

Enhancing electrocatalytic ammonia oxidation via surface concentration-gradient platinum alloying

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Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909171>

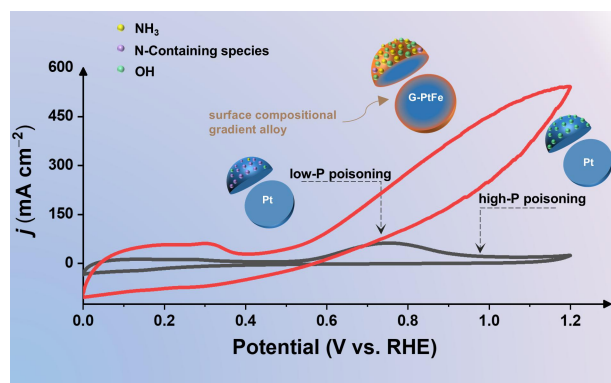
<https://www.sciopen.com/journal/1998-0124> on Sep. 7, 2026

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A surface compositional gradient G-PtFe alloy catalyst was developed for high-performance electrocatalytic ammonia oxidation, delivering an outstanding current density of 541.7 mA cm^{-2} in three-electrode cells and a peak power density of 43.0 mW cm^{-2} in direct ammonia fuel cells (DAFCs). Moreover, this unique structure enables balanced adsorption of reactants across a wide potential window, exhibiting excellent poisoning resistance over 0.5–1.2 V vs. RHE and thereby providing a design strategy for highly stable DAFC anodes.

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Received: 27 March 2026; Revised: 11 August 2026; Accepted: 7 September 2026

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 Cite this article: Nano Research, 2026, 19, 94909171 <https://doi.org/10.26599/NR.2026.94909171>

ABSTRACT: Electrocatalytic ammonia oxidation reaction (EAOR) remains hindered by the lack of catalysts that simultaneously achieve high activity and long-term stability. Herein, we report a surface compositional gradient PtFe alloy catalyst (G-PtFe) consisting of a Pt-Fe gradient shell and a PtFe alloy core. The G-PtFe delivers an EAOR current density of 541.7 mA cm⁻², representing an 8.7-fold improvement over pristine Pt, while exhibiting robust poisoning resistance across a wide potential range of 0.5–1.2 V vs. RHE. When employed as anode catalyst in direct ammonia fuel cells, the G-PtFe-based device achieves a peak power density 3.3 times higher than that of commercial Pt/C. Combined experimental analyses and density functional theory simulations reveal that EAOR deactivation on conventional Pt-based catalysts originates from potential-dependent adsorption imbalance: insufficient surface OH adsorption at low potentials promotes the accumulation of N-containing poisoning intermediates, whereas excessive OH binding at high potentials suppresses NH₃ adsorption and induces surface passivation. The surface compositional gradient structure enables dynamically balanced OH and NH₃ adsorption over a wide potential window, resulting in ultra-stable EAOR performance. This work provides mechanistic insights into potential-dependent catalyst poisoning and establishes a surface gradient alloy strategy for rational design of efficient and durable EAOR catalysts.

KEYWORDS: electrocatalytic ammonia oxidation reaction, poisoning mechanism, platinum, surface compositional gradient alloy

1 Introduction

Ammonia (NH₃), one of most widely produced industrial chemicals, is emerging as a zero-carbon energy carrier with exceptional gravimetric (22.5 MJ kg⁻¹) and volumetric (12.7 MJ L⁻¹) energy densities. In addition, ammonia's favorable liquefaction properties enable storage at modest pressures, approximately 8 bars at room temperature, further enhancing its practicality as an energy vector. These advantages render ammonia particularly attractive for energy conversion platforms, such as direct ammonia fuel cells (DAFCs) and on-site hydrogen production systems, with the electrochemical ammonia oxidation reaction (EAOR) serving as the key reaction for these platforms [1–11]. However, owing to the six electrons transfer process per NH₃ molecule (see eqs. (1–3)) [12], the EAOR generally faces several critical challenges including high overpotential, sluggish reaction kinetics, poor catalyst stability and low catalytic efficiency, collectively hindering practical

deployment [7, 13–17].

Anode: N₂(g) + 6H₂O(l) + 6e⁻ ↔ 2NH₃(aq) + 6OH⁻(aq)
(E₀ = -0.736 V vs. SHE) (1)

Cathode:
6H₂O(l) + 6e⁻ ↔ 3H₂(g) + 6OH⁻(aq) (E₀ = -0.828 V vs. SHE)
(2)

Overall: 2NH₃(aq) → N₂(g) + 3H₂(g) (E = -0.092 V)
(3)

Electrocatalysts for the EAOR are generally categorized into two main groups: noble metal-based catalysts, represented by platinum-based catalysts, and non-noble metal catalysts, represented by nickel-based and copper-based catalysts. Pristine nickel hydroxide Ni(OH)₂ suffers from sizable overpotentials and pronounced parasitic side reactions during EAOR, compromising its electrochemical performance and selectivity. Notably, strategic incorporation of copper dopants [18, 19], as well as the deliberate application of tensile strain [20], which can markedly

enhance both the intrinsic EAOR activity and the long-term operational stability of $\text{Ni}(\text{OH})_2$. Furthermore, initially inactive copper oxide (CuO) can achieve exceptional stability exceeding 400 hours at an elevated current density of approximately 200 mA cm^{-2} through oxygen vacancy engineering. Nevertheless, the onset potentials typically exceed 1.3 V versus reversible hydrogen electrode (RHE) and the N_2 faradaic efficiency remains limited to around 60% [21, 22]. Compared with non-precious metal catalysts, platinum-based electrocatalysts show significantly higher nitrogen selectivity (>90%) and substantially lower onset potentials (>0.5 V vs. RHE). However, Pt catalysts experience rapid deactivation when the potential exceeds 0.7 V vs. RHE, thus narrowing the effective potential window to 0.5 to 0.7 V vs. RHE [23–25]. Unfortunately, EAOR electrocatalytic performance remains suboptimal even within this narrow window due to inherent stability constraints. Although certain Pt catalysts maintain acceptable performance over hundreds of cyclic voltammetry (CV) cycles, they deactivate rapidly within two hours at 0.6 V vs. RHE in chronoamperometry (CA) tests [16, 26–29]. Such poor durability is confirmed in chronopotentiometry (CP) tests, where the catalysts fail within 9 h at 5 mA cm^{-2} [29–31], indicating insufficient operational robustness under practical conditions. Consequently, enhancing the stability of Pt-based catalysts in CA/CP environments constitutes the paramount technological challenge.

As demonstrated by eq. (1) and previous work [32], efficient EAOR requires balanced co-adsorption of NH_3 and OH on the catalyst surface. However, the adsorption of OH on pristine Pt is limited especially at lower potential, which leads to markedly sluggish kinetics. To address this, transition metals are commonly introduced to preferentially adsorb OH and enhance the EAOR activity [33–37]. Nevertheless, this strategy fails to fundamentally resolve the stability issues, thereby severely hindering its practical application. A mechanistic understanding is essential for attaining further improvements on catalysts, but current insights remain debated. In fact, the precise nature of toxic species, whether they are N-containing species [31, 38–41] or OH [7, 42, 43] remaining ambiguous due to the complex reaction pathways, thereby impeding further advancements.

Various Pt-transition metal alloys were synthesized and evaluated, among which the PtFe alloy exhibited the highest intrinsic EAOR activity (Fig. S1). However, similar to previously reported systems [44, 45], the PtFe alloy still shows limited stability (Fig. S2). Given that gradient structures can effectively modulate the adsorption behavior of reaction intermediates [46–48], we adopted this approach to develop a surface gradient-structured PtFe (G-PtFe) catalyst with a compositional gradient Pt-Fe shell and a PtFe alloy core. This structural design confers superior poisoning resistance together with enhanced EAOR activity and stability. The G-PtFe catalyst achieved an EAOR activity of 541.7 mA cm^{-2} , representing an 8.7-fold improvement over the conventional Pt catalyst, while maintaining poisoning resistance within the potential range of 0.5 to 1.2 V vs. RHE. When employed as anode in alkaline DAFCs, the G-PtFe delivered a peak power density of 43.0 mW cm^{-2} , which was

3.3 times that of the commercial Pt/C catalyst. By combining experimental analyses of adsorption species at different potentials with DFT calculations, we determined that the primary cause of Pt deactivation is competitive adsorption, leading to uneven surface coverage of different reactants and consequently imbalanced adsorption. Owing to its surface compositional gradient structure, the G-PtFe catalyst achieves a more balanced adsorption between OH and NH_3 reactants within 0.5–1.2 V vs. RHE, resulting in significantly improved electrocatalytic activity and operational stability. This work elucidates the poisoning mechanisms in EAOR and establishes an effective catalyst design strategy, thereby advancing the development of high-performance EAOR electrocatalysts.

2 Experimental

2.1 Materials

Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Adamas, 99%), Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Aladdin, AR 99%), manganese chloride (MnCl_2 , Adamas, 99%), copper chloride hexahydrate ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$, Aladdin, 99.99%), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot \text{H}_2\text{O}$, Aladdin, 99.9%), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot \text{H}_2\text{O}$, Macklin, 99.99%), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Adamas, 99%), Zinc Chloride (ZnCl_2 , Aladdin, $\geq 98\%$), Glycine (Aladdin, 99.9%), sodium iodide (Aladdin, 99.5%), Polyvinyl pyrrolidone (PVP, Aladdin, Mw=24000, k23-27), ethanolamine (Macklin, AR 99%), potassium hydroxide (Aladdin, 99.99%), sulphuric acid (Sinopharm Chemical, 95–98%), Nickel Foam (MA-EN-CU-03), Carbon cloth (CeTech, WOS1009), 2.0 mg cm^{-2} Pt on gas diffusion layer (SEN-23K, Sinero), and anion exchange membranes (PBI-35, Celazole) were used as received.

2.2 Synthesis of PtFe Electrocatalyst

The nickel foam (NF) or carbon cloth (CC) substrate was cut into $1 \text{ cm} \times 2 \text{ cm}$ and sequentially subjected to ultrasonication in acetone, ethanol and deionized water to remove impurities. In a typical procedure, glycine (150 mg), sodium iodide (300 mg), PVP (100 mg), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (40 mg), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mg) and ethanolamine (0.35 mL) were dissolved in the deionized water (3.65 mL) and homogenized via magnetic stirring for 30 min under ambient conditions. The resulting homogeneous solution and a pretreated NF or CC substrate was transferred into a 20 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was maintained at 160°C for 16 h in a programmable oven, followed by natural cooling to room temperature. The as-synthesized PtFe sample was collected, rinsed thoroughly with deionized water to remove residual reactants and dried under vacuum at 60°C for 12 h prior to characterization and electrochemical measurements.

2.3 Synthesis of G-PtFe Electrocatalyst

The as-synthesized G-PtFe sample was modified by electrochemical dealloying method in a three-electrode system using 0.5 M H_2SO_4 through Cyclic voltammetry (CV) processing between 0.0–1.2 V vs. RHE for 50 CV scans. The PtFe, graphite rod electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ served as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively.

2.4 Synthesis of Pt

The synthesis of Pt was similar that of PtFe in the absences

of Fe source.

2.5 Synthesis of PtM (M = Mn, Cu, Co, Ni, Zn, Sn, Cr)

All PtM samples were synthesized following the same procedure as PtFe, except that $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was replaced by an equimolar amount of the corresponding metal chloride.

2.6 Synthesis of PtFe (17:3) Electrocatalyst

The synthesis of PtFe (17:3) was similar to that of PtFe, except that the Pt:Fe molar ratio was adjusted from 3:1 to 17:3.

2.7 Catalyst Characterization

The crystallographic structure and phase composition of the as-synthesized catalysts were investigated by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source. Surface morphology and microstructural features were examined using a Hitachi Regulus 8230 field-emission scanning electron microscope (SEM). High-resolution imaging and nanostructural analysis were performed on a Thermo Fisher Scientific Talos F200X G2 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher ESCALAB Xi+, and the binding energies were calibrated using C 1s peak at 284.8 eV as standard. Depth-resolved chemical composition profiles were obtained through sequential XPS analysis combined with controlled monatomic Ar^+ ion etching (2000 eV, 2 μA) over a 2 mm $\times$ 2 mm area. The elemental composition and metal loading of the catalysts were quantitatively determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Fisher Scientific iCAP RQ instrument.

2.8 Catalyst Electrochemical Measurements

The electrocatalytic properties of the obtained catalysts were systematically evaluated as the working electrode using a Solartron 1470E electrochemical workstation, while using graphite rod electrode and Hg/HgO electrode as the counter electrode and the reference electrode, respectively. All measurements were conducted at room temperature unless specified otherwise. To standardize the results, all measured potentials were converted to the reversible hydrogen electrode (RHE) scale in accordance with the Nernst equation: $E(\text{V vs. RHE}) = E(\text{V vs. Hg/HgO}) + 0.098 + 0.059 \cdot \text{pH}$ or $E(\text{V vs. RHE}) = E(\text{V vs. Hg/Hg}_2\text{SO}_4) + 0.616 + 0.0592 \cdot \text{pH}$. Prior to all measurements, the electrolyte was purged with Ar gas for 15 min to eliminate dissolved oxygen, and the CV was carried out. The EAOR electrocatalytic stability was assessed through chronoamperometry (CA) measurements at 0.6 V and 0.8 V vs. RHE, as well as chronopotentiometry (CP) tests under various constant current densities to simulate practical operating conditions. Electrochemical impedance spectroscopy (EIS) was performed at 0.6 V, 0.7 V and 0.8 V vs. RHE potentials over a frequency range of 0.01-100 kHz with an AC amplitude of 10 mV.

2.9 Apparent Activation Energy Tests

The apparent activation energy (E_a) of Pt, PtFe and G-PtFe were collected using performing CV measurements under various temperature conditions following the Arrhenius equation: $\ln k = -\frac{E_a}{RT} + \ln A$, where k , R , A and T represent the reaction rate constant, gas constant, frequency factor and temperature, respectively. For variable temperature electrochemical tests, the Ag/AgCl (3.5 M KCl) electrode was

used as the reference electrode, and the potentials were converted to the RHE scale using: $E(\text{V vs. RHE}) = E(\text{V vs. Ag/AgCl}) + 0.205 + 0.0592 \cdot \text{pH} + 0.44(\text{mV}) \times (T - 25^\circ\text{C})$, where T is the working temperature in $^\circ\text{C}$.

