Identification of the active triple-phase boundary of a non-Pt catalyst layer in fuel cells

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The rational design of non-Pt oxygen reduction reaction (ORR) catalysts and catalyst layers in fuel cells is largely impeded by insufficient knowledge of triple-phase boundaries (TPBs) in the micropore and mesopore ranges. Here, we developed a size-sensitive molecular probe method to resolve the TPB of Fe/N/C catalyst layers in these size ranges. More than 70% of the ORR activity was found to be contributed by the 0.8- to 2.0-nanometer micropores of Fe/N/C catalysts, even at a low micropore area fraction of 29%. Acid-alkaline interactions at the catalyst-polyelectrolyte interface deactivate the active sites in mesopores and macropores, resulting in inactive TPBs, leaving micropores without the interaction as the active TPBs. The concept of active and inactive TPBs provides a previously unidentified design principle for non-Pt catalyst and catalyst layers in fuel cells.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are clean and efficient electrochemical energy devices, but their commercialization has been severely impeded by the high expense and scarcity of Pt catalysts. Pyrolyzed transition metal/nitrogen/carbon (M/N/C) materials, especially Fe/N/C, have been shown to be the most promising nonprecious metal catalysts to replace Pt for use in PEMFCs to catalyze the cathodic oxygen reduction reaction (ORR) (1, 2). Through active site structure probing (3, 4) and material innovation (5–7), the intrinsic activity of previously developed Fe/N/C catalysts, which has mostly been tested in aqueous rotating disk electrodes (RDEs), has been greatly improved and has even approached that of Pt in some cases. However, there exists a large gap between aqueous electrode tests and fuel cells, mainly originating from the considerable differences in reaction interfaces (8, 9). In the aqueous RDE test, the ORR takes place at the solid-liquid two-phase interface. Conversely, in fuel cells, the reactions mainly take place at the triple-phase boundary (TPB), where the electrocatalyst, electrolyte, and reactant gas come into contact. For this reason, many ORR catalysts that perform well in aqueous RDE tests do not show high working performance in fuel cells (10). In addition, to prevent electrolyte leaching, perfluorosulfonic acid polyelectrolytes (e.g., Nafion) are used in PEMFCs (11). Unlike that of the free acids (e.g., H2SO4 or HClO4) that are in aqueous tests, the sulfonic anion is fixed on the polymer backbone, and only H+ can migrate (12, 13). The single-ion mobility and large molecular size of Nafion make the TPB very complex, especially for heterogenous Fe/N/C catalysts with atomically dispersed active sites in porous structures.

To achieve high fuel cell performance, it is critical to construct a sufficiently efficient TPB. However, the rational construction of such a TPB is mainly impeded by insufficient knowledge of the TPB structure. First, recent studies of TPB in fuel cell catalyst layers have mainly relied on x-ray nanocomputed tomography (14, 15), x-ray scattering tomography (16, 17), helium ion microscopy (18), and focused ion beam scanning electron microscopy (SEM) (19). These advanced characterization methods can be used to image catalyst-electrolyte interfaces, which reflect the number and distribution of TPBs (20, 21). However, the spatial resolutions of these methods are tens of nanometers (22), which is not sufficient to resolve interface information in micropores (<2 nm) and mesopores (2 to 50 nm). Second, recent studies of TPBs have rarely considered catalyst-electrolyte interfacial interactions. These interactions are a determining factor that governs the efficiency of the TPBs. If a strong catalyst-electrolyte interfacial interaction exists that can deactivate active sites, then the typical TPB will no longer be efficient for electrochemical reactions. Coincidentally, pyrolyzed Fe/N/C catalysts inevitably contain some alkaline sites, such as pyridinic N species, which may be protonated by the H+ in Nafion (23). Ignoring these acid-alkaline interfacial interactions may result in an inaccurate understanding of the TPB in the Fe/N/C catalyst layer and consequently incorrect guidance on the design of catalysts and catalyst layers.

Molecular probe methods have important advantages in terms of selectivity and specificity and are suitable for in situ studies of complex systems. However, these methods were previously used only to identify the structures of active sites of M/N/C catalysts in aqueous solutions (24). Here, we developed a size-sensitive molecular probe method to reveal effective TPBs and interface interactions in an Fe/N/C catalyst layer in the micropore and mesopore ranges under fuel cell working conditions and gained a previously unidentified insight into the structural design of catalysts and catalyst layers. We found that the TPB formed in micropores between 0.8 and 2.0 nm contributes more than 70% of the ORR activity, although the fraction of the micropore area is as low as 29%. This observation contradicts the previous general hypothesis that ORR active sites in mesopores or macropores are more efficient than micropores because of fast mass

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transfer and ease of formation of the TPB (25, 26). This discrepancy originates from an acid–alkaline interaction of the catalyst–electrolyte interface, i.e., protonation of pyridinic N species in Fe/N/C by Nafion, which deactivates the active sites in mesopores or macropores, resulting in an inactive TPB. This interaction is absent in micropores due to the large size of Nafion, ensuring high catalytic activity and consequently an active TPB.

