
F-centre charge state and dynamism govern oxide electrocatalytic selectivity

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1	Table of Contents	
2	Supplementary Notes 1-9.....	2-5
3	Supplementary Figures 1-55.....	6-60
4	Supplementary Tables 1-19.....	61-79
5	Supplementary References 55-92.....	80-82
6		

Supplementary Notes

Supplementary Note 1. XRD peak broadening and Williamson-Hall analysis

XRD peak broadening has two independent physical origins, including limited coherent crystallite size and uniform lattice microstrain. For defective materials with severe lattice distortion, Scherrer-only analysis will misattribute strain broadening to smaller particle size. The Williamson-Hall method quantitatively separates these two contributions via the following equation:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4 \varepsilon \sin \theta$$

where D is the coherent crystallite size, K is the shape factor, λ is the X-ray wavelength, β is the FWHM, θ is the Bragg angle, and ε is the lattice microstrain. In this model, the intercept is related to the finite-size contribution, whereas the slope reflects the microstrain contribution to peak broadening.

Prior to fitting, all XRD patterns were processed with identical background correction, fitting ranges and peak shape functions to guarantee cross-sample consistency. Multiple independent diffraction peaks were used for linear regression, avoiding uncertainty from single isolated peak fitting. This workflow reliably distinguishes broadening from coherent domain size and defect-driven lattice distortion, enabling accurate quantification of microstrain in defective catalysts.

Supplementary Note 2. Influence of different cationic chloride templates on F center formation

To clarify the different thermal behaviors of the NH_4Cl and NaCl template systems during annealing, thermogravimetric analysis of NH_4Cl and NaCl was first performed (Supplementary Fig. 5). We further explored the potential influence of alternative cationic chloride templates, including KCl and CaCl_2 , under synthetic conditions identical to those used for the NaCl -template system. Specifically, 100 mg of the $\text{Zr}(\text{OH})_4$ precursor and 3.0 g of KCl or CaCl_2 were thoroughly mixed by ball milling for 10 min. The obtained solid mixture was then placed in a muffle furnace and heated to 500 °C at a ramping rate of 5 °C min⁻¹, followed by annealing at 500 °C for 4 h. After cooling to room temperature, the resulting products were washed with deionized water 3-4 times to remove residual chloride salts and then dried at 100 °C overnight. The obtained samples were denoted as KCl-ZrO_2 and $\text{CaCl}_2\text{-ZrO}_2$, respectively. XRD, HAADF-STEM, EDS mapping and EPR characterizations were performed to confirm

the influence of different chloride template systems on *F*-center formation, as shown in **Supplementary Fig. 6-8**.

Supplementary Note 3. Calibration and normalization XPS

XPS spectra were processed using Thermo Advantage software (version 6.9). The binding energy scale was internally calibrated by setting the adventitious C 1s peak at 284.8 eV to correct the surface charging effect. The background was subtracted via the Shirley model to properly address inelastic electron scattering of Zr 3d signals, which is essential for the accurate quantification of Zr oxide states. All peaks were fitted with a mixed Gaussian-Lorentzian product function with a fixed Lorentzian ratio of 30%^[55].

Supplementary Note 4. Atomic-resolution EELS acquisition and data processing

The atomic level electron energy loss spectroscopy EELS measurements were conducted using a JEOL JEM ARM200F NEO ARM instrument equipped with double aberration correction. After selecting representative nanoparticles the zone axis and astigmatism were carefully adjusted to facilitate the acquisition of aberration corrected high angle annular dark field scanning transmission electron microscopy Ac HAADF STEM images with atomic resolution as much as possible. Subsequently EELS spectrum scanning was performed on the targeted regions. During the data processing stage Gatan GMS 3 software was utilized to select three distinct local regions for EELS analysis. To minimize potential background interference and enhance the reliability of the signals to the greatest extent possible the background was subtracted using a baseline established at the pre-edge position where no peaks were present.

Supplementary Note 5. Calibration and normalization of Zr K-edge XANES

To minimize energy drift and ensure accurate edge-shift analysis, all samples including *F*²-Zr³⁺, *F*¹-Zr⁴⁺ and pristine ZrO₂ were measured in a single experimental batch. A Zr foil was measured simultaneously with each sample as the internal energy calibration reference. Synchronous acquisition of sample and Zr foil spectra enables precise alignment of photon energy and baseline, effectively suppressing instrumental artifacts and ensuring physical significance of relative edge shifts among different samples.

After data collection, raw spectra were normalized following standard protocols. Specifically, the pre-edge region was normalized to 0, and the post-edge absorption

jump was normalized to 1. Such standardized step normalization guarantees reliable analysis of near-edge energy shifts, and the obtained edge displacement can well reflect the overall Zr oxidation state in different *F* center configurations.

Supplementary Note 6. Data processing and fitting procedures of Zr K-edge EXAFS

EXAFS data processing and fitting procedures were conducted using the Athena and Artemis modules in the Demeter package, with theoretical scattering paths calculated via the FEFF6 program^[56, 57]. All sample spectra were calibrated against a simultaneously measured Zr foil reference to eliminate energy drift.