2.10 CO Stripping Tests

The electrochemically active area (ECSA) of catalysts was determined with CO adsorption and subsequent electrooxidation (CO stripping). CO was bubbled into 1.0 M KOH solution for 20 min at 0.0 V vs. RHE to form a saturated monolayer on the catalyst surface. Subsequently, Ar was then purged for 30 min to remove dissolved CO while maintaining the adsorbed CO monolayer. Then, CVs were recorded in the potential range between 0.0–1.2 V vs. RHE. The ECSA can be calculated as follows:

$$\text{ECSA} = \frac{Q_{\text{CO}}}{C_{\text{CO}} \times m_{\text{Pt}}}$$

where Q_{CO} is the integrated Coulombic charge of CO adsorbed on the surface of catalyst electrode, C_{CO} is 420 $\mu\text{C cm}^{-2}_{\text{Pt}}$, m_{Pt} is the platinum content on the catalysts used as working electrode.

2.11 Calculation of the Faradic Efficiency

The faradaic efficiency for EAOR was determined by quantifying the amounts of generated N_2 and H_2 gases. These products were collected during CP or CA tests under certain test conditions in a custom-built electrolytic cell. The catalysts electrode served as the working electrode, a Pt plate as the counter electrode, and a Hg/HgO electrode as the reference electrode.

The amounts of N_2 and H_2 were evaluated to determine the faradaic efficiency of the process using the formula:

$$\text{N}_2 \text{ faradic efficiency} = \frac{6 \times V_{\text{N}_2} \times F}{V_{\text{m}} \times Q} \times 100\%$$

$$\text{H}_2 \text{ faradic efficiency} = \frac{2 \times V_{\text{H}_2} \times F}{V_{\text{m}} \times Q} \times 100\%$$

Where V_{N_2} is the volume of collected N_2 and V_{H_2} is the volume of collected H_2 , F is the faraday constant (96485 C mol^{-1}), V_{m} is the molar volume of the gas (22.4 L mol^{-1}), and Q is the total charge consumed in the measurement.

The faradic efficiency of H_2 was calculated using the formula:

2.12 In Situ Differential Electrochemical Mass Spectrometry (DEMS) Analysis

The composition of gas products generated during EAOR were qualitatively analyzed using DEMS measurements (Linglu), including N_2 (28 m/z), N_2H_4 (32 m/z), NO (30 m/z), N_2O (44 m/z) and NO_2 (46 m/z), providing insights into the reaction pathway. The catalyst was employed as the working electrode, while the Pt wire and the Ag/AgCl electrode served as the counter electrode and reference electrode, respectively.

2.13 In Situ Attenuated Total Reflection Fourier-Transform Infrared (ATR-FTIR) Measurements

A custom-designed electrochemical setup integrated with spectroscopic capabilities was employed for real-time infrared characterization. The measurement system consisted of a specially fabricated three-electrode cell positioned on the reflectance platform of a variable angle ATR accessory (PIKE VeeMAX III). Catalyst materials were directly deposited onto the silicon prism surface and subsequently contacted with a glassy carbon electrode under controlled pressure, which functioned as the working

electrode component. The electrochemical cell was completed using Pt wire as the counter electrode and an Ag/AgCl reference system containing 3.5 M KCl solution. For accurate potential reporting, all measurements referenced to the Ag/AgCl electrode were mathematically converted to RHE. CA experiments at predetermined potential values were conducted using a Solartron 1470E electrochemical testing platform. Spectroscopic data acquisition was performed with a Thermo Fisher iS50 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT-A detector element. Each spectral dataset represented the accumulation of 100 consecutive scans collected at 4 cm^{-1} spectral resolution to optimize signal-to-noise characteristics while maintaining appropriate temporal resolution for the electrochemical processes under investigation.

2.14 Direct Ammonia Fuel Cells (DAFCs) Performance Tests

The performance of DAFCs was evaluated using the as-prepared G-PtFe catalyst (active area: 1.0 cm^2) as the anode, while a reference anode with 2.0 mg cm^{-2} Pt loading on GDL (SEN-23K, Sinero). For comparison, a commercial Pt/C reference DAFC (2.0 mg Pt cm^{-2} , SEN-23K) was employed. The DAFCs assembly incorporated a PBI-35 anion exchange membrane (Celazole, pre-treated in 6 M KOH). Under operational conditions, the anode was fed with an Ar-saturated aqueous electrolyte (6 M KOH + 3 M $\text{NH}_3\cdot\text{H}_2\text{O}$) at 0.2 mL min^{-1} , while the cathode was supplied with oxygen at 120 mL min^{-1} .

2.15 Density Functional Theory (DFT) Calculation

DFT calculations were performed using the CP2K software package. The exchange-correlation energy was described using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized-gradient approximation (GGA). The electronic wave functions were expanded using a molecularly optimized double-zeta Gaussian basis set (MOLOPT DZVP), together with an auxiliary plane-wave basis set, with a plane-wave cutoff energy of 500 Rydberg to ensure reliable convergence. The Pt (111) surface, PtFe (111) surface (with the atomic ratio of Pt to Fe in the top three surface layers being Pt:Fe = 70:30), and the G-PtFe (111) surface (where the atomic ratio of Pt to Fe varies: 85:15 at the surface, 78:22 in the third layer, and 75:25 in the sixth layer) were simulated by cleaving the corresponding slabs. A vacuum layer with a thickness of 15 Å was set along the z-

direction. All surface models were required to ensure full relaxation of all structures and the adsorption energies of intermediates. During the optimization of the structures of all models, only the atoms in the bottom three layers were fixed. For the integration over the Brillouin zone, only the point in the reciprocal-space mesh was used. Geometric structure optimization was performed based on the quasi-Newton BFGS method. The convergence criterion for geometric structure optimization was set as a maximum force not exceeding 0.01 eV/Å . Spin polarization was considered in all calculations. This study also took into account the influence of an electric field on the band structure. By adjusting the &FORCE_EVAL/&DFT parameters in CP2K, electric fields of different intensities were applied in the z-direction. The adsorption energy (ΔE_{ads}) of intermediates were calculated according to:

$$\Delta E_{\text{ads}} = E_{\text{ads+sur}} - E_{\text{ads}} - E_{\text{su}}$$

$E_{\text{ads+sur}}$, E_{ads} , E_{sur} are the energy of surface with adsorbate, single adsorbate, and single surface, respectively. The d-band center and p-band center were exported using the Multiwfn software.

3 Results and discussion

3.1 Materials Synthesis and Structural Characterization

The PtFe alloy catalyst was in situ grown on nickel foam (NF) or carbon cloth (CC) substrates via a facile one-pot hydrothermal synthesis. To obtain the surface gradient constructure catalyst, the as-synthesized PtFe electrocatalyst was electrochemically activated through CV treatment in $0.5\text{ M H}_2\text{SO}_4$ for 50 cycles between $0.0\text{--}1.2\text{ V}$ vs. RHE, yielding the G-PtFe catalyst (Fig. 1a). For comparison, the pure Pt catalyst was prepared using the same method. Scanning electron microscopy (SEM) characterization uncovered that both PtFe and G-PtFe displayed a highly uniform particle size of approximately 600 nm , as indicated in Figs. 1b and 1c. X-ray diffraction (XRD) patterns (Fig. 1d) verified that G-PtFe, PtFe and Pt all crystallized in a face-centered cubic (FCC) structure. The two-theta peaks of PtFe were slightly shifted to higher angles relative to Pt, which is attributed to the lattice contraction caused by the incorporation of smaller Fe atoms. Meanwhile, the peak positions of G-PtFe were located between those of PtFe and Pt, reflecting the partial leaching of Fe during the dealloying process.

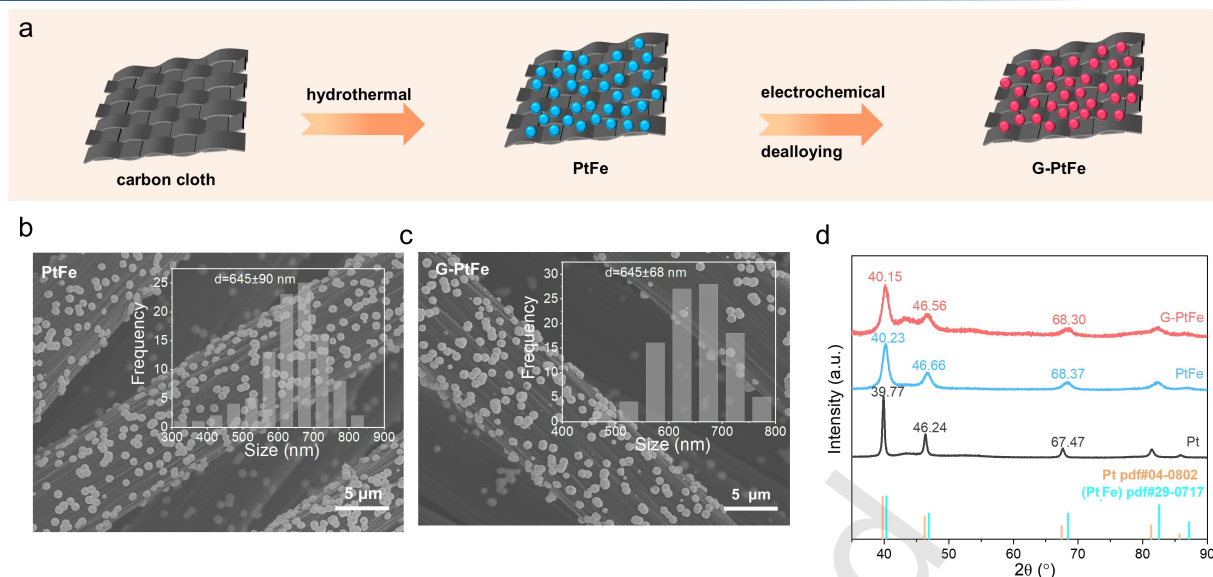


Figure 1 EAOR catalyst preparation and characterizations. (a) The scheme of material preparation for PtFe and G-PtFe. SEM images of (b) PtFe and (c) G-PtFe, the insets provide corresponding histograms charts detailing the particle size distribution. (d) XRD patterns of Pt, PtFe and G-PtFe.

To investigate the chemical composition at different depths, X-ray photoelectron spectroscopy (XPS) with Ar^+ sputtering was conducted and is provided in Figs. S3 and S4. Ar^+ sputtering rate was approximately 0.05 nm s^{-1} , allowing the XPS depth profiles to be presented in nanometers (Figs. 2a and 2b). For the PtFe, the atomic ratio of Pt to Fe remained constantly at 7:3 throughout the depth range of 35 nm, indicating a uniform composition. In contrast, the G-PtFe catalyst delivered a Pt-rich surface with a Pt:Fe ratio of 17:3, in sharp contrast to the completely Pt-terminated surface obtained in the previous work [49]. This distinction originates from the dynamic behavior of Fe during the electrochemical process [50]. As sputtering progressed, the Pt content gradually decreased while the Fe content increased, finally resulting in a stable Pt:Fe ratio of 7:3 at a depth of approximately 7.5 nm, almost identical to that of the PtFe sample. To further quantify this surface gradient distribution, high-resolution STEM-EDS line-scanning analysis was performed on individual nanoparticles (Fig. S5). The distributions of Pt and Fe in PtFe remain uniform from the particle edge to the interior, confirming its homogeneous alloy structure. In contrast, line-scan profiles of G-PtFe reveal a distinct Pt-rich region at the particle edge, where the Pt content gradually decreases while the Fe content correspondingly increases. At a depth of 2 nm, the relative composition approaches that of PtFe, further confirming a surface compositional gradient structure in G-PtFe.

To investigate the effect of Fe leaching on the surface chemical state, we analyzed the Pt 4f and O 1s XPS spectra of PtFe and G-PtFe (Fig. S6). The results reveal a 0.1 eV

negative shift of the Pt $4f_{7/2}$ peak after dealloying, indicating an increased electron density of surface Pt, in agreement with previous studies [51, 52]. Furthermore, the O 1s spectra confirms the evolution of the surface chemical state. For the PtFe sample, the O 1s spectrum can be fitted into three characteristic peaks, including metal-oxygen bonds (M-O) at $\sim 530.0 \text{ eV}$ assigned to surface Fe oxide species, C-O bonds at $\sim 531.4 \text{ eV}$, and adsorbed water at $\sim 533.0 \text{ eV}$. In contrast, the M-O peak intensity at $\sim 530.0 \text{ eV}$ is markedly decreased for the G-PtFe, providing robust evidence for the leaching of surface Fe species, which is fully consistent with the formation of a Pt-rich surface structure.

High-resolution transmission electron microscopy (HRTEM) was employed to precisely examine the microstructure of the catalysts. In the PtFe sample (Fig. 2c), both the interior and exterior (111) lattice spacings were measured to be 0.223 nm. The G-PtFe sample (Fig. 2d) exhibits an interior spacing of 0.224 nm, which is in good agreement with the XRD results. The surface region, however, shows a slightly expanded spacing of 0.225 nm, suggesting lattice relaxation arising from partial Fe leaching. This structural change is further supported by the XPS spectra, which evidence surface Fe depletion. Additional images (Figs. S7 and S8) reveal clear lattice fringes with an interplanar spacing of 0.231 nm, corresponding to Pt. Taken together, the combined XPS and HRTEM analysis confirm that electrochemical dealloying induced partial Fe dissolution from the near-surface region, yielding a surface compositional gradient alloy structure.