RESULTS AND DISCUSSION

The Fe/N/C catalyst used in this work was prepared from poly-m-phenylenediamine by a two-step pyrolysis under an Ar atmosphere and was termed PDA-Ar (24). The catalyst exhibited high ORR activity and a repeatable current density of 130 to 137 mA cm⁻² at 0.8 V_{irr-free} (after correction for ohmic loss R) at kinetic region in H₂–O₂ PEMFC (fig. S1). Consistent with most active M/N/C catalysts (27–30), the PDA-Ar catalyst was a typical microporous material with a micropore area and an external surface area (pore size: >2 nm) of 27 m² g⁻¹ of the sphere and controlled at 93 m² g⁻¹ of catalyst coverage area is determined by accumulating the projected area whose diameter is approximate to the dynamic diameter. The catalytic reaction for the PDA-Ar catalyst. The organics are taken as a sphere, and the contribution of pores of different sizes, we developed an electrochemical molecular probe method. As shown in Fig. 1A, organic compounds of different sizes (benzene, naphthalene, pyrene, perchloronaphthalene, tetraphenylporphyrin, C₅₀Cl₂₂, and C₉₀Cl₂₇H₃, labeled as Ph, Ph₂, Ph₄, C₁₁Cl₈, Ph₄Pp, C₆₀Cl₂₂, and C₉₀Cl₂₇, respectively) were selected as probe molecules. These chemically inert molecules do not react with the PDA-Ar catalyst, as evidenced by the unchanged background cyclic voltammetry (CV) peak after probe molecules were applied (fig. S3). However, they can be physically absorbed by the micropores or external surface of the catalyst. To exclude the pH interference, we conducted absorption before addition of acidic Nafion electrolyte. Physical absorbing molecules on the external surface are not expected to poison the catalytic sites. However, the organic compounds can block a fraction of micropores and impede the transport of reactants (mainly O₂, because its dynamic diameter is larger than those of H⁺ and H₂O) (31). The largest size (d_p) of pores that can be blocked by organic compounds is reasonably assumed to be the sum of the dynamic diameters of the organic compounds (d_i) and O₂ (d₂), that is, d_p = d_i + d₂. When the pore size is larger than d_p, the gap between the pore wall and the organic compounds is still large enough for reactants to access. Therefore, absorption cannot considerably decrease the fuel cell performance in the kinetic region, i.e., 0.8 V, where the mass transfer is not a limiting factor. By investigating the response of the PDA-Ar cathode toward organic compounds of different sizes, the contribution to ORR activity by pores of different sizes can be differentiated.

For the fuel cell activity test, the catalyst surface coverage by the organics should be kept constant because it can affect the fuel cell activity. The same surface coverage was achieved by optimizing the starting organics concentration for absorption. Figure S4 plots the curve of catalyst coverage area versus the starting organics concentration for the PDA-Ar catalyst. The organics are taken as a sphere, whose diameter is approximate to the dynamic diameter. The catalyst coverage area is determined by accumulating the projected area of the sphere and controlled at 93 m² g⁻¹ with <4% of deviation for each absorption molecule (fig. 1B). The size-dependent organics distribution was verified by measuring the Ar isothermal adsorption/desorption. The test was conducted after the organics were applied to the catalyst surface but before the catalyst was fabricated into the membrane electrode assembly (MEA). The Ph and Ph₄Pp decreased the micropore accessibility while affecting little on the mesopore or macropore region (fig. S5). The larger Ph₄Pp blocked more micropore than the smaller Ph even at the same catalyst surface coverage. By contrast, the largest C₉₀Cl₂₇ was mainly absorbed by the external surfaces and affected little on the micropore accessibility. This experimental observation is in good agreement with the assumption of size-selective pore blocking.

After clarifying these points, the fuel cell activity test was conducted, as shown in Fig. 1C. The current density at 0.8 V_{irr-free} of these samples relative to those of organic-free samples are shown in Fig. 1D. The ORR performance was dominated by the molecular size of the organic compounds. After the addition of Ph, only 9.0% of the ORR activity at 0.8 V_{irr-free} was lost relative to that of the bare sample. Ph can block active sites in pores smaller than 0.8 nm (d_p ≈ 0.8 nm; table S1). The observed activity loss suggests that pores smaller than 0.8 nm contribute, at most, 9.0% to the ORR activity. As the size of the organic molecules increases, the ORR activity of the PDA-Ar catalyst decreases. At a critical size of organic compounds, corresponding to Ph₄Pp (d_p ≈ 2.0 nm), the current density at 0.8 V_{irr-free} decreased by 86.3%. This result suggests that pores between 0.8 and 2.0 nm contribute 77.3% to the ORR activity. Larger probe molecules, e.g., C₅₀Cl₂₂ (d_p ≈ 2.4 nm) and C₉₀Cl₂₇ (d_p ≈ 3.0 nm), are too large to enter micropores; they are mainly absorbed on the external surfaces of the PDA-Ar catalyst. Correspondingly, less than 10% of the ORR activity was lost, supporting our expectation that physically absorbing molecules on the external surface do not poison the catalytic sites and have little impact on the intrinsic ORR activity. By means of the molecular probe experiment, the contribution of pores of different sizes to the ORR activity can be evaluated, as shown in Fig. 1E, and the efficient pore size was determined to be 0.8 to 2.0 nm for the PDA-Ar catalyst.