In Athena, a linear background was subtracted from the pre-edge region, followed by edge-jump normalization. The $\chi(k)$ function was extracted by subtracting a smooth third-order polynomial to remove the isolated atomic absorption background. Subsequently, the k^2 weighted data were Fourier-transformed into R space using a Hanning window with $\Delta k = 1.0 \text{ \AA}^{-1}$. Structural parameters, including coordination number (CN), bond distance (R), Debye Waller factor (σ^2) and energy shift (ΔE_0) were derived through nonlinear least squares fitting in R space with Artemis.

Supplementary Note 7. Normalization and fitting of EPR

All powder EPR tests were performed under identical experimental conditions to ensure reliable identification of paramagnetic centers and rational assignment of Zr oxidation states. In detail, 50 mg of each solid sample was loaded into identical 3 mm quartz tubes, and the measurements were carried out at a constant temperature of 100 K. Sample mass, tube position, microwave power and modulation amplitude were kept consistent across all measurements to ensure comparability of spectral position and line shape. Experimental EPR spectra were simulated and analyzed using the EasySpin toolbox (version 6.0.0) in MATLAB R2020a. Precise g-factors and hyperfine coupling constants were extracted according to standard simulation methods^[58], providing solid evidence for the existence of oxygen vacancies and the corresponding electronic structure of *F* center sites.

Supplementary Note 8. Counter-ion compensation for charged surface models

Under periodic boundary conditions, directly charged slab models often encounter convergence issues and ambiguous total-energy references due to the vacuum region. To address this problem in surface adsorption calculations, we employed a counter-ion compensation approach to simulate the charged states of various *F* centers.

For the electron-rich $F^2\text{-Zr}^{3+}$ surface, a single hydrogen atom was introduced for charge compensation. Bader charge analysis reveals that this H atom loses around 0.85 e^- , which effectively renders the rest of the surface electron-rich. This configuration reasonably reproduces the electronic character of the reduced $F^2\text{-Zr}^{3+}$ surface. In comparison, an OH group was placed on the $F^I\text{-Zr}^{4+}$ surface to mimic its positively charged nature. The OH group gains approximately 0.76 e^- , leaving the surrounding surface electron-deficient. This setup well approximates the intrinsic properties of the positively charged $F^I\text{-Zr}^{4+}$ surface.

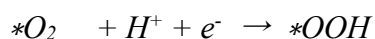
Supplementary Note 9. Adsorption-energy and free-energy calculations

The adsorption energy of O_2 was calculated as:

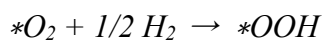
$$E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{adsorbate}}$$

Where E_{total} , E_{surface} and $E_{\text{adsorbate}}$ are the total energies of the O_2 -adsorbed surface, the clean catalyst surface, and the isolated gas-phase O_2 molecule, respectively.

The $*\text{OOH}$ intermediate was not treated as the direct adsorption of an isolated OOH radical. Instead, it was considered to be generated through the proton-coupled electron-transfer step:



Within the computational hydrogen electrode framework, this step is equivalently written as^[59]:



Accordingly, the CHE-referenced energy for $*\text{OOH}$ formation was defined as:

$$E_{\text{ads}} (*\text{OOH}) = E (*\text{OOH}) - E (*) - E (\text{O}_2) - 1/2 E (\text{H}_2)$$

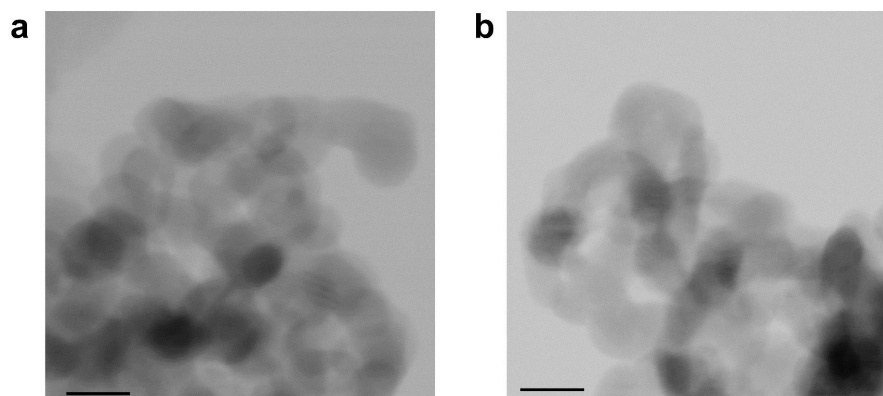
where $E (*\text{OOH})$, $E (*)$, $E (\text{O}_2)$, and $E (\text{H}_2)$ are the total energies of the OOH -adsorbed surface, the clean catalyst surface, the isolated O_2 molecule, and the isolated H_2 molecule, respectively.

The Gibbs free-energy change was calculated as^[60, 61]:

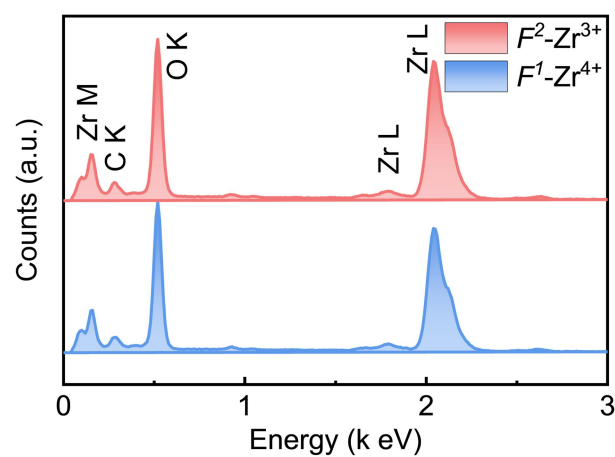
$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\phi} + \Delta E_{\text{w}}$$

where ΔE is the DFT reaction energy, ΔE_{ZPE} is the zero-point energy correction, $T\Delta S$ is the entropy contribution at 298.15 K, ΔG_{ϕ} accounts for the free-energy shift induced by the applied electrode potential, and ΔE_{w} represents the aqueous solvation correction.