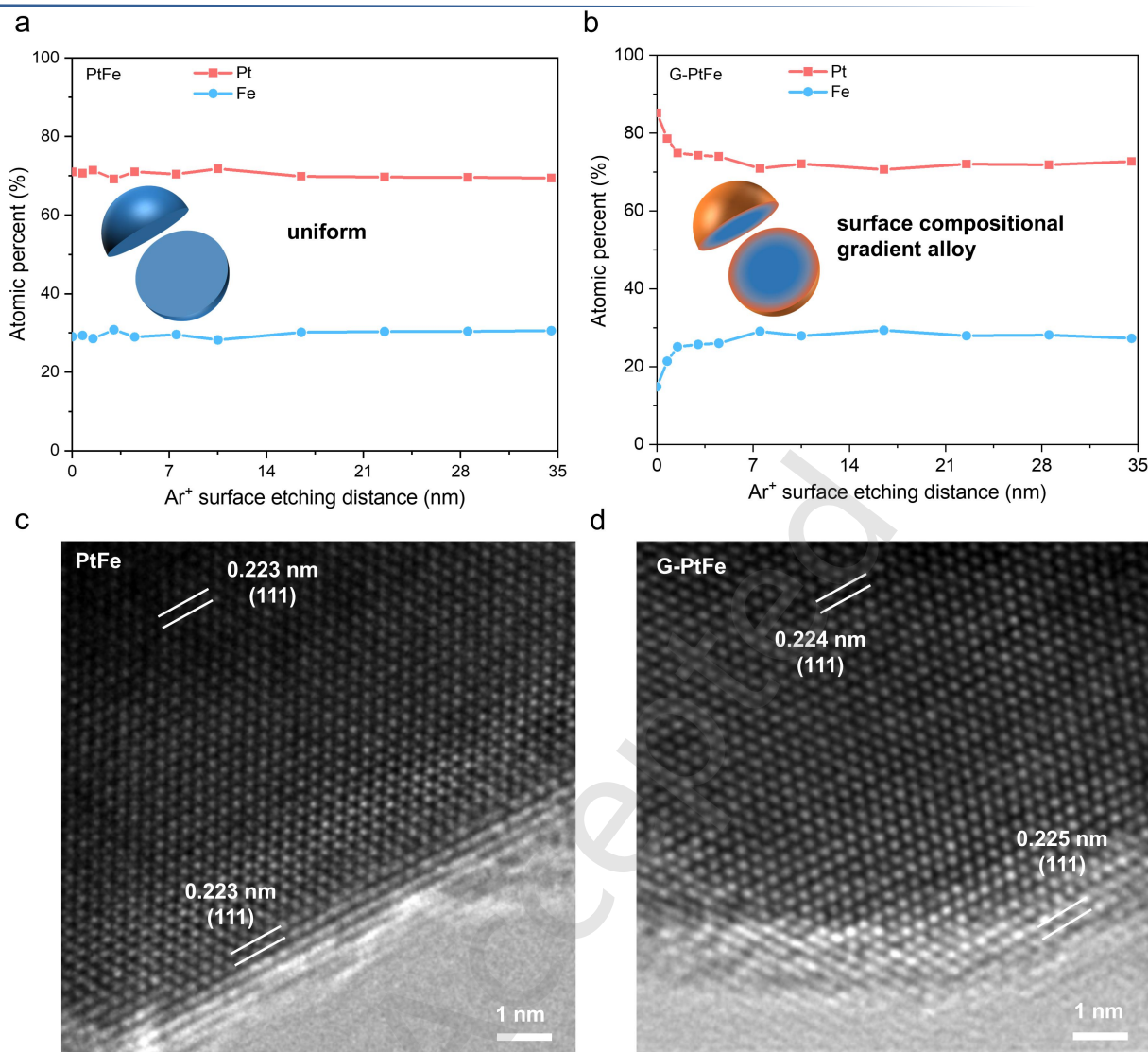


Figure 2 Microstructures of PtFe and G-PtFe. The atomic ratios of (a) PtFe and (b) G-PtFe characterized by XPS from surface to inner. HRTEM images of (c) PtFe and (d) G-PtFe.

3.2 EAOR performances

The EAOR performances of the catalysts were evaluated using a three-electrode system in an Ar-saturated 1 M KOH + 1 M NH₃·H₂O electrolyte. As illustrated in Figs. 3a and S9, the onset potential and peak potential for the Pt catalyst were 0.54 and 0.75 V vs. RHE, respectively. The EAOR current density rapidly decreased when the potential continued to increase, reflecting a typical poisoning phenomenon for Pt-based catalysts [53–55]. For the PtFe catalyst, the onset and peak potentials were 0.50 and 0.90 V vs. RHE, respectively, suggesting a broader operating potential range. Remarkably, the G-PtFe catalyst displayed the widest electrochemical window with the onset potential decreasing to 0.46 V vs. RHE and no signs of poisoning phenomenon upon 1.20 V vs. RHE, while the peak current density reached 541.7 mA cm⁻², which is 1.8 times and 8.7 times that of PtFe (299.3 mA cm⁻²) and Pt (62.3 mA cm⁻²), respectively. After normalizing the activity to the electrochemical active surface areas (ECSA) (Figs. S10 and S11), the trend remained consistent with the apparent activities illustrated in Fig. 3a. To verify whether the activity

enhancement originates from the compositional- gradient rather than composition alone, a control catalyst was synthesized using a precursor feeding ratio of Pt:Fe = 17:3, corresponding to the surface composition of G- PtFe. As depicted in Fig. S12, this control sample yielded a markedly lower current density of 266.1 mA cm⁻² and a higher peak potential at 0.98 V vs. RHE, thereby supporting the importance of the in situ-formed Pt- Fe compositional gradient in facilitating EAOR. Moreover, electrochemical impedance spectroscopy (EIS) measurements further evidenced that G-PtFe had the smallest charge transfer resistance than PtFe and Pt, validating enhanced electrochemical kinetics during the EAOR process (Fig. S13).

Building upon these electrochemical results, we next employed differential electrochemical mass spectrometry (DEMS) to gain molecular- level insights into the gaseous products evolved during the EAOR over G- PtFe. For comparison, the Pt and PtFe catalysts were also examined under identical conditions. According to Figs. 3b, 3c and S14, N₂H₄ intermediate can be found in all the DEMS spectra of three catalysts, corroborating that the EAOR proceeds via

the G-M reaction pathway [56]. Furthermore, it was evident that the G- PtFe catalyst generated the highest amount of N_2 gas under identical conditions, followed by PtFe and then Pt, a trend that aligns closely with the EAOR performance shown in Fig. 3a. To quantitatively correlate gas evolution with reaction efficiency, we then evaluated the faradaic efficiencies of both anodic and cathodic reactions using a water- displacement method, as depicted in Figs. 3d and S15. In Fig. 3e, the faradaic efficiencies for H_2 of all three catalysts were approximately 99.0%. Notably, G- PtFe achieved the highest N_2 selectivity of 99.0%, confirming the nearly complete conversion of NH_3 to N_2 . To gain deeper mechanistic insight into the reaction kinetics, the apparent activation energy (E_a) during the EAOR process was investigated at different potentials. Based on the Butler-

Volmer charge transfer kinetics equation, the catalytic rate is expected to increase with rising overpotential, accompanied by a corresponding decrease in E_a [57]. The E_a values of three catalysts at various potentials were determined using the Arrhenius method (Fig. S16) [58], and subsequently plotted as a function of applied potentials (Fig. 3f). Interestingly, both Pt and PtFe exhibited an unexpected increase in E_a beyond 0.8 V vs. RHE, which can be attributed to catalyst poisoning during the reaction. More notably, the E_a values of G-PtFe continuously decreased from 23.51 kJ mol⁻¹ to 14.91 kJ mol⁻¹ over the potential range of 0.6 to 1.0 V vs. RHE, which is in excellent agreement with the Butler-Volmer theoretical framework and confirms the accelerated charge- transfer kinetics of G- PtFe.

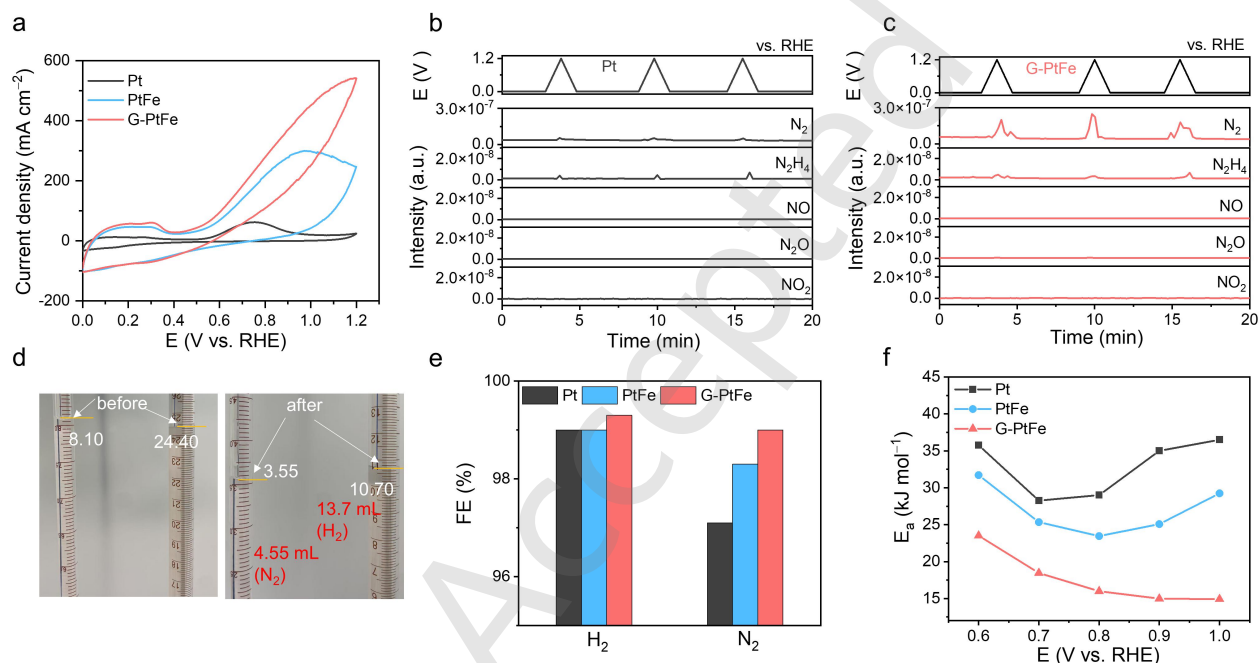


Figure 3 EAOR performances of G-PtFe, PtFe and Pt. (a) CV curves between 0.0–1.2 V vs. RHE. The DEMS spectrum of (b) Pt and (c) G-PtFe. (d) Collection of the cathodic (H_2) and anodic (N_2) gas products for G-PtFe catalyzed EAOR by the drainage method. (e) The faradaic efficiencies of H_2 and N_2 . (f) Apparent activation energies at different potentials.

Electrochemical stability is a critical parameter for assessing catalyst performance, nevertheless, achieving long-term operation under practical conditions remains a major challenge for EAOR. To evaluate the durability of the catalysts, chronoamperometry (CA) and chronopotentiometry (CP) were conducted, and the results are presented in Fig. 4. Specifically, Fig. 4a demonstrates the Pt catalyst illustrated the initial current density of 18.1 mA cm⁻² at 0.6 V vs. RHE, which rapidly decayed by 80% within 0.3 h and became completely deactivated after 1.8 h, with no recovery even after electrolyte replenishment. For the PtFe catalyst, the initial current density was 19.0 mA cm⁻², decreasing by 47% to 10.0 mA cm⁻² after 4 h. By sharp contrast, the activity of G-PtFe was almost fully recovered to 40 mA cm⁻² after an 8 h stability test, showing only a 29% decrease relative to its initial 56.7 mA cm⁻². Notably, to the best of our knowledge, G- PtFe outperforms most reported Pt- based EAOR catalysts, which typically deliver current densities of 0.07 to 2.5 mA cm⁻² after 0.05–2 h at the applied

potential of 0.6–0.7 V vs. RHE (Fig. 4b). Moreover, G-PtFe operated stably even at the higher potential of 0.8 V vs. RHE, whereas PtFe underwent moderate deactivation and Pt rapidly lost activity under the same condition (Fig. S17). Under constant current density of 10 mA cm⁻² (Fig. 4c), the G-PtFe catalyst demonstrated exceptional durability, maintaining stable operation for 89.5 h, which is 447.5 times longer than Pt (0.2 h) and 22.3 times longer than PtFe (4.0 h). After CA and CP tests, almost identical XPS pattern of Pt 4f (Fig. S18) and little Fe leaching (Fig. S19) can be found confirms the high stability of the as-prepared G-PtFe. Under harsher conditions, at a higher current density of 50 mA cm⁻², the G-PtFe retained operation for 2.1 h and 12.5 h at 25 °C and 80 °C, respectively (Fig. S20). Significantly, this represents the longest reported operational stability for EAOR in 1 M KOH electrolyte to date (Fig. 4d).

Having confirmed the high activity and outstanding durability of G- PtFe in a three- electrode configuration, we further evaluated its EAOR performance under realistic

device conditions. The DAFC was assembled with a G-PtFe anode (1.0 cm²), a commercial Pt/C cathode (SEN-23K) and a PBI-35 membrane. For comparison, a symmetric DAFC employing Pt/C as both the anode and cathode was also fabricated. As presented in Figs. 4e and 4f, the Pt/C-DAFC recorded an open circuit voltage (OCV) of 0.49 V and a peak power density of 12.9 mW cm⁻², consistent with previous report [28]. In stark contrast, the G-PtFe-DAFC obtained an enhanced OCV to 0.55 V and a peak power density of 43.0

mW cm⁻², which is 233% improvement over Pt/C-DAFC and superior to representative literature values [6, 59–61]. These results collectively highlight the outstanding durability and high activity of G-PtFe in both half- cell and full- cell configurations. However, the enhanced catalytic performance of G-PtFe can only be fully understood by elucidating the EAOR poisoning mechanism inherent to conventional Pt-based catalysts.