To further strengthen the reliability of the molecular probe method and as-derived conclusion, we conducted several exclusion experiments. The factors that are relevant to the fuel cell activity were examined, e.g., the thickness and surface wettability of the catalyst layer and the conductivity of the MEA, so as to verify that the decrease in performance is actually caused by size-dependent pore blocking rather than other factors. The wettability of the catalyst layer was compared by measuring the surface contact angle (fig. S6). The change in the cathode thickness was determined by comparing the cross section using SEM (fig. S7). The proton transport resistance (R_H⁺) of the MEA was measured by electrochemical impedance spectroscopy (fig. S8), and data analysis and fitting were according to a previously reported method of the transmission line mode in an H₂/N₂ atmosphere (32, 33). It was observed that the thickness and wettability of the catalyst layer as well as the conductivity of the MEA are not changed by the addition of organics, further supporting the notion that the size-dependent pore blocking dominates the fuel cell activity loss.

The PDA-Ar catalyst is a typical microporous material. To demonstrate the universality of the probe method and determine efficient pore size ranges for the ORR, we prepared five Fe/N/C catalysts with different pore structures by altering the synthetic process. The synthetic process of PDA-CO₂ series catalysts was similar to that of the PDA-Ar catalyst, except that a CO₂–Ar mixture (1.25, 7, 8.5, and 10% CO₂, respectively) was used instead of pure Ar in the first pyrolysis step (34). CO₂ can etch carbon under high temperatures (CO₂ + C → 2CO) to create more pores. To date, the most active Fe/N/C catalysts have been derived from zeolitic imidazolate frameworks (ZIFs) (35–37). Therefore, a ZIF-Ar catalyst was prepared by
a one-step pyrolysis of Fe-doped ZIF-8 particles under an Ar atmosphere (38). Figure 2A shows the Ar absorption-desorption isotherms for the six Fe/N/C catalysts, including the PDA-Ar catalyst. Table S2 lists the micropores and external surface area of the six catalysts. Their micropore surface fraction is shown in Fig. 2B and follows the order ZIF-Ar (62%) > PDA-Ar (55%) > PDA–1.25% CO₂ (47%) > PDA–7% CO₂ (36%) > PDA–8.5% CO₂ (33%) > PDA–10% CO₂ (29%), ranging from microporous type to hierarchically porous type. The five PDA series catalysts showed similar carbon morphology and consisted of roughly 100-nm aggregated particles, which is different from the ZIF-Ar consisting of polyhedral carbon structures (fig. S9).

The Fe loading of the six catalysts was given by inductively coupled plasma mass spectrometry (ICP-MS), as shown in table S3. The five PDA series catalysts showed a low Fe content of no more than 0.78 weight (wt) %. The combination of x-ray absorption spectroscopy (XAS; fig. S10) and x-ray diffraction (fig S11) confirmed the atomically dispersed Fe species in the five PDA series catalysts. By contrast, the ZIF-Ar exhibited a high Fe content of up to 4.22 wt %, which was attributed to the formation of Fe₃C particles. Among them, the three catalysts, i.e., PDA–7% CO₂, PDA–8.5% CO₂, and PDA–10% CO₂, can be regarded as a group of near model catalysts. They exhibited the same Fe status and the high similarity in Fe content.
(<15% of the variation), carbon morphology (fig. S12), carbon defect degree (fig. S13), and surface wettability (fig. S14). Therefore, the six Fe/N/C catalysts not only contain three rigorous near-model comparison samples but also show catalyst diversity. If the probe method can be applied to the six Fe/N/C catalysts, then the reliability and universality of as-derived conclusion will be strengthened.

Similar to the PDA-Ar case, the plots of catalyst coverage area versus starting organics concentration were plotted for the five catalysts (fig. S15). For a specific Fe/N/C catalyst, the catalyst coverage area remained constant for different-sized organics (fig. S16). Then, the electrochemical molecular probe experiment was conducted (fig. S17). As shown in Fig. 2C, the five Fe/N/C catalysts showed a similar molecular size–dependent activity change trend to the PDA-Ar catalyst. This similarity supports that the 0.8– to 2.0-nm micropores contribute most to the ORR activity, >70% (Fig. 2D), for the six Fe/N/C catalysts, regardless of their micropore surface fraction (Fig. 2B) and pore distributions (fig. S18).

In general, active sites in mesopores or macropores are considered more efficient than those in micropores for the ORR (25), because the former allows fast mass transfer and facile formation of the TPB via Nafion agglomeration (39). However, active sites in micropores with sizes from 0.8 to 2.0 nm contribute more than 70% to the ORR activity in PEMFC, even for the Fe/N/C catalyst PDA–10% CO₂ with a micropore surface fraction of only approximately 29%. This finding is unexpected and needs to be clarified.

The cathode catalyst layer consists of an Fe/N/C catalyst and a polymer electrolyte (i.e., Nafion). Nafion, composed of a fluoro-polymer backbone with sulfonic acid side chains, exists in the form of clusters in solution, with aggregation sizes of approximately 4 nm (13, 40). The sulfonic acid in Nafion can protonate pyridinic N species (logarithmic acid dissociation constant $K_a$, $pK_a = 5.4$; fig. S19) in the mesopores and macropores of the Fe/N/C catalyst but cannot easily neutralize those basic species in micropores (Fig. 3A). This conclusion is supported by the negative correlation between the micropore surface fraction and the protonation degree of pyridinic N species (fig. S20 and table S4). Specifically, for a typical microporous catalyst, 71% of pyridinic N exists in an unprotonated state in the presence of Nafion. For hierarchically porous catalysts (e.g., PDA–10% CO₂), almost 100% of pyridinic N is protonated on the near surface where mesopores or macropores dominate, as detected by x-ray photoelectron spectroscopy (XPS), where the band with a binding energy of approximately 402 eV is assigned to protonated pyridinic N (Py-NH⁺, Fig. 3B) (23, 41). In the interior, where micropores dominate, 95% of pyridinic N still remains in the unprotonated state (398.5 eV), as detected by XPS after Ar ion etching at approximately 50 nm.