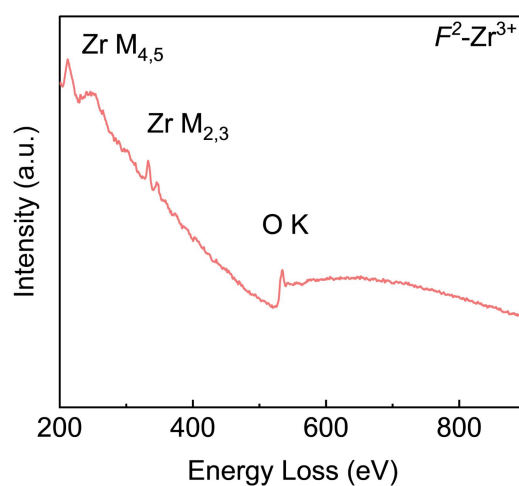
136 **Supplementary Figures**



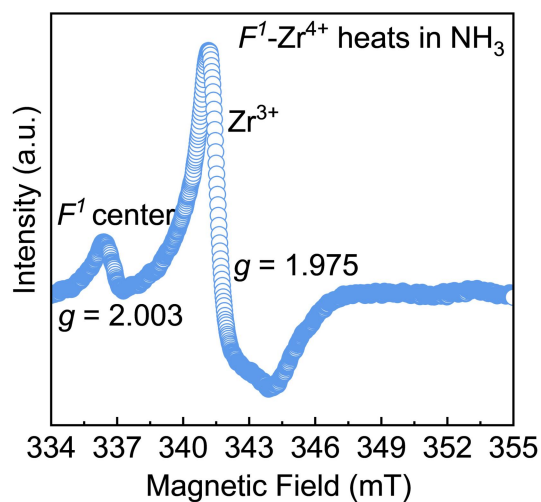
Supplementary Figure 1. Bright Field images of (a) F^2 -Zr $^{3+}$, (b) F^I -Zr $^{4+}$ (Scale bar = 10 nm).



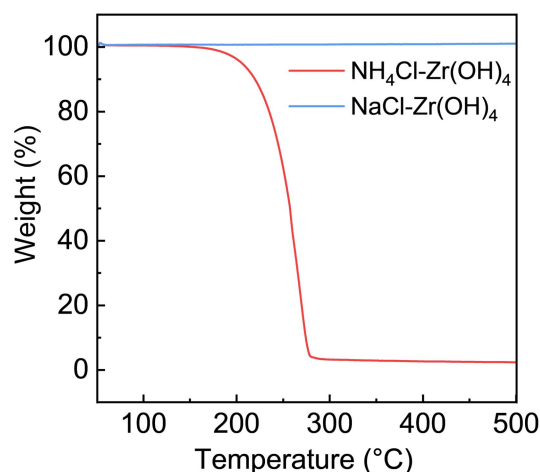
Supplementary Figure 2. STEM-EDS corresponding to Fig. 2f, g for $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$.



Supplementary Figure 3. Full-range EELS spectrum of F^2-Zr^{3+} , showing characteristic Zr M_{4,5}, Zr M_{2,3} and O K edges.

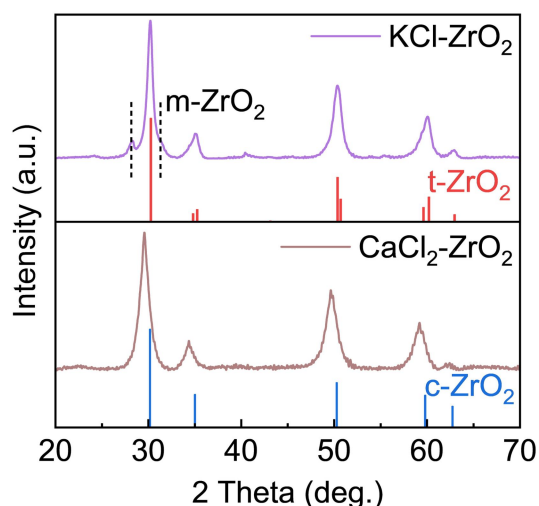


Supplementary Figure 4. X-band experimental EPR of $F^l\text{-Zr}^{4+}$ after heating in NH_3 . For the secondary NH_3 annealing experiment, the pre-synthesized $F^l\text{-Zr}^{4+}$ obtained using the NaCl template was placed in a tube furnace and further annealed under a pure NH_3 atmosphere. The NH_3 flow rate was maintained at 60 mL min^{-1} . The temperature was increased to $500 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ and held for 2 h, followed by natural cooling to room temperature under the same NH_3 flow.