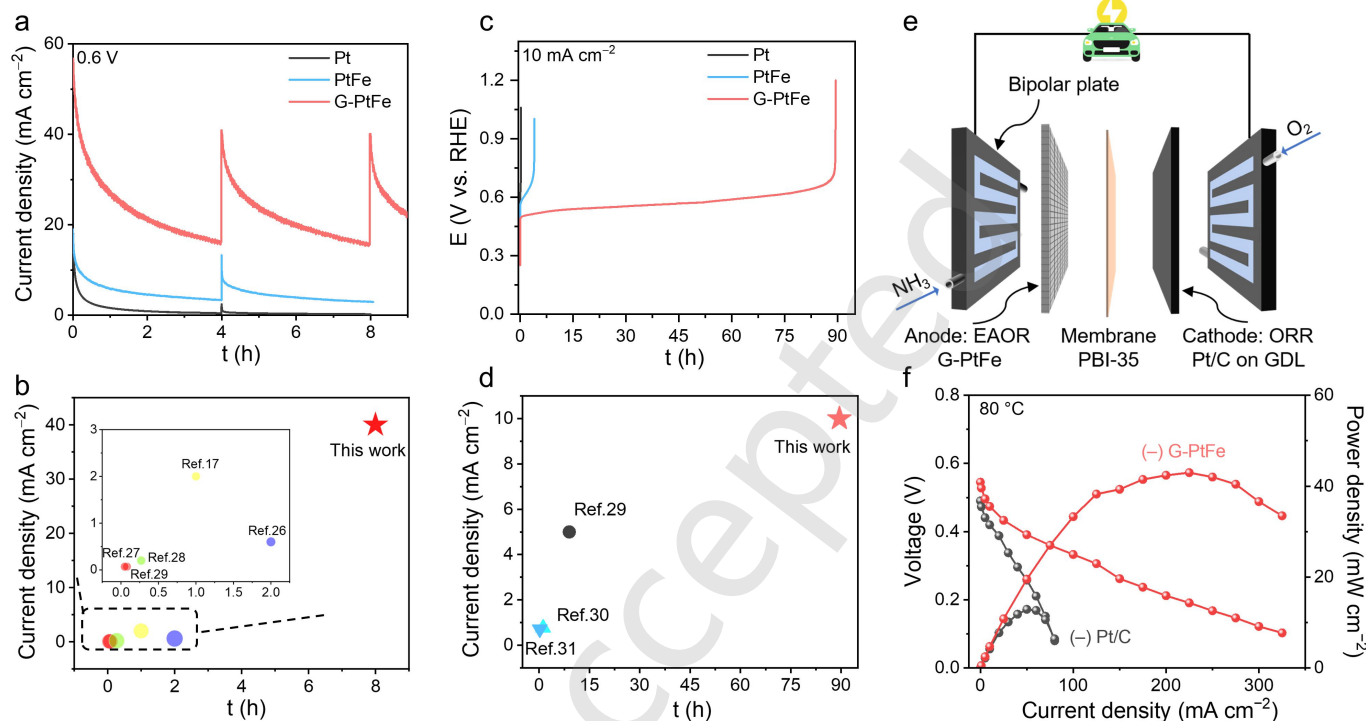


Figure 4 EAOR stability evaluation of Pt, PtFe and G-PtFe. (a) CA tests at 0.6 V vs. RHE at room temperature. (b) The comparison of CA stability on different Pt-based electrocatalysts. (c) CP tests at constant current density of 10 mA cm⁻² at room temperature. (d) The comparison of CP stability on different Pt-based electrocatalysts. (e, f) EAOR performances of DAFCs at 80 °C: (e) The schematic illustration of DAFC, (f) The polarization and power density curves for G-PtFe and Pt/C. The electrolyte is Ar-saturated aqueous solution of 1 M KOH + 1 M NH₃·H₂O.

3.3 EAOR anti-poisoning mechanism

Previous studies have revealed that the co-adsorption of NH₃ and OH is a prerequisite for EAOR [32], yet the identification of toxic species (N-containing species or OH) remains debated. To uncover the origin of different performances and anti-poisoning behaviors, the potential-dependent surface adsorption of Pt, PtFe and G-PtFe was systematically investigated. CA polarization at 0.6 and 0.8 V vs. RHE for 10 mins were first performed to deliberately accumulate the toxic species on the studied catalysts at low- and high-potential regimes (Fig. 5a). Then XPS measurements were conducted on the post-CA catalysts to identify the poisoning species. As depicted in Figs. 5b and 5c, the pristine Pt shows notable increased signal intensities of N 1s and O 1s after 10 mins' CA measurement at 0.6 V vs RHE as compared to the reference sample (immersed in the electrolyte without applied potentials). This intensity augmentation reflects substantial N-O accumulation on the Pt surface, which could cause surface passivation, in agreement with previous studies [13, 41, 62]. By contrast, G-PtFe shows a different behavior with neglectable N-O-containing species under identical

conditions. The different contents of N-O-containing species for Pt and G-PtFe correspond to their different anti-poison abilities, suggesting that the N-O-containing species is highly relative to the catalytic poisoning at the low potential.

In situ attenuated total reflection Fourier transform infrared spectroscopy (in situ ATR-FTIR) was employed to study the adsorption behavior of OH on catalyst surfaces through quantitative monitoring of the characteristic O–H stretching vibrations associated with adsorbed OH (OH_{ads}) in the spectral region of 3000–3500 cm⁻¹ [63, 64]. Since Pt surfaces undergo OH adsorption at potentials exceeding 0.5 V vs. RHE, spectra recorded at open circuit potential (OCP) served as reference background (Fig. 5d). Comparative spectroscopic analysis (Fig. 5e) revealed a pronounced enhancement of O–H stretching modes for both G-PtFe and PtFe relative to Pt at 0.6 V vs. RHE, indicating that Fe-containing catalysts possess a superior OH adsorption capability at low potentials. This enhanced OH adsorption originates from the electronic modulation induced by the alloying ligand effect and/or surface concentration-gradient configuration, and thus, accelerates EAOR kinetics by facilitating the oxidative removal of N-based intermediates.

In contrast, the limited OH adsorption on pristine Pt leads to incomplete ammonia oxidation and the accumulation of N-O species on the surface, thereby causing severe poisoning. Notably, when the potential was increased to 0.8 V vs. RHE, the Pt catalyst achieved dramatically enhanced OH_{ads} capability, reaching a level comparable to PtFe (Fig. 5f). However, both Pt and PtFe demonstrated a poor EAOR performance at the high potential (Fig. 5a), implying that the excessive adsorption of OH species block the active sites, leading to EAOR deactivation.

To verify this assumption, the subsequent NH_3 adsorption experiments were conducted to elucidate the underlying cause of the observed activity loss. We assessed the NH_3 adsorption capability based on the changes in OCP and reaction current density before and after the introduction of NH_3 . As depicted in Fig. 5g, the changes in OCP upon NH_3 injection were 0.50 V, 0.45 V, 0.33 V for G-PtFe, PtFe, Pt,

respectively, indicating that all three catalysts possess somewhat NH_3 adsorption capacity, with the strongest adsorption observed for G-PtFe and the weakest for pristine Pt. To evaluate the NH_3 adsorption capability at elevated potentials, the catalysts were pre-adsorbed with OH at 0.6 and 0.8 V vs. RHE in 1 M KOH solution before NH_3 injection. As evident from Fig. 5h, PtFe and G-PtFe feature high EAOR current densities at 0.6 V vs. RHE, directly reflecting their continuous NH_3 adsorption surpassing pristine Pt under these conditions. When the potential increased to 0.8 V vs. RHE (Fig. 5i), only G-PtFe displayed a rapid increase in current upon NH_3 injection, reflecting its sustained ability to adsorb NH_3 , whereas Pt and PtFe delivered negligible EAOR current responses after NH_3 injection, indicating an incapability of NH_3 adsorption that may be caused by the excessive OH absorption under this high potential.

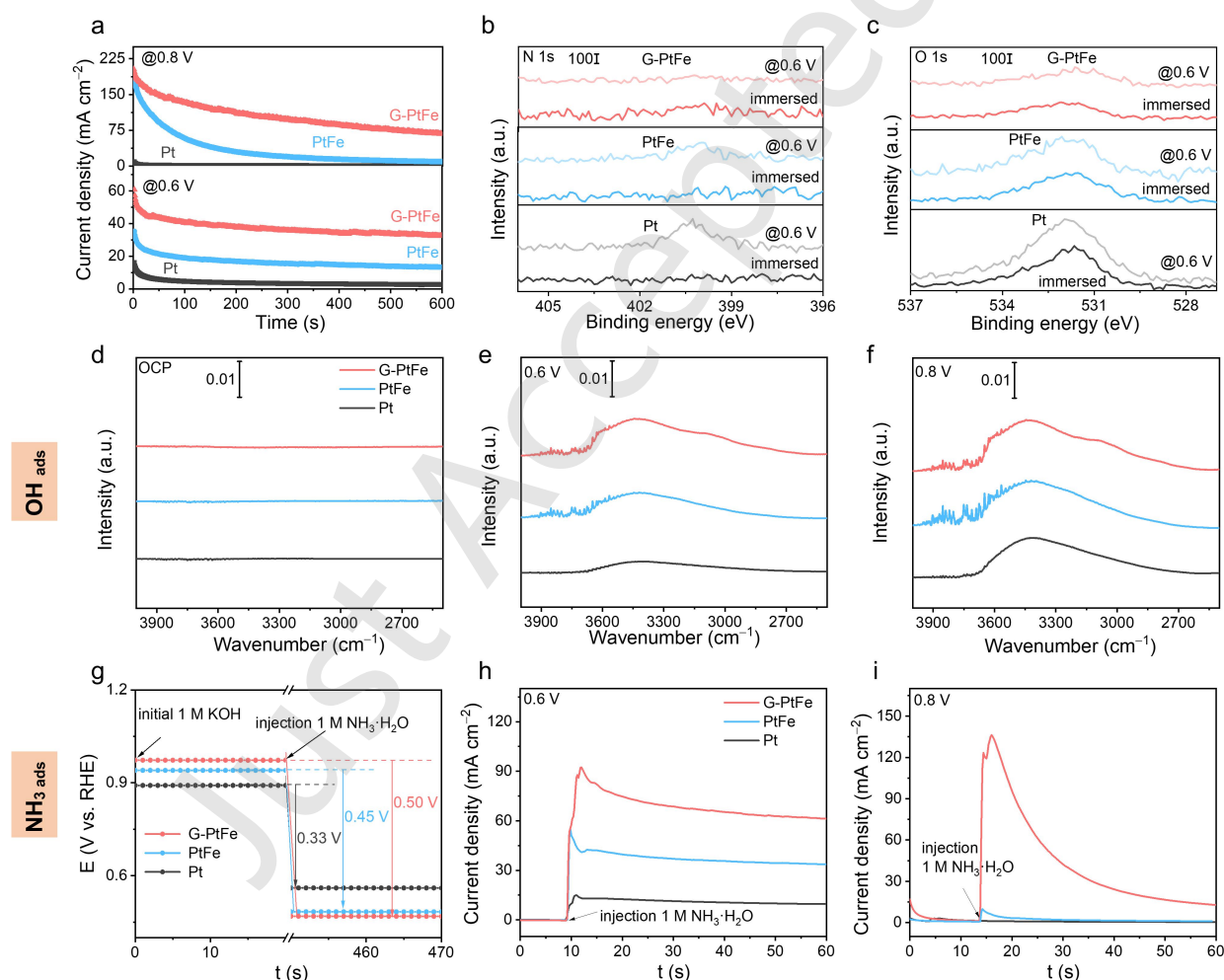


Figure 5 Comparative study of anti-poisoning electrochemical behavior on the G-PtFe, PtFe and Pt catalysts. (a) CA tests at 0.6 V vs. RHE and 0.8 V vs. RHE for 10 min. (b, c) XPS spectra of (b) N 1s and (c) O 1s after 10 mins' CA tests at 0.6 V vs. RHE. The samples immersed in the electrolyte without applied potentials were used as references. (d-f) Hydroxyl adsorption (OH_{ads}) observed by in situ ATR-FTIR spectra at (d) OCP, (e) 0.6 V vs. RHE and (f) 0.8 V vs. RHE. (g-i) Evaluation of NH_3 adsorption: (g) Changes of OCP, Changes of current density in CA tests at (h) 0.6 V vs. RHE and (i) 0.8 V vs. RHE after injecting 1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ into 1 M KOH electrolyte.

DFT calculations were conducted to understand the different adsorption capabilities of OH and NH_3 reactants upon different potentials. First, the adsorption energies of

the reactants ($\Delta E_{\text{ads-OH}}$ and $\Delta E_{\text{ads-NH}_3}$) were evaluated across a range of applied potentials. As depicted in Figs. 6a and S21–25, the OH adsorption energies for G-PtFe and PtFe were

markedly higher than that for pure Pt, which suggested a strengthened OH binding due to the ligand effect of Fe. Simultaneously, the NH_3 binding affinity follows the descending order of $\text{G-PtFe} > \text{PtFe} > \text{Pt}$. This unique dual-adsorption capability allows G-PtFe to facilitate the co-adsorption of both reactants, sustaining high EAOR activity and thereby offering superior tolerance to poisoning at low potentials. Conversely, under a more oxidative condition of 0.8 V vs. RHE, the adsorption energy of OH increases rapidly and becomes higher than that of NH_3 for Pt and PtFe, thereby resulting in OH poisoning with their capacity to capture NH_3 diverges drastically with $\text{G-PtFe} \gg \text{PtFe} > \text{Pt}$. This sharp contrast underscores that the surface gradient-regulated electronic configuration of G-PtFe is critical for preserving efficient NH_3 activation even in highly oxidative environments.

From an electronic structure perspective, the d-band center was investigated to rationalize these energetic trends (Fig. S26). The calculated d-band centers of the catalysts correlate well with the OH adsorption energy, indicating that the Fe ligand effect upshifts the d-band center and thereby enhances OH adsorption. Notably, while the surface Fe content of G-PtFe decreases after dealloying compared to the pristine PtFe alloy, the synergistic interplay of the ligand effect and the surface compositional gradient structure in G-PtFe leads to a significant upward shift in the d-band center of its surface Pt atoms. This electronic modulation greatly enhances the intrinsic OH adsorption capability of these Pt sites, which is sufficient to compensate for the loss of Fe sites, ultimately rendering the overall OH adsorption strength of

G-PtFe outperforming conventionally homogeneous PtFe alloy. To understand the variation in NH_3 adsorption energy at higher potentials, a detailed PDOS analysis of the Pt-N interaction was further performed. As shown in Figs. 6b and 6c, the Pt-N PDOS overlap area decreases slightly from 0.215 to 0.213 for PtFe, suggesting a weakened NH_3 adsorption at high potentials, which leads to OH^- induced poisoning. In contrast, the Pt-N overlap area increases significantly from 0.263 to 0.296 for G-PtFe, indicating that strong NH_3 adsorption is preserved even under high-potential conditions. This balanced adsorption between NH_3 and OH effectively suppresses OH poisoning.