To demonstrate the absence of acid-alkaline interface interactions in micropores resulting in high ORR activity, we selected small H₂SO₄ as a probe molecule. Unlike large Nafion, H₂SO₄ can easily enter micropores and protonate pyridinic N species. Figure 3C shows the polarization curves of the PDA–10% CO₂ cathode with and without
H$_2$SO$_4$ treatment (1.0 $\mu$mol mg cat$^{-1}$). In the presence of Nafion alone, the cathode showed a current density of 0.078 A cm$^{-2}$ at 0.8 V$_{iR}$-free. After H$_2$SO$_4$ treatment, the current density at 0.8 V$_{iR}$-free decreased by 85%, which may be attributed to protonation of the micropores by H$_2$SO$_4$. A similar degree of ORR activity loss after treatment with H$_2$SO$_4$ was also observed for nine other Fe/N/C catalysts (Fig. 3D and fig. S21). These observations suggest that the ORR activity in the Fe/N/C cathode is mainly attributed to the micropores, where the acid-alkaline interaction of the catalyst-electrolyte interface is absent.

To clarify the deactivation mechanism of protonation, we conducted a series of physical characterizations and control experiments. Both H$_2$SO$_4$ and HClO$_4$ treatments resulted in an ORR activity loss greater than 70% (fig. S22), excluding the specific adsorption of SO$_4^{2-}$ on active sites. Mössbauer (fig. S23 and table S5) and XAS analyses (fig. S9) revealed that acid treatments have little impact on the coordination structure and number of Fe-N$_x$ active sites, excluding the possibility that the acids destroy the active sites. Therefore, an indirect deactivation mechanism was proposed: The protonation of pyridinic N decreases the catalytic efficiency of adjacent Fe-N$_x$ active sites. Such a mechanism was supported by the following experimental evidence: (i) The neutralization of Py-NH$^+$ to pyridinic N by alkaline treatment led to a 60% recovery of the ORR activity (fig. S24), and (ii) molecular iron phthalocyanine (FePc) with FeN$_4$ active site but without pyridinic N showed an activity loss of 24% after acid treatment versus 75% loss for the PDA-Ar catalyst (fig. S25). The deactivation phenomenon of Fe/N/C catalysts by protonation has been observed by several groups, but the mechanism is still under debate. Changing the electronic structure of the catalyst by the protonation of pyridinic N (42) and incorporating anions with Py-NH$^+$ cations to suppress the ORR (43) have been proposed. To better understand the deactivation mechanism of Py-NH$^+$ on adjacent Fe-N$_x$ active sites, density functional theory calculations were carried out. Two types of Fe-N-C moieties (C$_{35}$-FeN$_4$-N and C$_{73}$-FeN$_4$-N) with different pyridinic N sites were constructed to simulate the ORR processes (fig. S26). It was found that the protonation of pyridinic N weakens the adsorption of O$_2$ on adjacent FeN$_4$ sites (fig. S27). Correspondingly, the O–O bond length is shorter than that without protonation, resulting in a higher energy barrier for the cleavage of O–O bonds and consequently a slower ORR (44, 45).

Another question that needs to be answered is why Fe/N/C catalysts can still show high ORR activity under aqueous RDE tests with H$_2$SO$_4$ or HClO$_4$ as the electrolyte (fig. S28). Because pyridinic N can be rapidly protonated by small molecular acids, the Fe/N/C catalyst should quickly lose its high ORR activity (46). We found that the key factor is Nafion, the most frequently used binder. During the RDE test, the catalyst is first mixed with Nafion in the ink, dispersed and dried on the electrode, and immersed in aqueous solution to lastly perform the ORR. After the mixing and drying processes, Nafion coats the catalyst particles and forms a cation-selective thin film, which limits the entrance of H$_2$SO$_4$ into the micropores by blocking the anion. Therefore, high ORR activity can still be observed in the aqueous RDE test. When acid contact was carried out before coating with Nafion, 72% of the mass activity at 0.8 V$_{RHE}$ was lost (fig. S29). Moreover, if the binder was replaced by polyvinylidene
fluoride without a cation-selective function, then rapid activity loss was observed (fig. S30). These observations support the notion that Nafion protects the micropores. Because of the heterogeneity in particle morphology, Nafion cannot completely cover the catalyst particles. However, N species on the external surface may help the Nafion to coat most of the particles via chemical interaction (47).