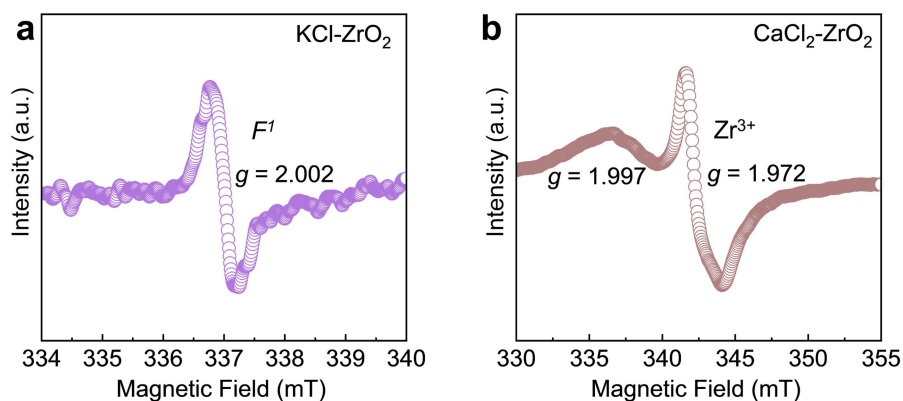
Supplementary Figure 5. Thermogravimetric analysis profiles of the different salt templates $\text{NH}_4\text{Cl-Zr(OH)}_4$ and NaCl-Zr(OH)_4 recorded under a simulated air atmosphere from room temperature to 500 °C.

Thermogravimetric analysis was performed to compare the thermal behaviors of $\text{NH}_4\text{Cl-Zr(OH)}_4$ and NaCl-Zr(OH)_4 precursors under the annealing temperature used for synthesis. The precursors were prepared with a chloride salt/ Zr(OH)_4 mass ratio of 30:1 and heated to 500 °C in air. The NaCl-derived precursor shows negligible mass loss before 500 °C, consistent with the high thermal stability of NaCl and excluding obvious volatile release from the NaCl template. In contrast, NH_4Cl undergoes pronounced decomposition at lower temperature, generating a local NH_3 -rich reductive microenvironment.



Supplementary Figure 6. Powder X-ray diffraction pattern of KCl-ZrO₂ and CaCl₂-ZrO₂.

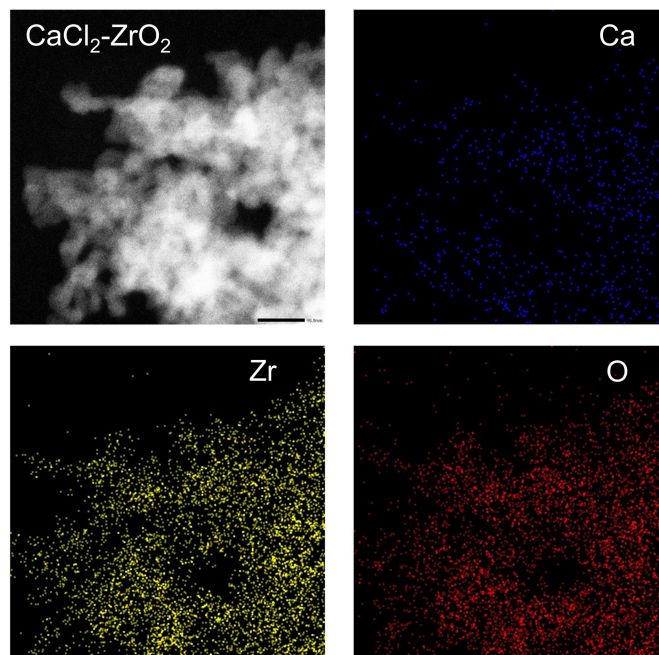
XRD patterns were collected to evaluate the structural influence of different cationic chloride templates. The KCl-ZrO₂ exhibits mixed tetragonal ZrO₂ with a minor monoclinic phase, indicating that K⁺ does not stabilize a pure tetragonal structure as effectively as Na⁺. In contrast, the CaCl₂-ZrO₂ shows diffraction features corresponding to cubic ZrO₂, clearly deviating from the target tetragonal matrix. These results suggest that different chloride template cations mainly affect the crystallographic phase of ZrO₂, with K⁺ inducing slight phase segregation and Ca²⁺ strongly altering the crystal structure.



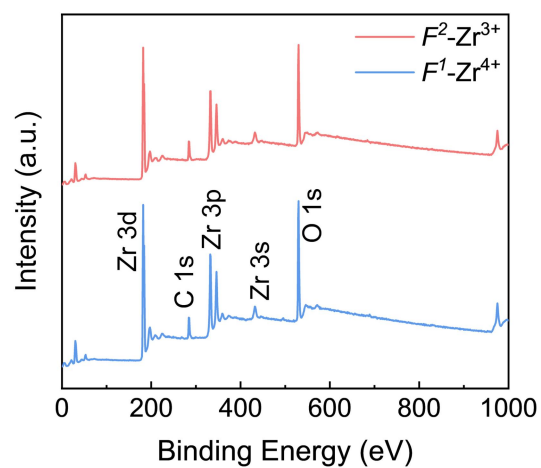
Supplementary Figure 7. X-band experimental EPR of (a) KCl-ZrO₂. (b)

CaCl₂-ZrO₂ at 100 K.