Based on these atomistic insights, the anti-poisoning mechanism is schematically proposed in Fig. 6d. For pure Pt, weak OH binding at low potentials induces the accumulation of poisoning N-O intermediates, whereas excessively strong OH binding at high potentials competitively blocks NH_3 adsorption, leading to rapid deactivation and a narrow EAOR potential window. Although the PtFe alloying improves low-potential performance by enhancing OH adsorption, it fails to prevent NH_3 starvation at high potentials due to overwhelming OH adsorption. In distinct contrast, the surface compositional gradient G-PtFe overcomes this limitation, simultaneously strengthening the adsorption of OH at low potentials and NH_3 at high potentials. This synergistic modulation creates a "dual-active" surface that can well balance the reactants' adsorption in a wide potential window, and thus, enhance the EAOR activity and durability of G-PtFe.

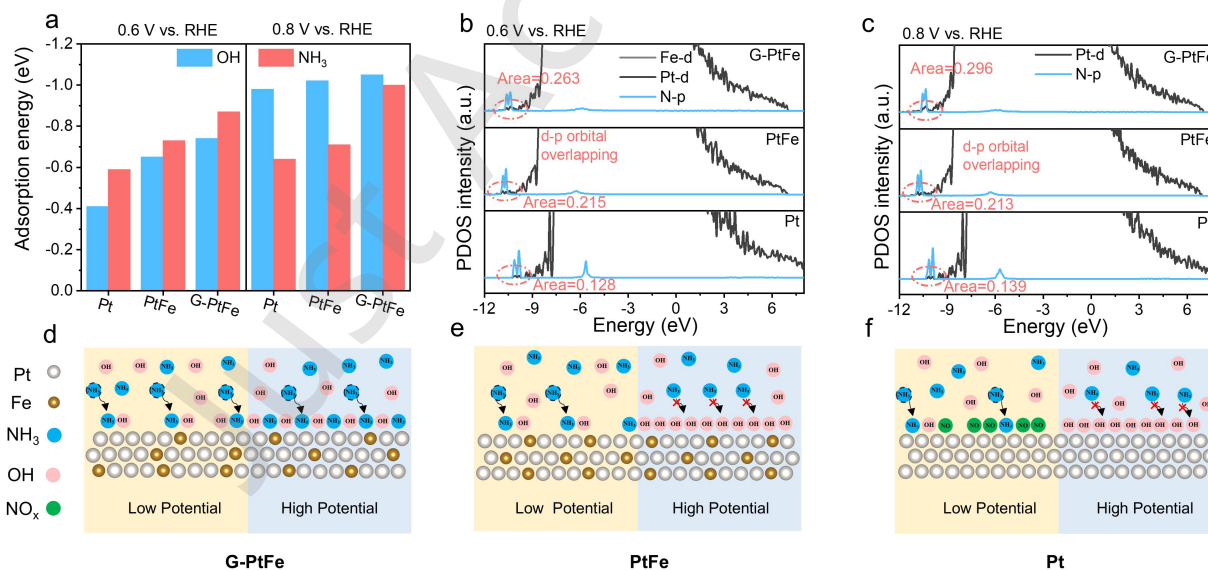


Figure 6 DFT calculations elucidated the potential-dependent of NH_3 /OH on G-PtFe, PtFe and Pt. (a) Adsorption energies of NH_3 and OH at 0.6 V and 0.8 V vs. RHE. The calculated of overlap area of d-p orbital at (b) 0.6 V vs. RHE, (c) 0.8 V vs. RHE. The competition adsorptions of NH_3 and OH at different potentials during EAOR of (d) G-PtFe, (e) PtFe, (f) Pt.

4 Conclusions

In this study, we synthesized a surface compositional gradient PtFe alloy catalyst (G-PtFe) catalyst featuring a Pt-Fe gradient shell and a PtFe alloy core through a facile hydrothermal synthesis followed by electrochemical dealloying. The G-PtFe catalyst exhibits markedly enhanced

EAOR performance, achieving a peak current density of 541.7 mA cm^{-2} and maintaining stable activity for 89.5 h in a three-electrode cell at room temperature and 10 mA cm^{-2} . Furthermore, when employed as the anode in a DAFC equipped with a commercial Pt/C cathode and a PBI-35 membrane, G-PtFe delivers substantial improved open-

circuit voltage, peak power density, and long-term durability, showing its potential for practical applications. Systematic adsorption analysis reveals that EAOR deactivation stems from potential-dependent competitive adsorption imbalance among key reaction species. Specifically, insufficient OH adsorption at low potentials causes the accumulation of N-containing intermediates and surface poisoning, whereas excessive OH adsorption relative to NH₃ induces surface passivation at potentials above 0.8 V vs. RHE. Although ligand-effect modulation through conventional alloying can improve low-potential EAOR stability, it remains insufficient to overcome high-potential poisoning. The surface compositional gradient design enables potential-dependent regulation of OH and NH₃ adsorption energetics, achieving balanced adsorption behavior across 0.5–1.2 V vs. RHE and thereby enhancing both EAOR activity and operational stability. Overall, this work provides fundamental understanding of potential-driven catalyst poisoning and introduces a surface gradient alloying strategy for developing high active and poisoning-resistant EAOR catalysts.

Electronic Supplementary Material: Supplementary Figures S1–S26 are available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909171>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was partially supported by Scientific Research Fund of Zhejiang Provincial Education Department (Y202351294) and Zhejiang Provincial Higher Education Domestic Visiting Scholars Program Faculty Professional Development Project (FX2025187). The authors thank Dr. Qike Jiang from Instrumentation and Service Center for Physical Sciences (ISCPS) and Dr. Huanhuan Huang from Micro/Nano Fabrication at Westlake University for HRTEM characterization, Dr. Changle Mu and Mrs. Min Zhou from ISCPS for XPS and ICP-MS measurements, and Dr. Xu Chen from Micro/Nano Fabrication at Westlake University for XRD characterization.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Author 1: Conceptualization, investigation, data curation, visualization, validation, funding acquisition, project administration, writing – original draft. Author 2: Data curation, validation, writing – review & editing. Author 3: Investigation, data curation. Author 4: Investigation, data curation. Author 5: Investigation, data curation. Author 6: Project administration, conceptualization, supervision, funding acquisition, writing – review & editing. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Enhancing electrocatalytic ammonia oxidation via surface concentration-gradient platinum alloying

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Supporting information to <https://doi.org/10.26599/NR.2026.94909171>

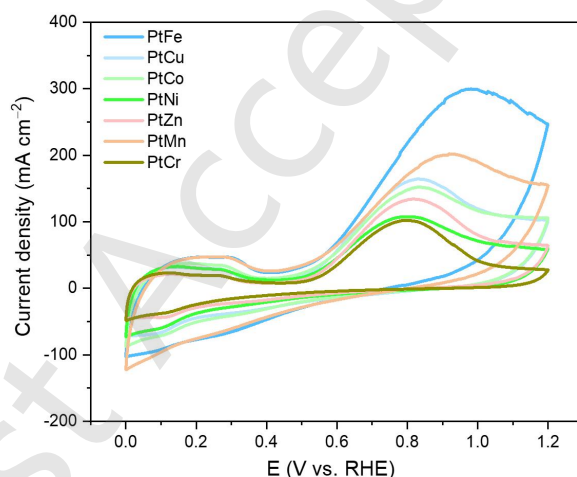


Figure S1 The CV curves of Pt-based binary alloy catalysts in Ar-saturated 1 M KOH + 1 M NH₃·H₂O electrolyte.

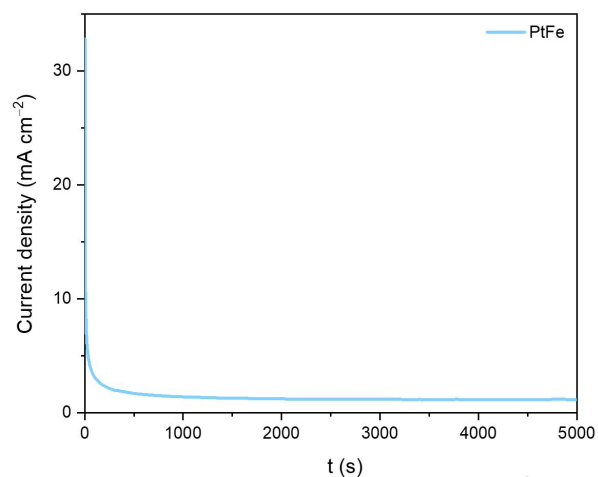


Figure S2 CA test of PtFe at 0.6 V vs. RHE in Ar-saturated 1 M KOH + 1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ electrolyte.

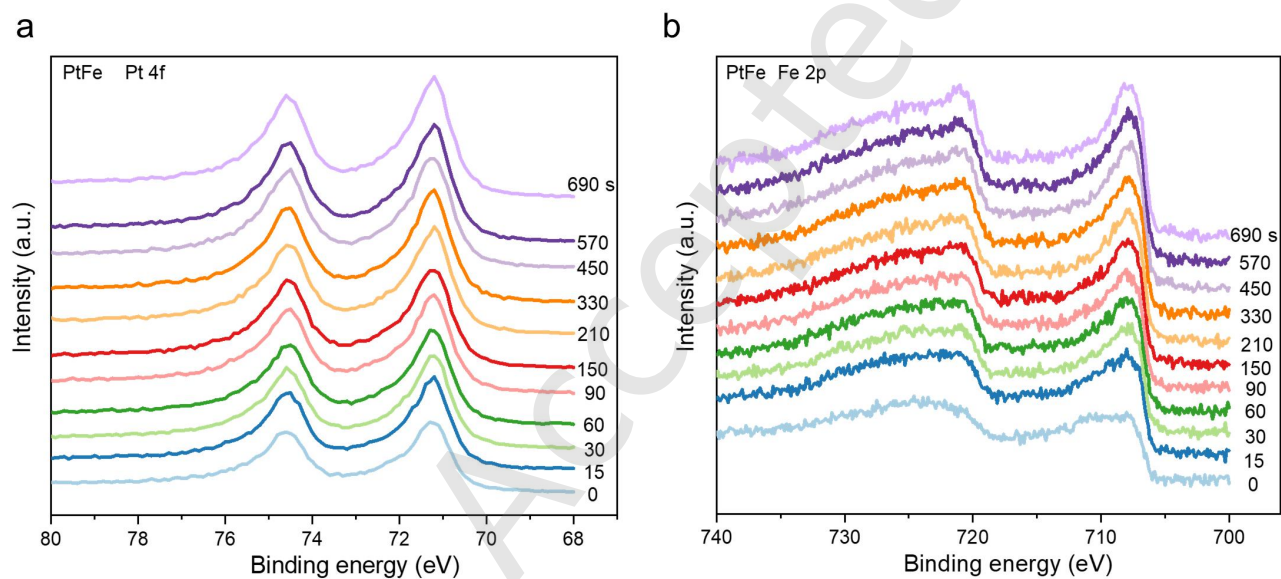


Figure S3 XPS patterns with Ar⁺ surface etching measurements of (a) Pt 4f and (b) Fe 2p for PtFe.

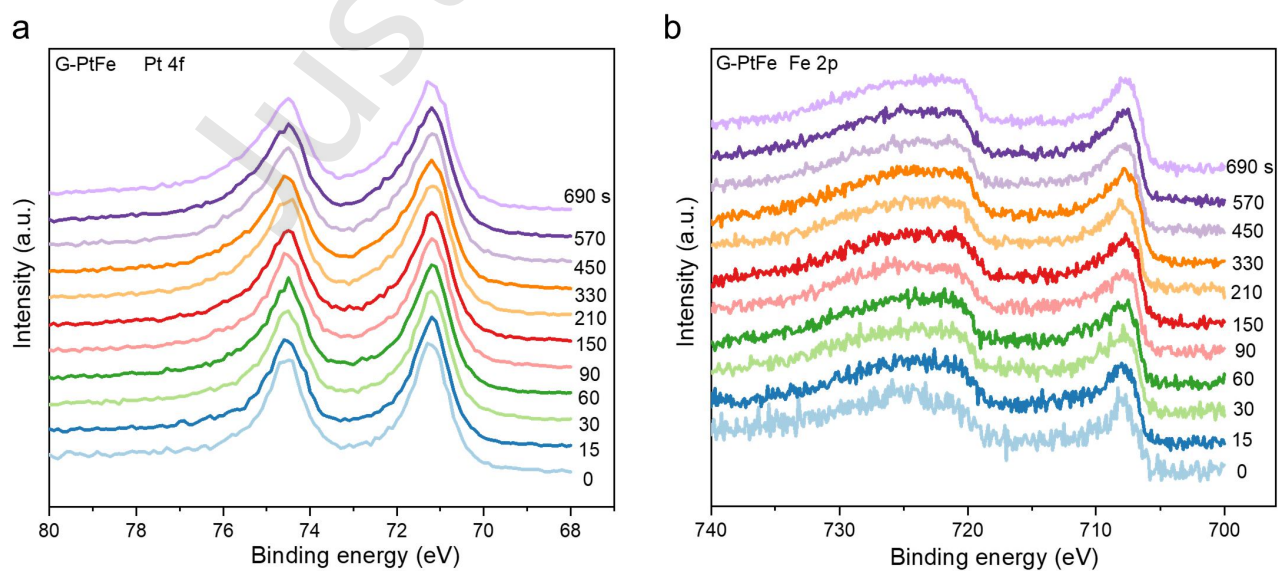


Figure S4 XPS patterns with Ar⁺ surface etching measurements of (a) Pt 4f and (b) Fe 2p for G-PtFe.

