-NH is utilized in the hydrogenation process.



As discussed above, near the onset potentials at pH 1 and pH 13, only the 2-electron reduction leading to H_2O_2 formation occurs. However, since the first electron reduction potentials for pyri-NH formation and adsorption of oxygen molecules are higher than the onset potential (Figures 2 and 3), the rate-determining step should exist in the second electron process (Equations (5) and (6)). We assume that Equations (5) and (6) include the reduction of $O_{2,a}$ to OOH_a and the thermal hydrogenation process between pyri-NH and OOH_a , and the thermal process is rate-determining step. This mechanism can explain the Tafel slopes of 60 mV/dec observed at both pH 1 and pH 13 (Figure S9)

A Mechanism of Activity Decrease in N-Doped Carbon Catalysts for ORR

In this study, we systematically investigated the pH dependence of the formation potential of pyri-NH coupled with adsorption of

oxygen molecules (Equations (2) and (3)). As shown in Figure 3, this coupled reaction proceeded at approximately 1.0 V vs. RHE at pH 7 and 13, whereas at pH 1, the reaction occurred at about 0.6 V vs. RHE. Therefore, at higher than 0.6 V vs. RHE, oxygen molecules cannot adsorb, and ORR does not proceed. This is a major cause of degradation of the activity in acidic electrolytes. Figures 4A and S11 present Pourbaix diagrams related to the acid-base equilibrium of pyri-N (Supporting Information). These diagrams allow for a quantitative explanation of the potentials for pyri-NH formation coupled with adsorption of oxygen. A critical point is that the pathway for pyri-NH formation differs depending on whether it starts from pyri-N or pyri-NH⁺. In basic electrolytes, adsorption of oxygen and pyri-NH formation occur starting from pyri-N at a calculated potential of about 1.0 V vs. RHE. In contrast, at pH 1, $O_{2,a} + \text{pyri-NH}$ forms from pyri-NH⁺, at a potential of about 0.6 V vs. RHE, which is 0.4 eV lower than the corresponding potential starting from pyri-N. This difference (−0.4V) corresponds to the potential change due to the acid-base equilibrium of pyri-NH⁺ by about 0.3 V (5 pH units × 59.2mV/pH). In other words, the difference in the formation potentials of $O_{2,a} + \text{pyri-NH}$ between pH 1 (0.6V) and pH 13 (1.0V) arises from the acid-base equilibrium of pyri-N. Moreover, as shown in Figure S11, in the absence of oxygen molecules, the formation potential of pyri-NH is lower. This suggests, as we have already pointed out, that the potential in reactions (2) and (3) are elevated by the potential corresponding to the adsorption energy of oxygen molecules. Furthermore, Figure 4B presents the Gibbs free energy diagram redrawn from the Pourbaix diagram in Figure 4A. The formation potential of pyri-NH coupled with adsorption of oxygen molecules corresponds to the changes in Gibbs free energy involved in the reaction. In basic electrolytes, the coupled reaction starts from pyri-N, with a free energy change of 1.0 eV, whereas the free energy change for pyri-NH formation without adsorption of oxygen molecules is 0.6 eV. This 0.4 eV difference, derived from equations (3) and (4), corresponds to the adsorption energy of oxygen molecules, indicating that adsorption of oxygen molecules raises the formation potential of pyri-NH. Conversely, in acidic electrolytes, the coupled reaction starts from pyri-NH⁺, with a free

energy change of 0.6 eV. Here, the energy level of pyri-NH⁺ calculated using pK_a (0.3 eV) and DFT calculation (0.32 eV) coincides. Therefore, this approximate 0.3 eV change in free energy corresponds to the degradation of the activity. The important point is that the difference between the reduction potentials of 0.6 V at pH 1 and 1.0 V at pH 13 for pyri-NH formation is a key factor contributing to the degradation of the catalytic activity in acidic electrolytes. To enhance the activity in acidic electrolytes, the energy drop associated with pyri-NH⁺ formation, as depicted in Figure 4, must be minimized. One potential approach to achieve this is by lowering the pK_a of pyri-N, which can be accomplished by increasing the hydrophobicity of the region surrounding the active site. In fact, the introduction of a macroscopic cage-like structure into nitrogen-doped graphene, which increases the hydrophobicity near the active sites, has successfully improved the onset potential.^[33,34] In the future, it will be desirable not only to suppress the stabilization of pyri-NH⁺ but also to increase the adsorption energy of oxygen molecules, thereby enlarging the energy drop from pyri-NH⁺ to pyri-NH + O_{2,a} and raising the redox potential to approximately 1.0 V.

Conclusions

This study elucidated, at the elementary process level, the mechanism behind the activity degradation in acidic electrolytes, the issue preventing the widespread adoption of pyridinic nitrogen (pyri-N)-doped carbon as a fuel cell catalyst. Using a model catalyst with a uniform pyri-N local structure, we focused on the formation of pyri-NH coupled with oxygen molecule adsorption and elucidated the mechanism of the activity degradation of nitrogen-doped carbon catalysts in acidic electrolytes. By measuring the state changes of pyri-N, catalytic activity, reaction pathways, and the behavior of pyri-NH in both acidic and basic electrolytes, it was found that the degradation of the ORR activity in nitrogen-doped carbon catalysts in acidic electrolytes is attributed to the stabilization of pyri-NH⁺, driven by the basicity of pyri-N. In other words, in acidic electrolytes, the redox potential for pyri-NH formation is lowered because the reaction starts from the stabilized pyri-NH⁺. In contrast, in basic electrolytes, pyri-NH formation proceeds directly from pyri-N without proton adsorption, allowing the ORR to proceed at higher potentials. Therefore, improving hydrophobicity or designing functional groups to reduce the proton adsorption energy of pyridinic nitrogen—in other words, lowering its pK_a—can enhance catalytic activity.

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Author Contributions

K.T. and J.N. conceptualized the study. K.H., J.N., and K.T. developed the methodology. K.H. conducted the investigation and data visualization, with support from K.T. Funding acquisition was handled by K.H., J.N., and K.T. K.T. managed the project and supervised the work with J.N. K.H. wrote the original draft, and K.T. and J.N. contributed to review and editing.

Competing Interests

Authors declare that they have no competing interests.

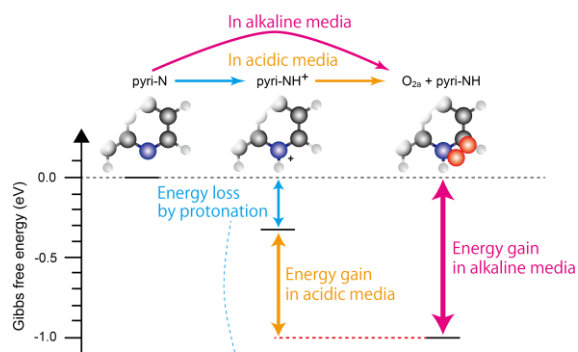
Data Availability Statement

All data are available in the main text or the supporting information.

Keywords: Carbon catalyst, oxygen reduction reaction, reactivation mechanism, surface science.

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A reason why the ORR activity decreases in acidic media

The oxygen reduction reaction (ORR) of nitrogen-doped carbon catalysts proceeds through electron injection into the π^* orbital, triggered by the hydrogenation of pyridinic nitrogen. By closely tracking the changes in the electronic state during the reaction, we have reported that the decrease in ORR activity in acidic electrolytes is due to the protonation of pyridinic nitrogen, which precedes its hydrogenation.