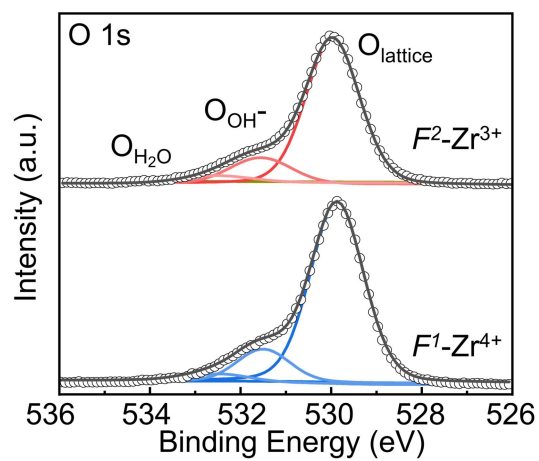
EPR spectra were measured at 100 K to compare the F -center-related electronic structures of the KCl-ZrO₂ and CaCl₂-ZrO₂. Despite slight phase segregation, the KCl-ZrO₂ exhibits an EPR response consistent with the characteristic F^I -Zr⁴⁺ signal observed in the NaCl-template system, suggesting that monovalent alkali cations do not fundamentally restructure the intrinsic F^I -type oxygen vacancies formed under air annealing. In contrast, the CaCl₂-ZrO₂ displays distinct Zr³⁺-related EPR signals, which are mainly associated with Ca²⁺-induced lattice distortion and charge compensation rather than the dopant-free intrinsic F centers targeted in this study.



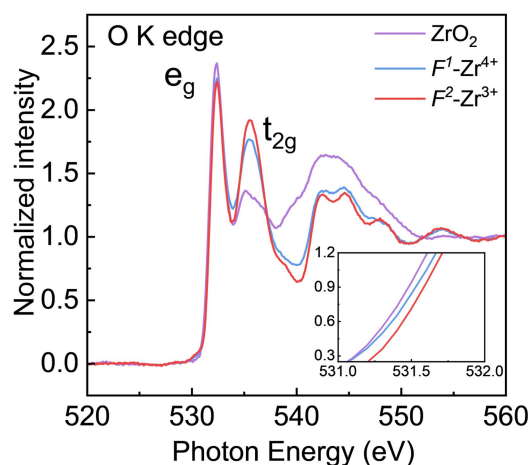
Supplementary Figure 8. HAADF-STEM and EDS-mapping images of $\text{CaCl}_2\text{-ZrO}_2$ (Scale bar = 10 nm). HAADF-STEM and EDS elemental mapping were performed on the $\text{CaCl}_2\text{-ZrO}_2$ to examine the distribution of Ca species. The uniform Ca signal across the ZrO_2 matrix confirms the incorporation of Ca into the oxide lattice during thermal treatment. Such Ca doping is known to promote the formation of doped zirconia solid solutions. The introduced Ca^{2+} dopants disrupt the native lattice charge balance and modify the electronic configuration of oxygen vacancies. Therefore, the $\text{CaCl}_2\text{-ZrO}_2$ should be regarded as an extrinsically doped ZrO_2 system rather than a dopant-free intrinsic F center model.



Supplementary Figure 9. XPS spectra of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$.

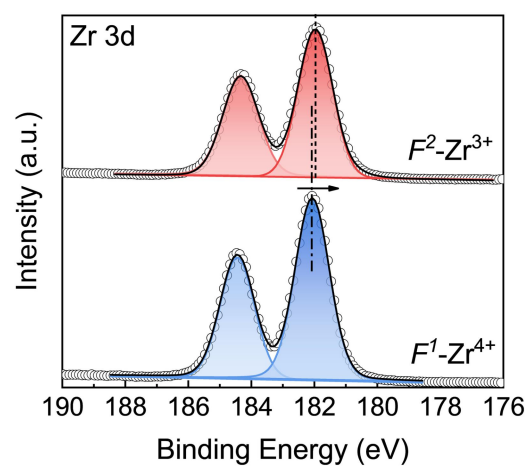


Supplementary Figure 10. O 1s XPS spectra of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$.