On the basis of the above results, we proposed a model for the TPB of Fe/N/C catalyst layers, as shown in Fig. 4. There are two types of TPBs: (i) Mesopores or macropores (>2.0 nm) in which acid-alkaline interactions exist at the catalyst-electrolyte interface and (ii) micropores (0.8 to 2.0 nm) without these interactions. Because the catalyst-electrolyte interaction, i.e., protonation of pyridinic N, deactivates the active sites, the mesopores or macropores contribute less than 30% to the ORR activity. In contrast, micropores (0.8 to 2.0 nm) without the protonation of pyridinic N contribute more than 70% to the ORR activity. To distinguish the two types of TPBs, we defined the former as an inactive TPB and the latter as an active TPB. In active TPBs, Nafion does not directly contact the active sites in the micropores, and proton transfer may occur via a hopping mechanism assisted by one-dimensional water chains (48, 49). Furthermore, this model clarifies the mechanism of mesopores or macropores improving the ORR activity of Fe/N/C catalysts (36). It is not via hosting active sites with faster mass transfer but rather via exposing active sites that are secluded in micropores.

ORR needs H⁺ to pass through micropores to access the active sites. An interesting question is arising: Why do H⁺ cannot protonate the pyridinic N inside the micropores? Most pyridinic N species in the micropores exist as the unprotonated state after the ORR, which is confirmed by the comparison of XPS N1s species before and after five cycles of fuel cell polarization test (fig. S31). Because of large size, Nafion and the attached sulfonic anions cannot enter the micropores. If the pyridinic N species in the micropores are massively protonated without anions, then micropore environment cannot hold the electroneutrality and thus is thermodynamically unfavorable. In contrast, ORR (O₂ + 4H⁺ + 4e⁻ → 2H₂O) will not result in the accumulation of the net charges in the micropores so that this process can occur continuously.

In summary, we developed a size-sensitive molecular probe method to reveal that more than 70% of the ORR activity can be attributed to micropores with sizes from 0.8 to 2.0 nm in the Fe/N/C catalyst layer of PEMFCs, regardless of the micropore surface fraction. The acid-alkaline interaction between the catalyst (pyridinic N) and electrolyte (Nafion) deactivates the active sites in mesopores or macropores, leading to an inactive TPB, although they have faster mass transfer. The absence of these interactions results in the formation of an active TPB in micropores. This study provides insight into the design and construction of advanced Pt-free ORR catalysts and catalyst layers for fuel cells.

**MATERIALS AND METHODS**

**Chemicals**

M-phenylenediamine (98.5%; Shanghai Wulian), p-aminobenzene sulfonic acid (98.5%; Alfa Aesar), chloroform (99%; Sinopharm), sodium hydroxide (99%; Sinopharm), sodium nitrite (99%; Sinopharm), ammonium persulfate (98.5%; Sinopharm), iron trichloride hexahydrate (99%; Sinopharm), FePc (98%; Sigma-Aldrich), dimethyl formamide (DMF; analytical reagent, AR, Sinopharm), Ketjenblack EC600J carbon black (KJ600, AkzoNobel), Ph₄Pp (99%; Macklin), C₁₀Cl₈ (99%; Macklin), C₆₀Cl₂₂ (homemade), C₉₆Cl₃₇ (homemade), Ph (99%; Macklin), Ph₃ (99%; Macklin), Ph₄ (99%; Macklin), sulfuric acid (96%; Sinopharm), hydrochloric acid (37%; Sinopharm), reduced iron powder (98%; Sinopharm), isopropyl alcohol (AR, Sinopharm), ethanol (AR, Sinopharm), dimethyl sulfoxide (AR, Sinopharm), acetonitrile-d₃ (99.8%; Aladdin), Nafion (20 wt%; DuPont), Nafion 212 membrane (DuPont), gas diffusion layer (3260; Ballard), and commercial Pt/C gas diffusion electrodes (0.4 mgPt cm⁻²; Johnson Matthey, JM) are used in this study.

**Synthesis of PDA-Ar Fe/N/C catalyst**

The Fe/N/C-Ar catalyst was prepared through a two-step high-temperature pyrolysis method in combination with an acid leaching process, according to a previously reported method (24). First, 2 g of KJ600 carbon black was dispersed in 60 ml of deionized (DI) water under an ice bath condition (<3°C). In another flask, 1.418 g of p-aminobenzene sulfonic acid was dissolved in 60 ml of DI water under an ice bath condition, followed by successive addition of 18 ml of NaOH solution (1 mol/liter), 42 ml of HCl solution (1 mol/liter), and finally, 8 ml of NaN₃ (1 mol/liter) by dropping slowly to prepare diazonium salt. After stirring for 50 min, the as-prepared diazonium salt was poured into the carbon black solution. After stirring for 15 min, 1.396 g of iron powder was added to accelerate the surface grafting of sulfophenyl groups on KJ600 carbon black. Then, concentrated HCl (36 wt %, 50 ml), m-phenylenediamine (15.22 g), (NH₄)₂S₂O₈ (2 M, 140 ml), and FeCl₃ (1 M, 45 ml) were added to the slurry successively. After stirring for 17 hours, the slurry was processed by extraction filtration and washing and vacuum drying to obtain a black powder. The powder was then subjected to milling. A total of 0.6 g of the powder was dissolved in 60 ml of DI water, followed by the addition of 1.6 ml of FeCl₃ solution (1 mol/liter). Subsequently, the dispersed powder was dried in a rotary evaporator at 50°C. The obtained precursors were pyrolyzed under an Ar atmosphere at 950°C for 1 hour. The resulting carbonized material was subjected to acid treatment (1 M HCl, 100 ml) at 80°C for 12 hours. After centrifugation and washing, the as-prepared powder was again pyrolyzed at 950°C for 3 hours to obtain the final catalyst. The
main purpose of the first pyrolysis process was to drive the formation of Fe-N_x catalytic sites. However, some inactive Fe particles may also be formed in this process. Therefore, an acid leaching step was carried out, during which inactive or less active Fe particles exposed on the surface were removed, and those metal ions dissolved in the aqueous solution were redistributed on the catalyst surface. In the second pyrolysis process, these surface Fe sites would transform into Fe-N_x active sites to increase the density of active sites of Fe/N/C catalyst. The selection of 950°C for the pyrolysis process was because the optimal pyrolysis temperature for the active site formation was in the range of 900°C to 1000°C.