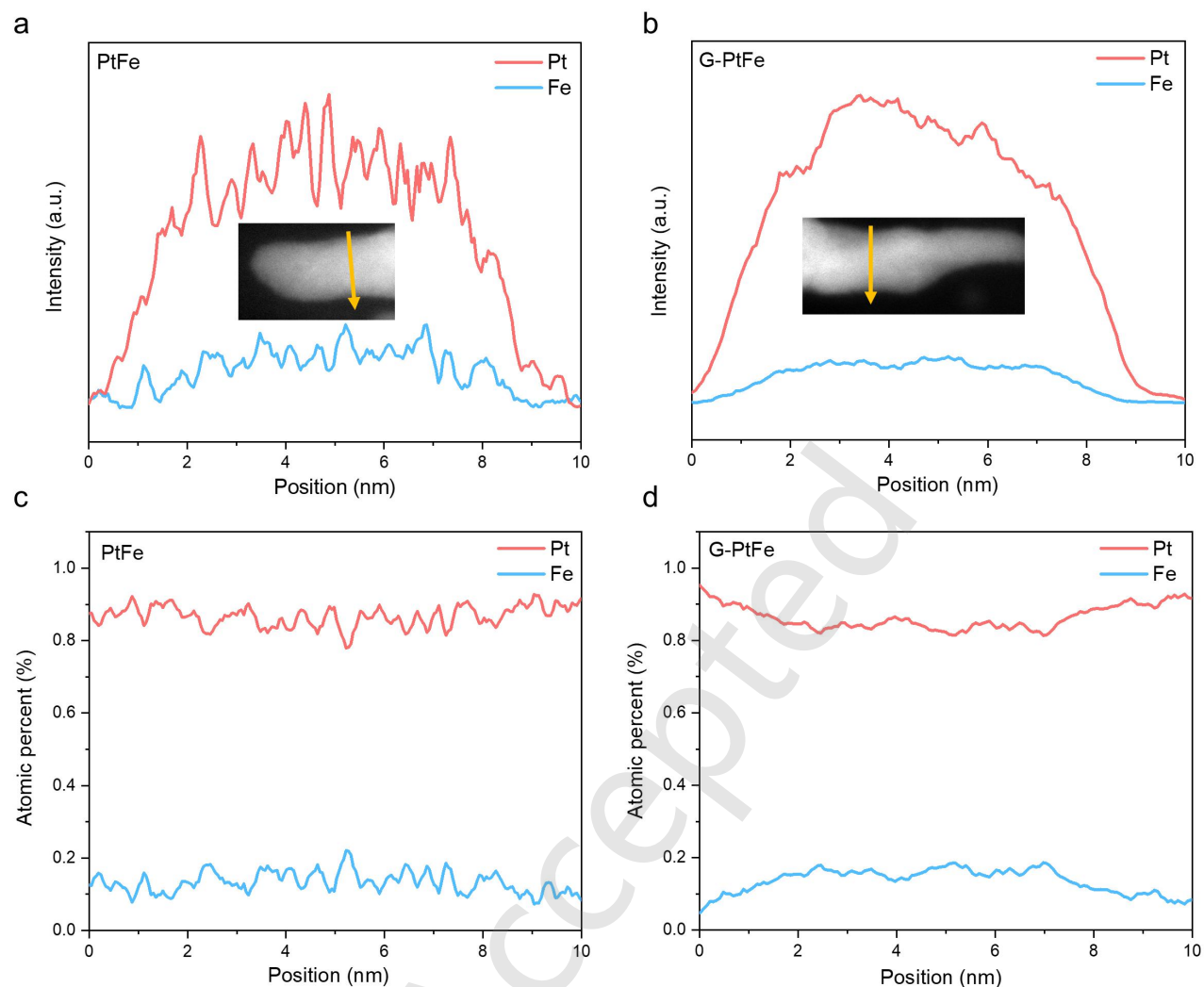


Figure S5 STEM-EDS line-scan profiles along the orange line in particle of (a, c) PtFe and (b, d) G-PtFe.

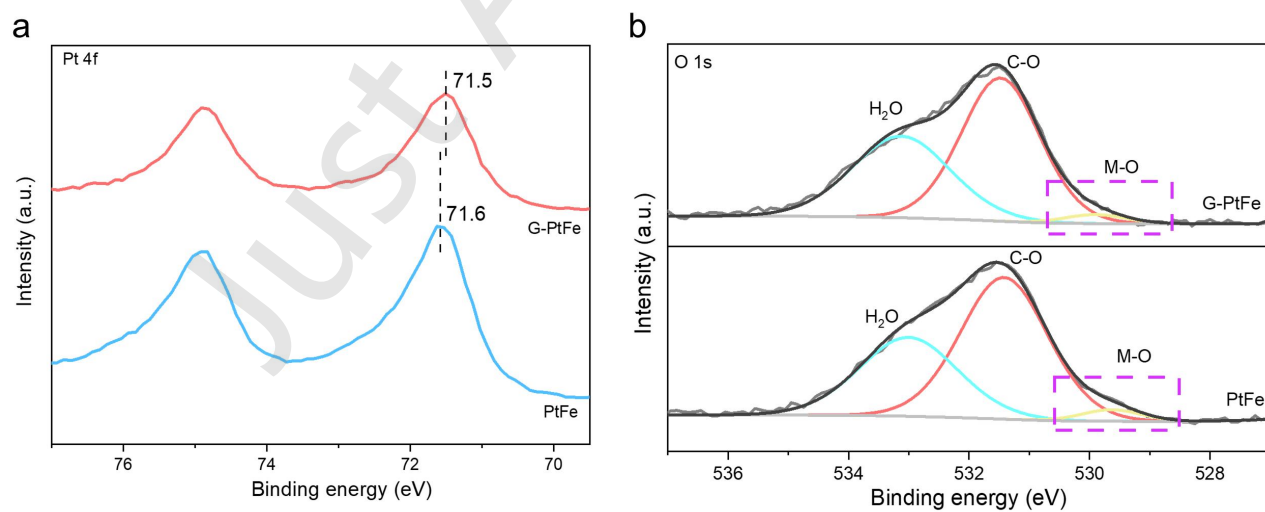


Figure S6 XPS patterns of PtFe and G-PtFe (after electrochemical dealloying in 0.5 M H_2SO_4): (a) Pt 4f and (b) O 1s.

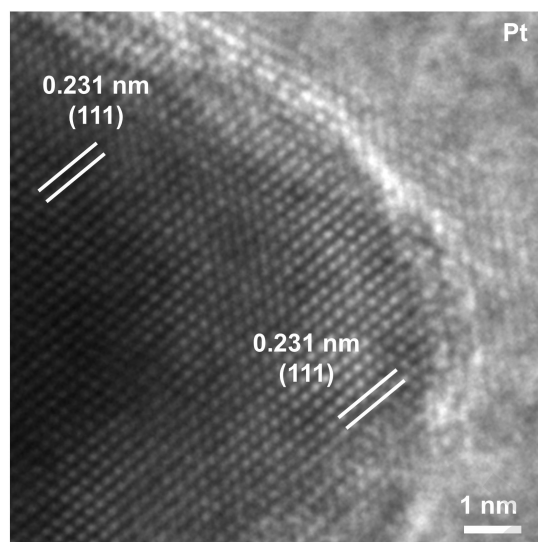


Figure S7 HRTEM image of pristine Pt.

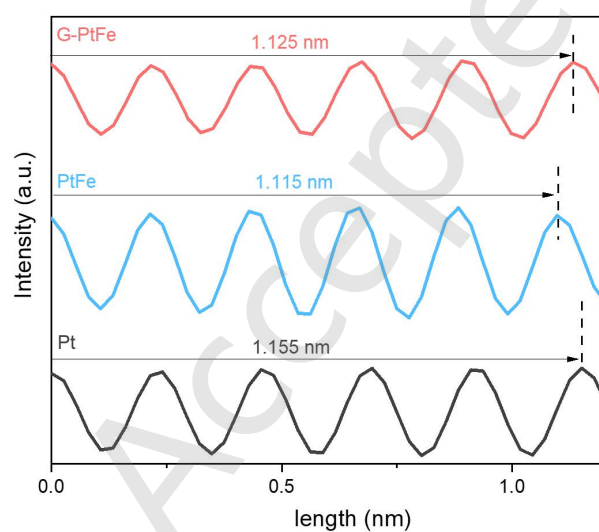


Figure S8 The integrated intensity profiles along (111) spacing directions (perpendicular to the facets) of Pt, PtFe and Pt surface of G-PtFe. The peaks and valleys represent the atoms and gaps, respectively.

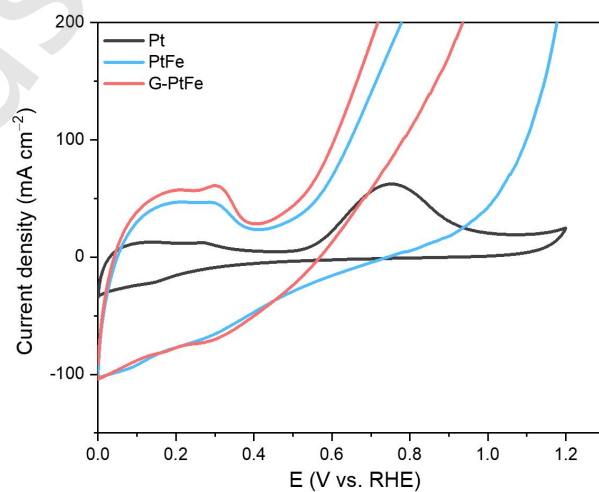


Figure S9 Illustration of the onset potential of Pt, PtFe and G-PtFe.

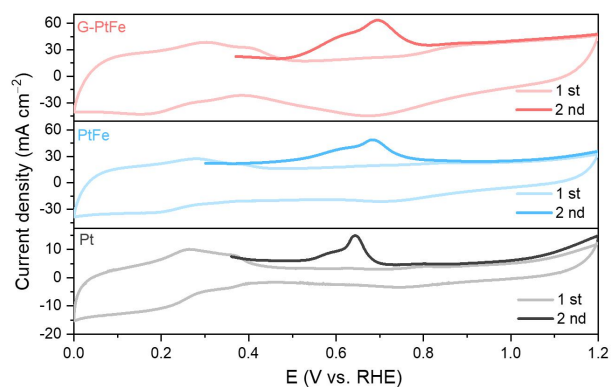


Figure S10 CO-ECOA evaluation process for G-PtFe, PtFe and Pt.

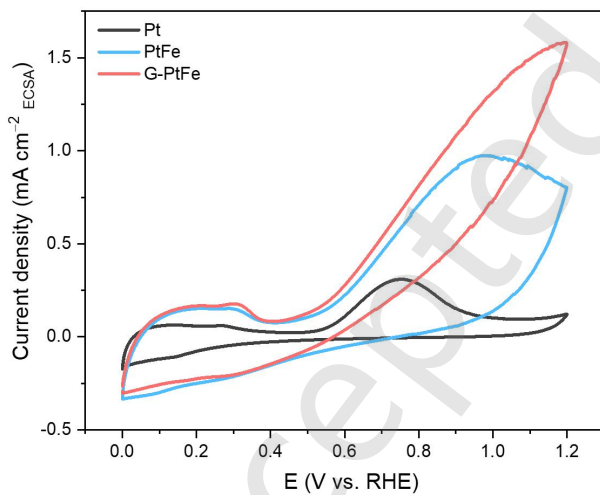


Figure S11 ECSA normalized CV curves for G-PtFe, PtFe and Pt.

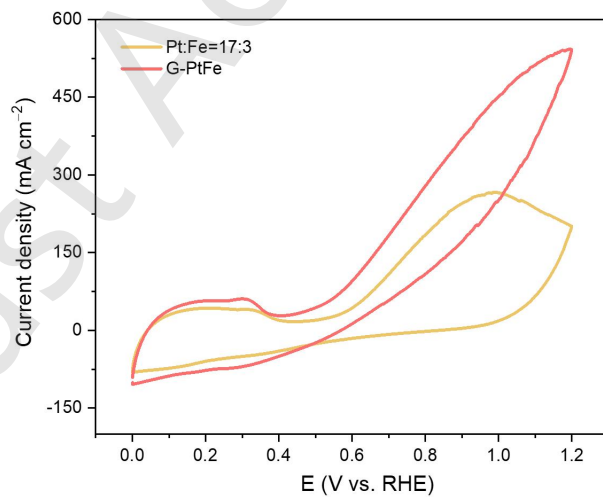


Figure S12 Comparison of CV curves for G-PtFe (with surface composition of Pt:Fe=17:3) and reference PtFe sample (with bulk composition of Pt:Fe=17:3).

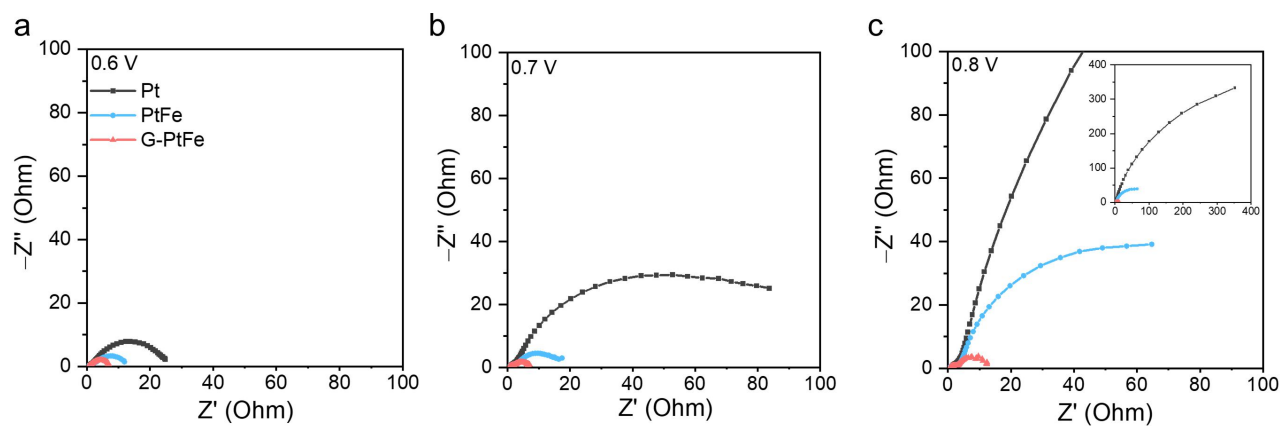


Figure S13 EIS Nyquist plots for G-PtFe, PtFe and Pt at different potentials: (a) 0.6 V vs. RHE, (b) 0.7 V vs. RHE and (c) 0.8 V vs. RHE, the inset shows the full view of EIS Nyquist plot.