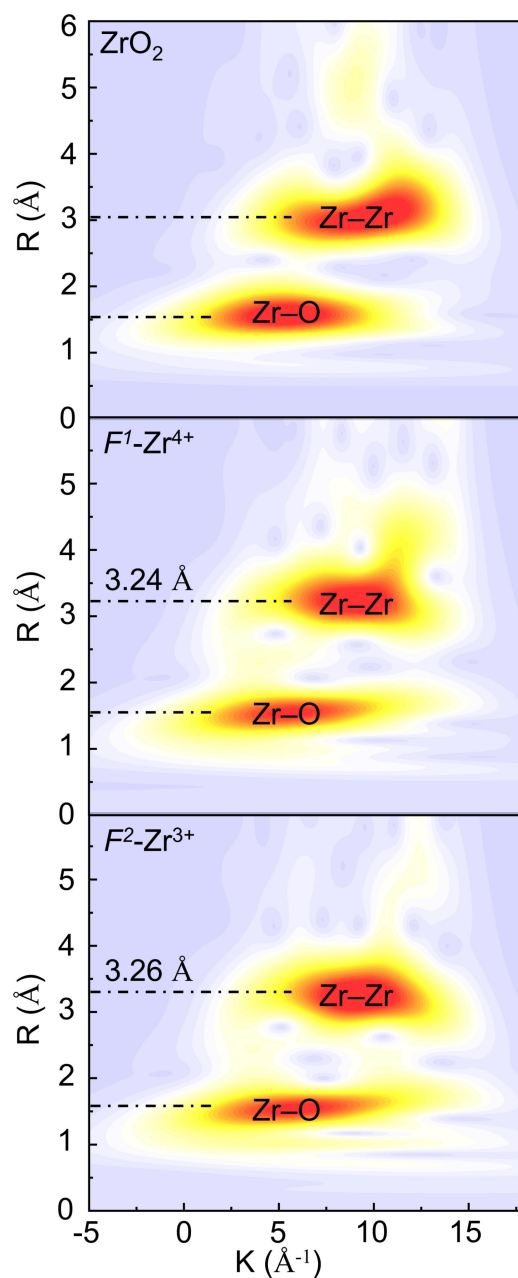


Supplementary Figure 11. O K edge XAS of $F^2\text{-Zr}^{3+}$, $F^I\text{-Zr}^{4+}$ and ZrO_2 .

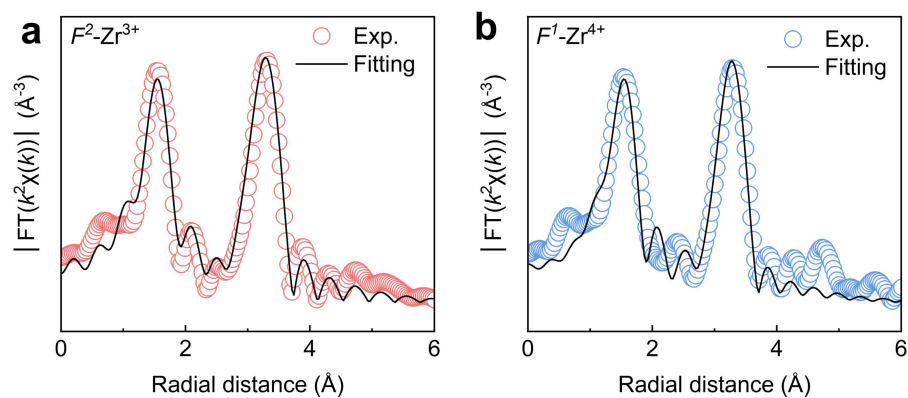
All data acquisition was performed at the XMCD A beamline of the Hefei Light Source HLS. To minimize potential experimental variations as much as possible the $F^2\text{-Zr}^{3+}$ and $F^I\text{-Zr}^{4+}$ were measured alongside a commercial ZrO_2 reference in a single experimental batch. The raw data files acquired at the beamline typically contain four distinct channels including X-ray energy (ERGE), background current intensity (IOR), sample current intensity (ISR) and the ratio of ISR to IOR (DIVR). To strive for a high level of methodological rigor the data were processed using the standard Athena software package. The threshold energy E_0 was defined by identifying the maximum of the first derivative of the absorption edge. Standard edge step normalization was then applied by fitting the pre-edge background to 0 and the post-edge step to 1.



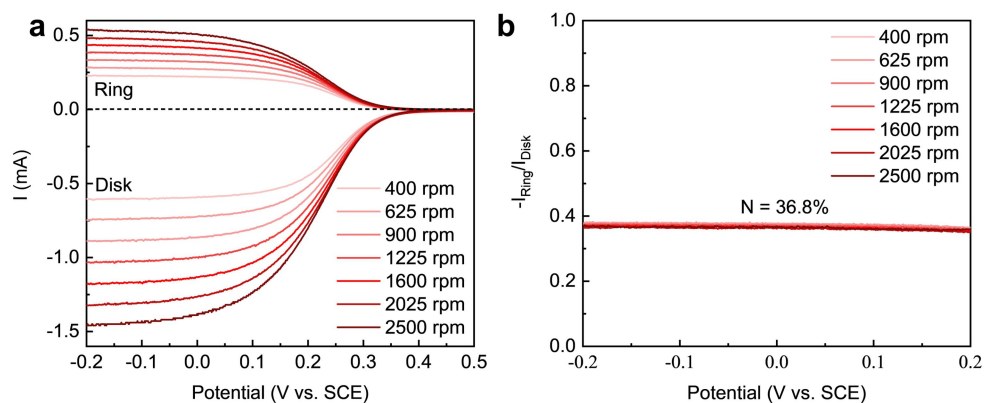
Supplementary Figure 12. Zr 3d XPS spectra of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$.