**Synthesis of PDA-CO_2 series Fe/N/C catalysts**

The synthetic process for the PDA-CO_2 series catalysts is similar to that of the PDA-Ar catalyst, except for the replacement of Ar atmosphere by a CO_2-Ar gas mixture in the first pyrolysis process. At first, the obtained catalyst precursors were pyrolyzed under Ar/CO_2 gas mixture (CO_2 volumetric proportion was 0, 0.25, 0.75, 1.25, 2.5, 5, 7, 8.5, and 10%) at 950°C for 1 hour, followed by acid treatment (1 mol/liter HCl solution at 80°C for 12 hours), and lastly pyrolyzed for the second time in Ar at 950°C for 3 hours.

**Synthesis of ZIF-Ar catalyst**

The ZIF-Ar catalyst was synthesized by one-step pyrolyzing Fe-doped ZIF-8 particles under Ar atmosphere according to a previously reported method (38). The ZIF-8 particles were prepared as follows: 1.6 g of Zn(NO_3)_2·6H_2O and 74 mg of FeSO_4·7H_2O were dissolved in 100 ml of methanol, followed by the addition of 2-methylimidazole (3.7 g), and stirred for 24 hours at room temperature. The product was purified by centrifugation and washed thoroughly with ethanol for three times and lastly dried overnight at 80°C. The as-obtained ZIF sample was subjected to heat treatment at 1000°C under Ar atmosphere for 1 hour.

**Synthesis of FePc@KJ600 catalyst**

The FePc@KJ600 catalyst was synthesized by loading FePc on KJ600 carbon black. First, 0.16 g of FePc was dissolved in 100 ml of DMF, followed by the addition of 0.32 g of KJ600 carbon black. Successively, the slurry was subjected to sonication for 1 hour and stirred for 5 hours. Last, the powder product was obtained by rotary evaporation and vacuum drying for 12 hours at 90°C.

**RDE test of bare sample**

The ORR polarization curves of Fe/N/C catalysts were recorded on a CHI-760D biopotentiostat in a standard three-electrode system with a glassy carbon (GC; ø = 5.61 mm) disk Pt ring electrode coated with Fe/N/C catalyst as the working electrode, a GC plate as the counter electrode, and the reversible hydrogen electrode (RHE) as a reference electrode. Initially, a catalyst ink was prepared. Six milligrams of Fe/N/C catalyst and 50 μl of 5 wt % Nafion were ultrasonically dispersed in 1 ml of a mixed ethanol-water solvent with a volumetric ratio of 1:1. The concentration of the catalyst in the ink is 6 mg cm^-2. Then, 25 μl of above ink was coated on the GC disk electrode and dried at room temperature to obtain a controlled catalyst loading of 0.6 mg cm^-2. Second, the as-prepared working electrode was immersed in an O_2-saturated H_2SO_4 solution (0.1 mol liter^-1) at 30°C. The CV experiment was performed by potential cycling between 0.2 and 1.0 V (RHE) at a scan rate of 10 mV s^-1. Then, purging gas was switched to high-purify Ar for at least 30 min to record the background current. The final ORR polarization curve was obtained by correcting the background current and compensating for the ohmic drop.

**Fuel cell polarization performance test of the bare sample**

The fabrication of MEA consisted of three steps: preparing the cathode ink, coating the ink on a gas diffusion layer (GDL), and a hot-pressing process. The cathode catalyst ink was prepared by adding 10 mg of ORR catalyst (Fe/N/C or FePc@KJ600) and 280 μl of Nafion solution (5 wt %; DuPont) into 1.5 ml of ethanol. The concentration of the catalyst in the ink is 6.66 mg ml^-1. After ultrasonic dispersing for 1 hour (T < 10°C), the ink was coated on a GDL equipped with a microporous layer at a catalyst loading of 4 mg cm^-2. The MEA was fabricated by hot pressing (3 MPa) a cathode, a commercial Pt/C anode with a Pt loading of 0.4 mg cm^-2, and an Nafion 212 membrane (DuPont) at 135°C for 2 min. The active area of MEA was 1.21 cm^2. The weight ratio of Fe/N/C catalyst (or FePc) to Nafion was nearly 1:1.3. Polarization and durability curves were measured at 80°C on a Model 850e fuel cell test system (Scribner Associates Inc.). H_2 and O_2 loaded with 100% relative humidity (RH) were fed as fuel and oxidant, respectively, at a flow rate of 0.3 standard liters per minute (SLPM). A backpressure of 1 bar was applied.