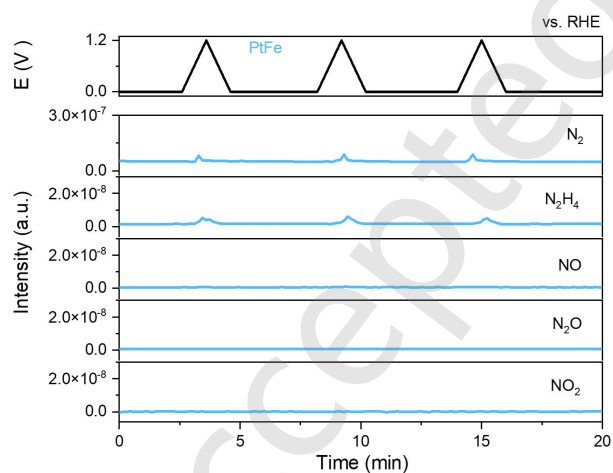


Figure S14 The DEMS spectrum of PtFe.

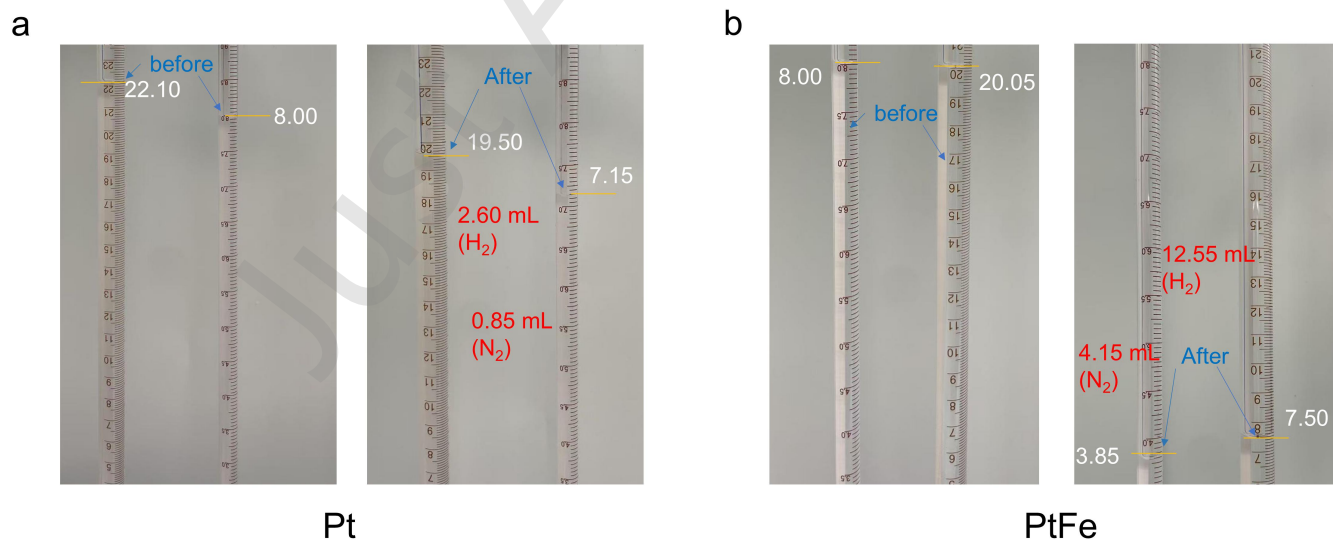


Figure S15 Collection of the cathodic (H_2) and anodic (N_2) gas products for (a) Pt and (b) PtFe catalyzed EAOR by the drainage method.

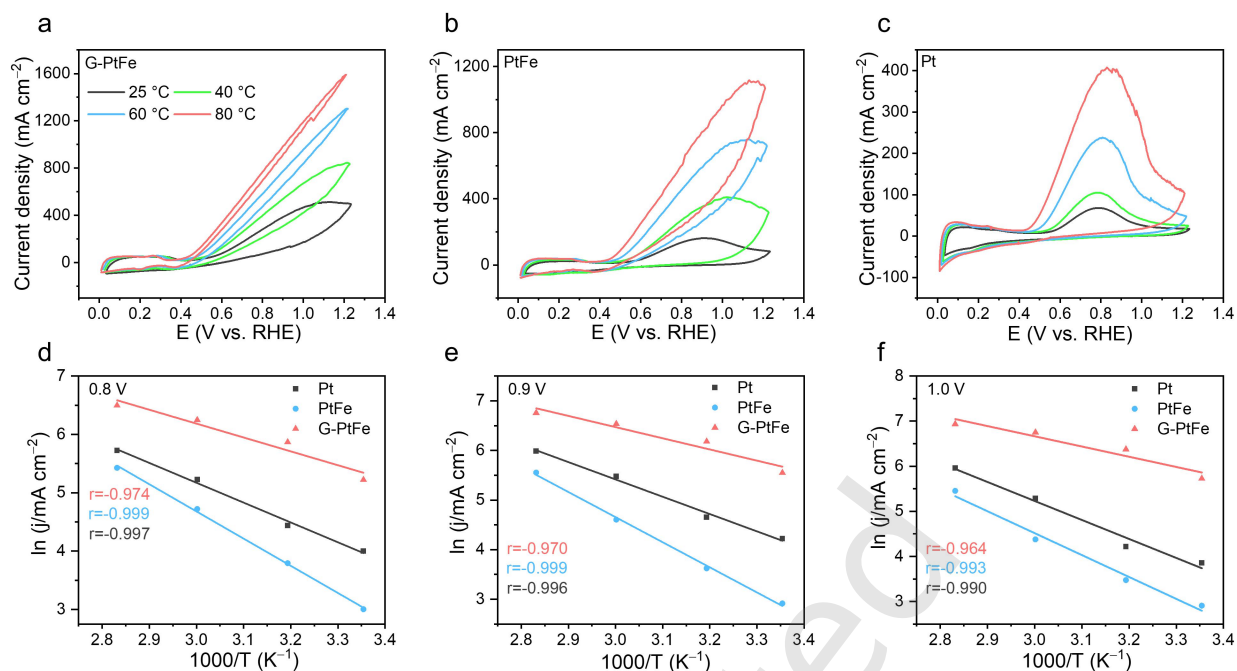


Figure S16 CV curves of (a) G-PtFe, (b) PtFe and (c) Pt in Ar-saturated 1 M KOH + 1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ electrolyte at various temperatures from 25 °C to 80 °C. Arrhenius plots at (d) 0.8 V vs. RHE, (e) 0.9 V vs. RHE and (f) 1.0 V vs. RHE, respectively.

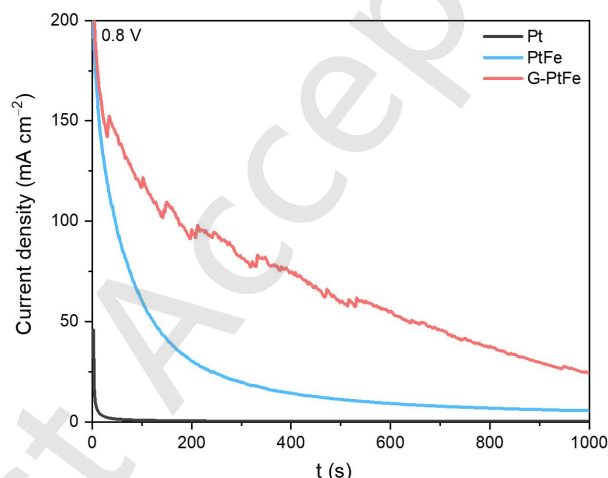


Figure S17 CA tests at 0.8 V vs. RHE at room temperature.

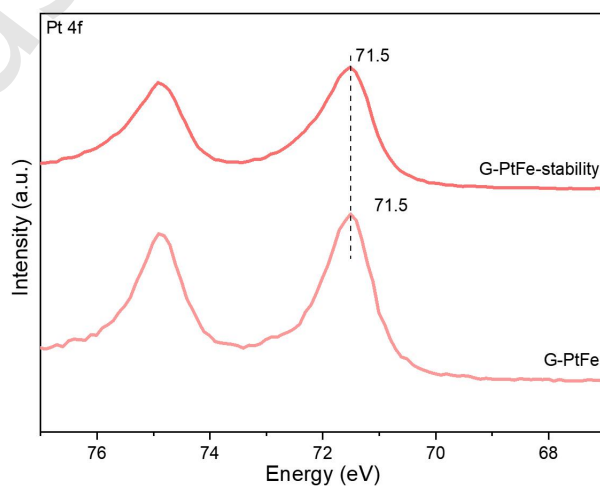


Figure S18 XPS patterns of Pt 4f for G-PtFe before and after the CP test at 10 mA cm⁻² at room temperature.

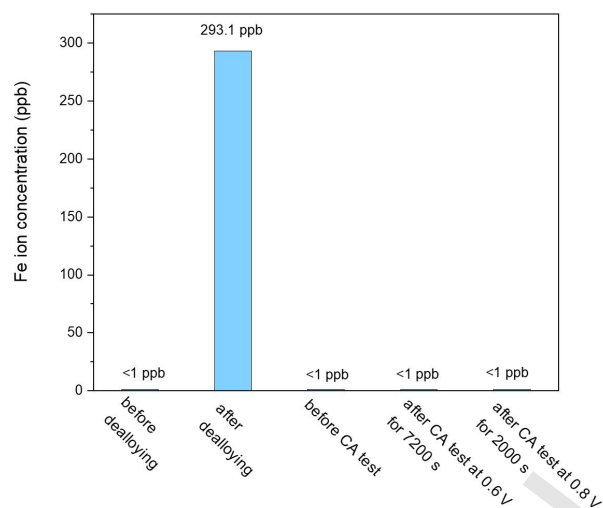


Figure S19 ICP-MS analysis of Fe ion concentration in the electrolyte during dealloying and after CA tests for G-PtFe. Dealloying was carried out in 0.5 M H₂SO₄ for 50 cycles between 0.0–1.2 V vs. RHE. The CA tests were carried out at 0.6 V vs. RHE for 7200 s and 0.8 V vs. RHE for 2000 s. Because the G-PtFe had underwent the dealloying treatment at a high potential of 1.2 V vs. RHE that is significantly higher than the 0.6 and 0.8 V vs. RHE applied in subsequent CA tests. Thus, no further Fe leaching from G-PtFe can be detected any longer.

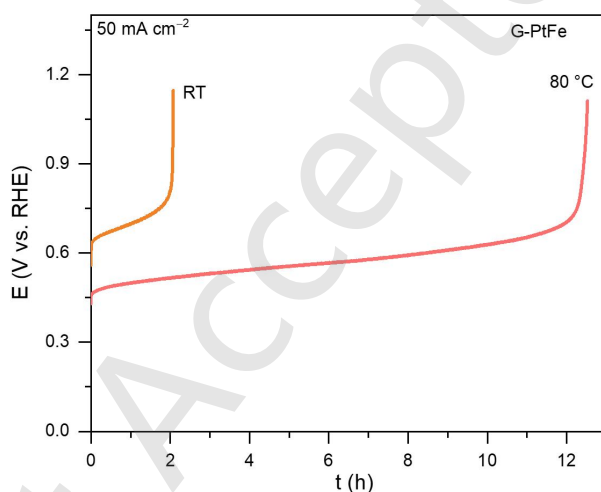


Figure S20 CP tests at constant current density of 50 mA cm⁻² at room temperature and 80 °C.

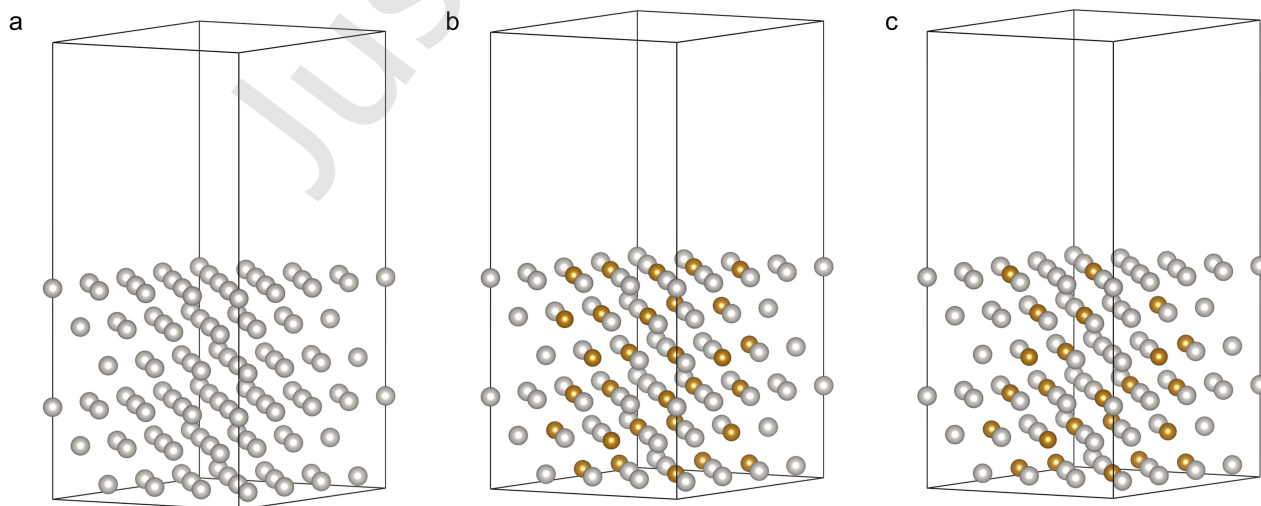


Figure S21 The computational model (111) of (a) Pt, (b) PtFe and (c) G-PtFe.