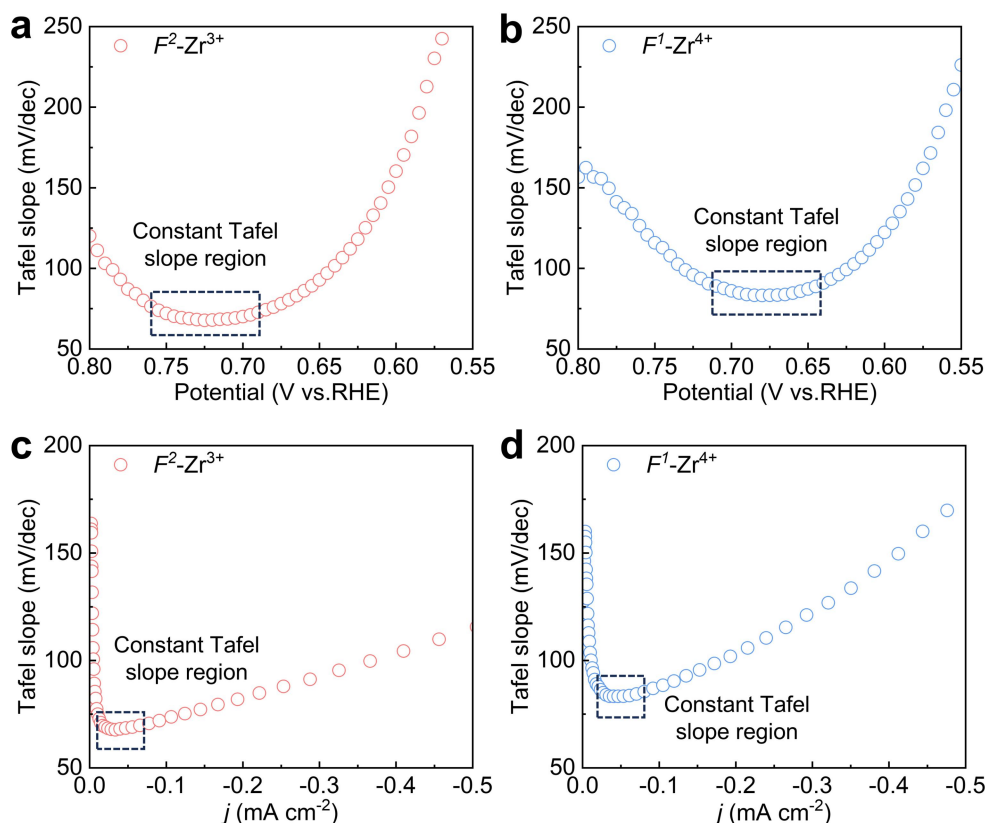
Supplementary Figure 13. The corresponding wavelet transform (WT)-EXAFS contour plots of ZrO_2 , $F^1\text{-Zr}^{4+}$ and $F^2\text{-Zr}^{3+}$.



Supplementary Figure 14. The Zr K-edge EXAFS spectra and fitting results of (a) $F^2\text{-Zr}^{3+}$ and (b) $F^1\text{-Zr}^{4+}$ are shown in R-space.

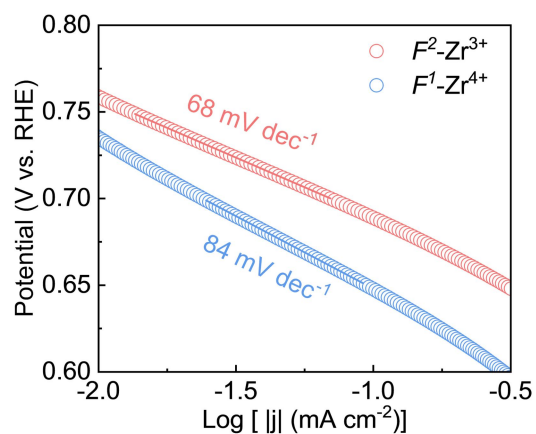


Supplementary Figure 15. (a, b) Derivation of the collection efficiency (N) of the rotating ring-disk electrode. The RRDE was placed in a 0.1 M KOH electrolyte solution containing a small concentration (~ 10 mM) of $\text{K}_3\text{Fe}(\text{CN})_6$.

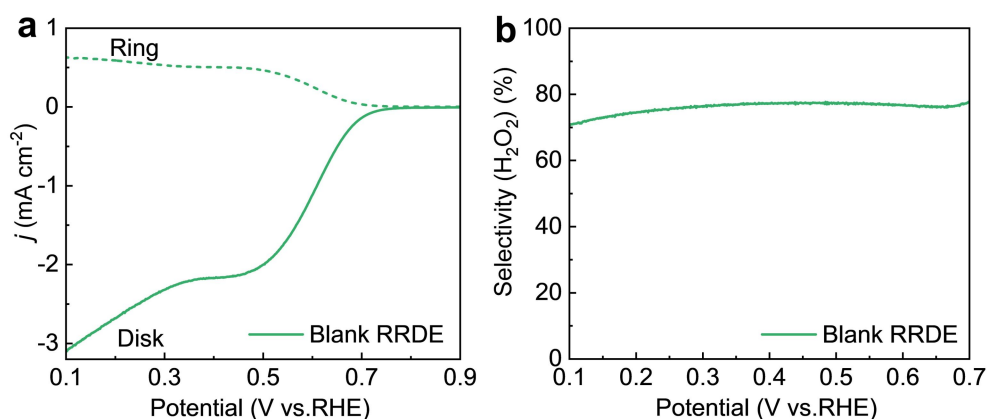


Supplementary Figure 16. Tafel slope plots of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ with the Tafel slope values calculated over ranges of 10 mV and plotted (a, b) the average potential and (c, d) the average current density.

The Tafel data were analyzed using the Tafel slope plot method proposed by Koper and co-workers^[62]. The original E- $\log|j_k|$ data were divided into sliding 10 mV potential windows, and the local Tafel slope in each window was obtained by linear regression of E versus $\log|j_k|$. The absolute value of the fitted slope was reported as the local Tafel slope for the cathodic ORR process. These local Tafel slopes were then plotted as a function of the average potential or average current density of each window, allowing relatively constant kinetic regions to be identified before the obvious high-current/nonlinear response.