**Electrochemical molecular probe experiments in H_2-O_2 PEMFC**

The molecular probe method consists of the following two processes: (i) absorption of organics by Fe/N/C catalysts and (ii) fuel cell polarization curve tests in H_2-O_2 PEMFC. First, a desired concentration of organics in the ethanol-chloroform solvent was selected. The volume ratio of ethanol to chloroform was 1:2, and the solvent volume was 1.5 ml. Afterward, 10 mg of Fe/N/C catalyst was added to the solution. The slurry was then subjected to ultrasonic dispersion for 2 hours and standing overnight at 50°C, during which organics can be fully absorbed by the catalyst. In the followed process, the solvent was not refreshed, which avoids breaking the absorption equilibrium and changing the absorption number of organics by the catalyst. Subsequently, 5 wt % Nafion solution was added to form the cathode ink. The weight ratio of Fe/N/C catalyst to Nafion was 1:1.3. The MEA fabrication and cell performance tests were the same as the bare sample. In the probe experiment, a mixed solvent was selected to dissolve the organics, which is different from that in the bare sample using the ethanol solvent. To exclude the possible influence of the solvent in the MEA preparation process, the polarization performance of the PDA-Ar catalyst prepared with different solvents was compared (fig. S32). Only 7% of performance variation at 0.8 V (iR-free) was observed, excluding the impact of solvents on fuel cell performance.

**Deactivation of ORR catalysts by acids in H_2-O_2 PEMFC**

The deactivation experiment consists of two processes: (i) the addition of acids in the cathode ink preparation process and (ii) followed by polarization test in H_2-O_2 PEMFC. First, 2.5 or 10 μmol of H_2SO_4 (or HClO_4) and 10 mg of ORR catalyst (Fe/N/C or FePc@KJ600) were dispersed in 1.5 ml of ethanol, and the dispersion was stirred for 1 hour. Then, 280 μl of Nafion solution (5 wt %) was added to form the cathode ink. The MEA fabrication and cell performance tests were executed analogous to that for the bare sample.

**Deactivation of ORR catalysts by acids in RDE test conditions**

**Acid treatment before Nafion coating**

First, 6 mg of the ORR catalyst and 10 μmol of H_2SO_4 were ultrasonically dispersed in 1 ml of ethanol-water mixture with a volumetric ratio of 1:1. Then, the mixture was stirred for 1 hour at 10°C, and then, the mixture was subjected to sonication for 1 hour before adding 10 mg of ORR catalyst (Fe/N/C or FePc@KJ600) and 280 μl of Nafion solution (5 wt %; DuPont) into 1.5 ml of ethanol. The concentration of the catalyst in the ink is 6.66 mg ml^-1. After ultrasonic dispersing for 1 hour (T < 10°C), the ink was coated on a GDL equipped with a microporous layer at a catalyst loading of 4 mg cm^-2. The MEA was fabricated by hot pressing (3 MPa) a cathode, a commercial Pt/C anode with a Pt loading of 0.4 mg cm^-2, and an Nafion 212 membrane (DuPont) at 135°C for 2 min. The active area of MEA was 1.21 cm^2. The weight ratio of Fe/N/C catalyst (or FePc) to Nafion was nearly 1:1.3. Polarization and durability curves were measured at 80°C on a Model 850e fuel cell test system (Scribner Associates Inc.). H_2 and O_2 loaded with 100% relative humidity (RH) were fed as fuel and oxidant, respectively, at a flow rate of 0.3 standard liters per minute (SLPM). A backpressure of 1 bar was applied.

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ratio of 1:1 for 1 hour. Then, 50 µl of 5 wt % Naﬁon was added. After ultrasonic dispersion for another 1 hour, 25 µl of the ink was coated on a GC disk electrode and dried at room temperature to obtain a catalyst loading of 0.6 mg cm⁻². The following RDE test was the same as the bare sample.

**PVDF was used as binder**

First, 6 mg of ORR catalyst and 0.23 mg of polyvinylidene diﬂuoride (PVDF) were ultrasonically dispersed in 1 ml of ethanol-water solvent with a volumetric ratio of 1:1. Then, 25 µl of the ink was coated on a GC disk electrode and dried at room temperature with a catalyst loading of 0.6 mg cm⁻². The following RDE test was the same as the bare sample.

**ORR activity recovery experiment in H₂-O₂ PEMFC**

First, 10 mol of H₂SO₄ was added into the slurry consisting of 8, eadd8873 (2022) 2 November 2022 Wang et al., Sci. Adv. 8, eadd8873 (2022) 2 November 2022 2 November 2022 Wang et al., Sci. Adv. 8, eadd8873 (2022) 2 November 2022 first, 10 µmol of H₂SO₄ was added into the slurry consisting of 10 mg of Fe/N/C catalyst and 1.5 ml of ethanol. After ultrasonic dispersion for 1 hour, 20 µmol of NaOH was added to neutralize the solution. Subsequently, the slurry was subjected to centrifugation, followed by washing with ethanol until the pH was close to 7. Afterward, 280 µl of Naﬁon solution (5 wt %) and 1.5 ml of ethanol were added to prepare the cathode ink. The following MEA fabrication and cell performance test were the same as stated before.