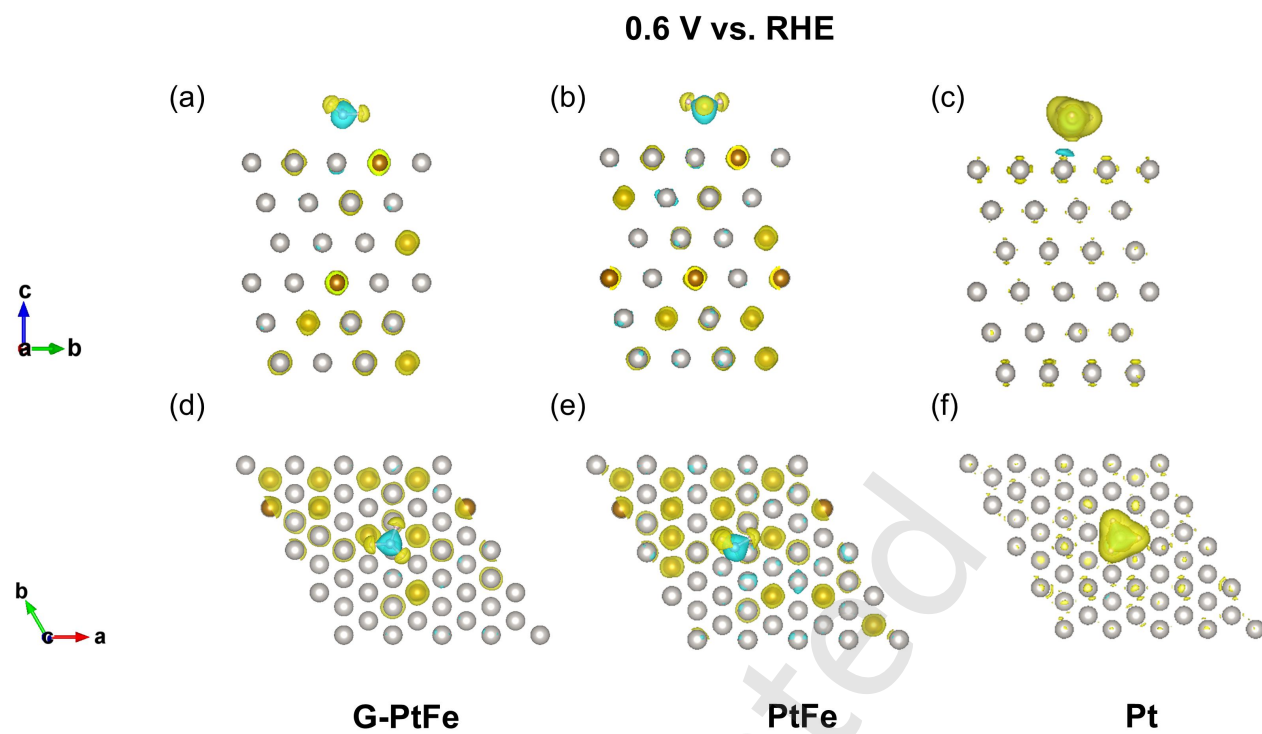


Figure S22 The charge density difference of NH_3 on (a, d) G-PtFe, (b, e) PtFe and (c, f) Pt at 0.6 V vs. RHE. The yellow and blue regions denote electron accumulation and depletion, respectively.

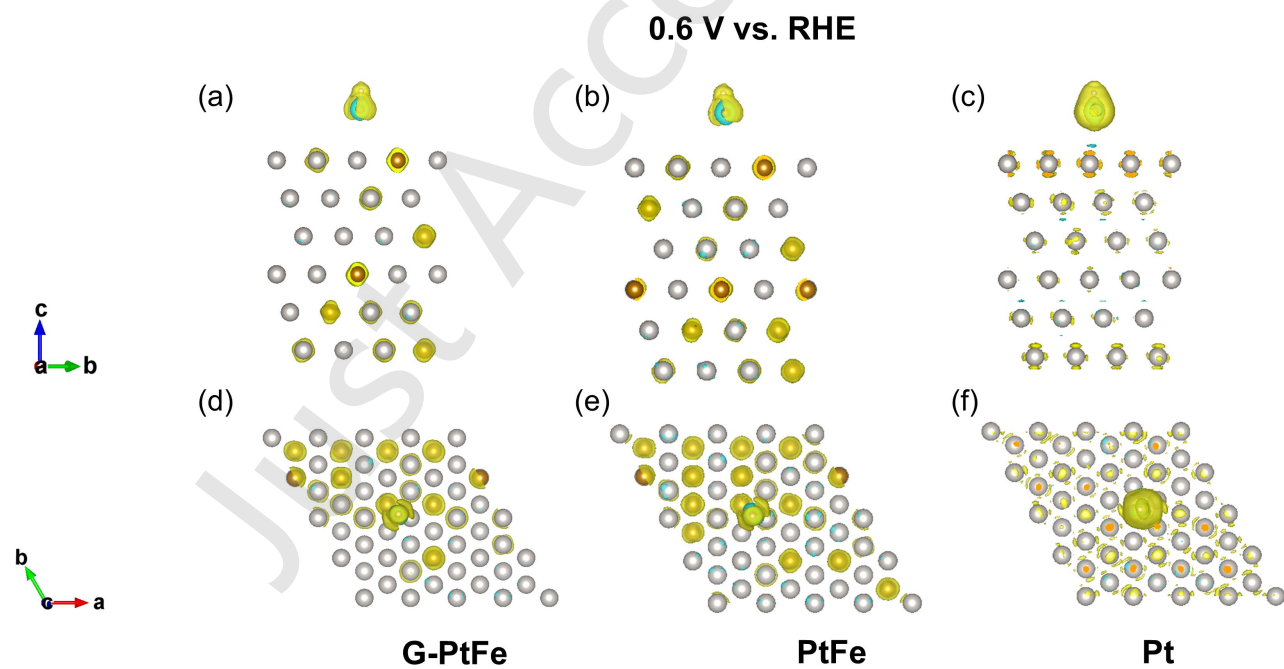


Figure S23 The charge density difference of OH on (a, d) G-PtFe, (b, e) PtFe and (c, f) Pt at 0.6 V vs. RHE. The yellow and blue regions denote electron accumulation and depletion, respectively. In the charge density difference plot, the backlit or shadowed side of the yellow isosurface is rendered in dark yellow or orange.

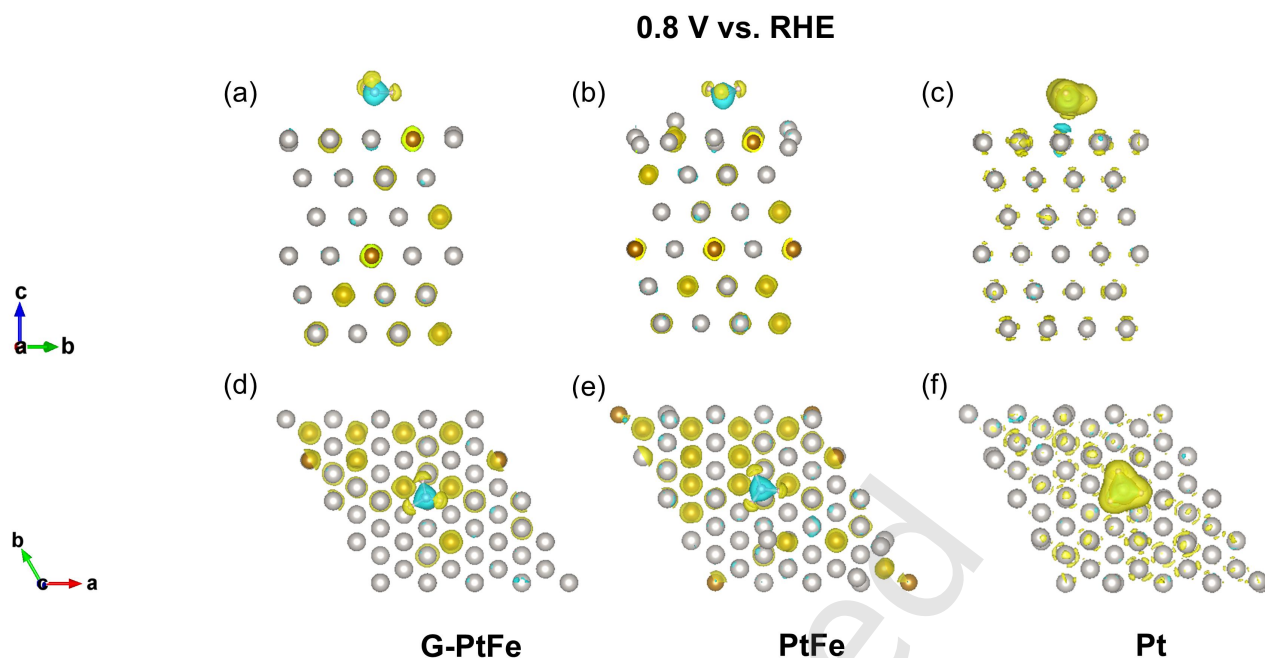


Figure S24 The charge density difference of NH_3 on (a, d) G-PtFe, (b, e) PtFe and (c, f) Pt at 0.8 V vs. RHE. The yellow and blue regions denote electron accumulation and depletion, respectively.

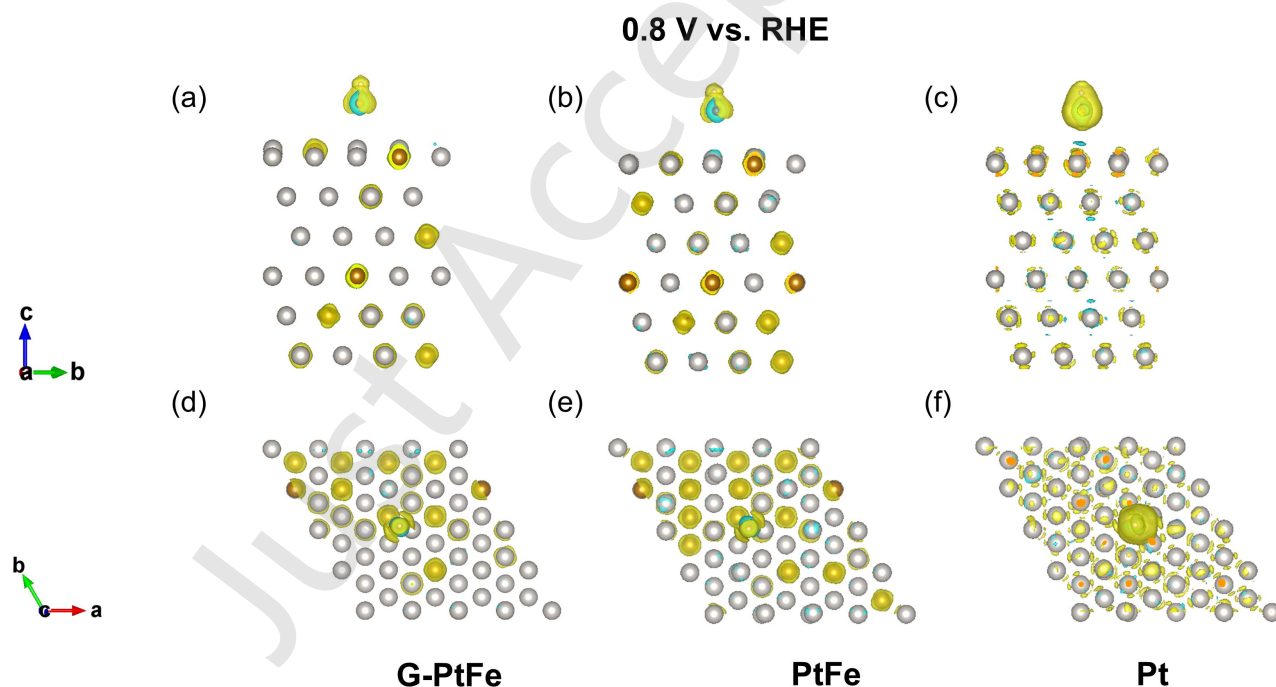


Figure S25 The charge density difference of OH on (a, d) G-PtFe, (b, e) PtFe and (c, f) Pt at 0.8 V vs. RHE. The yellow and blue regions denote electron accumulation and depletion, respectively. In the charge density difference plot, the backlit or shadowed side of the yellow isosurface is rendered in dark yellow or orange.

To elucidate the adsorption characteristics of different catalyst surfaces, charge density difference calculations were performed for NH_3 and OH adsorption (Figs. S22–S25). For NH_3 adsorption, the G-PtFe surface exhibits pronounced charge redistribution near the adsorption sites (Figs. S22a,d and S24a,d), indicating its superior adsorption affinity and electronic modulation capability. While charge transfer is also observed on the PtFe surface, it shows less intense compared to G-PtFe (Figs. S22b,e and S24b,e), whereas the charge variation on pure Pt remains relatively limited (Figs. S22c,f and S24c,f). Regarding OH adsorption (Figs. S23 and S25), pure Pt shows a weak charge response at low potentials. However, increasing the potential or incorporating Fe (as in PtFe and G-PtFe) significantly enhances surface electronic modulation and charge transfer, thereby facilitating the oxidation process.

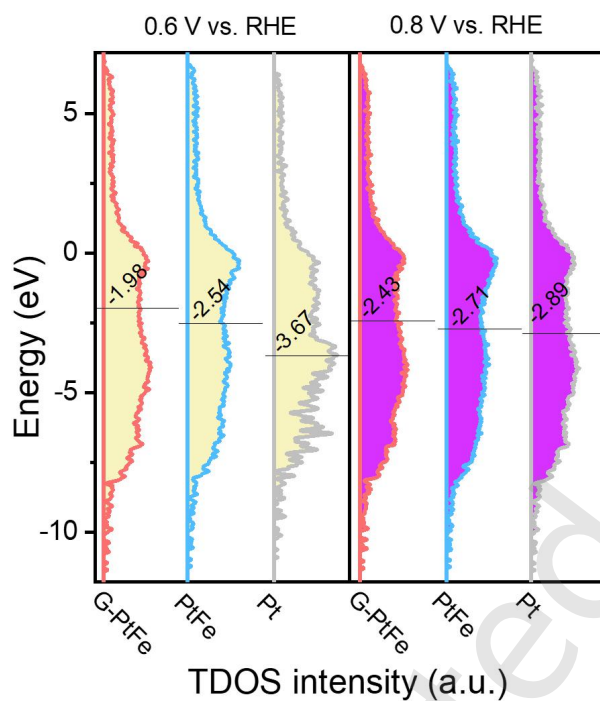


Figure S26 Total density of states (TDOS) and d-band center positions under 0.6 V vs. RHE (yellow) and 0.8 V vs. RHE (purple). Fermi level (E_F) = 0 eV.