**Absorption capacity test**

The amount of organics absorbed to the Fe/N/C catalysts was determined by measuring the concentration of organics in the solution before and after the absorption process via ultraviolet-visible (UV-Vis) spectrophotometry. The absorption process was the same as the probe experiment. In detail, a desired concentration of organics in 1.5 ml of ethanol-chloroform solvent was selected. The volume ratio of ethanol to chloroform was 1:2. Afterward, 10 mg of Fe/N/C catalyst was added to the solution. The slurry was subjected to ultrasonic dispersion for 2 hours and standing overnight at 50°C. The supernatant liquor was obtained by centrifugation and pipetted for consequent concentration test. The concentration of organics in the solution before and after the absorption was analyzed by UV-Vis spectroscopy. The test process was as follows: The test sample was diluted by a factor of 1 to 600 times (Ph₁, 1 time; Ph₂, 25 times; Ph₄, 200 times; C₁₀Cl₈, 200 times; Ph₃Pp, 600 times, C₆₀Cl₂₂, 300 times, and C₆₆Cl₂₇, 100 times). Then, the absorption spectra from 600 to 200 nm were measured with the Varian Cary 5000 spectrophotometer. Pure solvents were measured beforehand as reference (blank). The concentration of organics was determined by an external reference method.

**Isothermal absorption/desorption test**

The change of micropore accessibility was examined by measuring the Ar isothermal adsorption/desorption curves of Fe/N/C catalysts after the organics were applied to the catalyst surface but before the catalyst was fabricated into the MEA. The adsorption process was the same as the probe experiment. In detail, a desired concentration of organics in 7.5 ml of ethanol-chloroform solvent was selected. The volume ratio of ethanol to chloroform was 1:2. Afterward, 50 mg of Fe/N/C catalyst was added to the solution. The slurry was subjected to ultrasonic dispersion for 2 hours and standing overnight at 50°C. Then, the solvents were removed via centrifugation and vacuum drying at 40°C overnight. The obtained catalysts were then subjected to the Ar isothermal adsorption/desorption test. The degassing condition was 80°C at vacuum for 10 hours. The reference data were obtained by measuring the catalyst that went through the same treatment process but without the organics.

**Acid-alkaline titration experiment**

First, 12 pieces of aqueous solution (10 ml) with a given pH (ranging from 1 to 12) were prepared. The pH of the solutions was adjusted by addition of 0.1 M H₂SO₄ or 0.1 M NaOH aqueous solution. Twenty milligrams of PDA-Ar catalyst was then added into the above 12 different solutions. Each sample was left for equilibration for 10 hours. Last, the pH value of resultant aqueous solution was measured.

**Physical characterizations**

XPS (Qlic 100 LEISS-XPS instrument) was performed to characterize the surface composition of Fe/N/C catalysts. The Ar absorption/desorption isotherm was measured with an ASAP 2020 physisorption analyzer (Micromeritics). Micropore size distribution was obtained by the Horvath-Kawazoe method, and the mesopore size distribution was obtained by the Barrett-Joyner-Halenda method. The absorption branch data were used. UV-Vis spectroscopy was performed with a Varian Cary 5000 spectrophotometer to quantify the concentration of organics before and after the absorption experiments. The content of Fe element in the samples is determined by the ICP-MS (PerkinElmer, NexION 300). Extended x-ray absorption fine structure data of Fe K-edge were acquired at the Beijing Synchrotron Radiation Facility (1W1B) in fluorescence mode. The incident x-rays were monochromatized using Si (111) double crystals. The raw data were processed and fitted by the standard procedures with Athena and Artemis programs. The x-ray absorption near-edge structure fitting was processed using the MXAN package. A 27-W black light lamp (FPL27BLB, Sankyo Denki, Japan) was added between the gamma-ray detector and the catalyst sample holder to perform Mössbauer measurements under UV irradiation. The spectra were ﬁtted with the appropriate superpositions of Lorentzian lines using the MossWinn 3.0i computer program.

**Computational methods**

**Calculation of O₂ adsorption energy and O—O bond length**

All spin-polarized computations were performed by ORCA in this work (50). The Def2-TZVP basis set combined with the resolution of identity (RI) approximation was applied (51). All molecular structures were studied with the Perdew-Burke-Ernzerhof function in combination with the dispersion correction (52–54). The dipole correction was included for all the computations. For the FeN₄ molecular structures with the protonated pyridine N, the net charge was set to be 1. The O₂ adsorption energy was calculated according to the following equation

\[ E_{\text{ads}} = E_{\text{molecule-O}_2} - E_{\text{molecule}} - E_{\text{O}_2} \]

where \( E_{\text{molecule-O}_2} \), \( E_{\text{molecule}} \), and \( E_{\text{O}_2} \) were the total energy of the molecule with O₂ adsorption, the molecule, and the O₂ in gas phase, respectively.

**Calculation of dynamic diameter**

The organic molecules were optimized on the same theory level with the computation of O₂ adsorption. The optimized geometry of the organic molecules was measured in terms of length, width, and height by placing them completely into the smallest cuboid box.
The cross-sectional area of the box in the horizontal plane was chosen because it showed the largest area (55). The molecules were approximated to be in a circular shape, and the dynamic diameter of the molecule was calculated according to the following equation

\[ d = 2 \sqrt{\frac{A}{\pi}} \]

where \( d \) and \( A \) were the dynamic diameter and the cross-sectional area in the horizontal plane, respectively.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.add8873

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