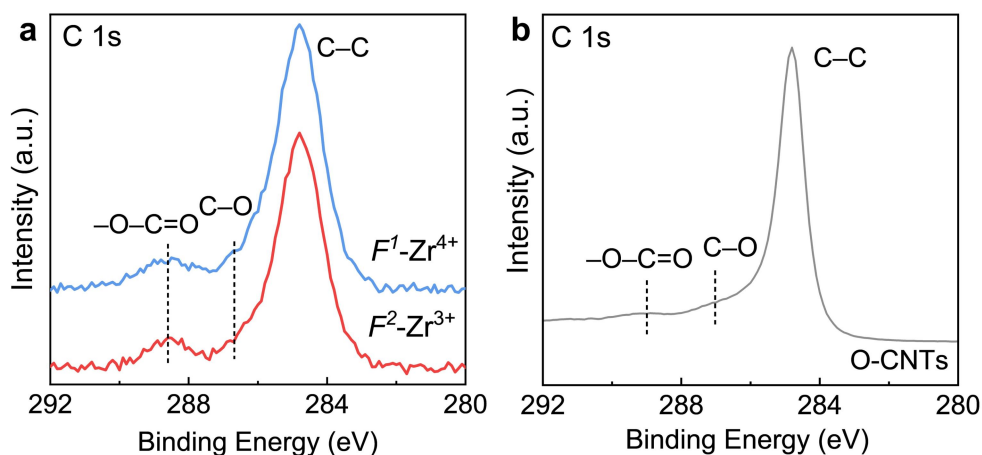


Supplementary Figure 17. Extracted apparent Tafel slopes from the stable kinetic windows of 0.75-0.70 V vs. RHE for $F^2\text{-Zr}^{3+}$ and 0.70-0.65 V vs. RHE for $F^1\text{-Zr}^{4+}$.



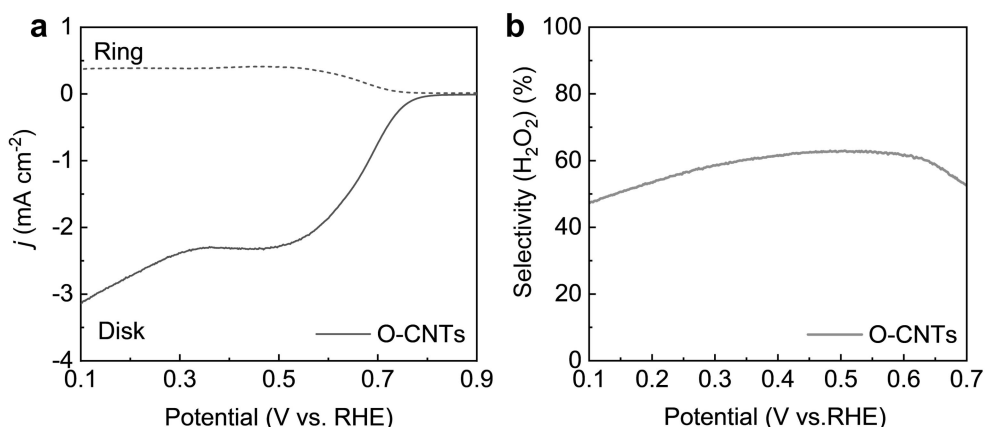
Supplementary Figure 18. (a) LSV curves and (b) corresponding H₂O₂ selectivity of bare glassy carbon electrode.

To rule out substrate interference, the bare GC electrode was tested under identical conditions, showing a H₂O₂ selectivity of ~75%. This baseline contrasts sharply with $F^2\text{-Zr}^{3+}$ (98%) and $F^I\text{-Zr}^{4+}$ (44%). Specifically, the superior selectivity of $F^2\text{-Zr}^{3+}$ originates from its dynamic electronic structure for moderating *OOH adsorption and desorption. In comparison, excessively strong *OOH adsorption on $F^I\text{-Zr}^{4+}$ active sites hinders intermediate release, resulting in selectivity even lower than the GC baseline. These comparisons clearly confirm that the ORR pathway and selectivity are governed by the intrinsic properties of $F^2\text{-Zr}^{3+}/F^I\text{-Zr}^{4+}$ centers, rather than the GC substrate background.



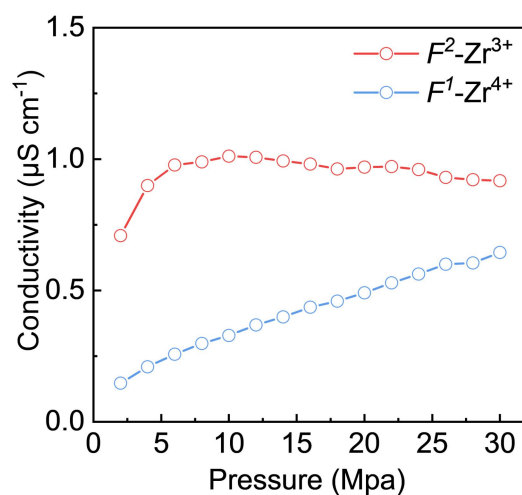
Supplementary Figure 19. C 1s XPS spectra of (a) $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$, (b) O-CNTs.

The C 1s spectra of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ show characteristic peaks at 284.8, 286.7 and 288.6 eV, corresponding to C-C, C-O and -O-C=O species, respectively^[63]. To assess the possible influence of adventitious surface carbon, commercial oxidized carbon nanotubes (O-CNTs) with similar surface functional groups were adopted as a control sample to simulate the effect of carbon contamination^[64].

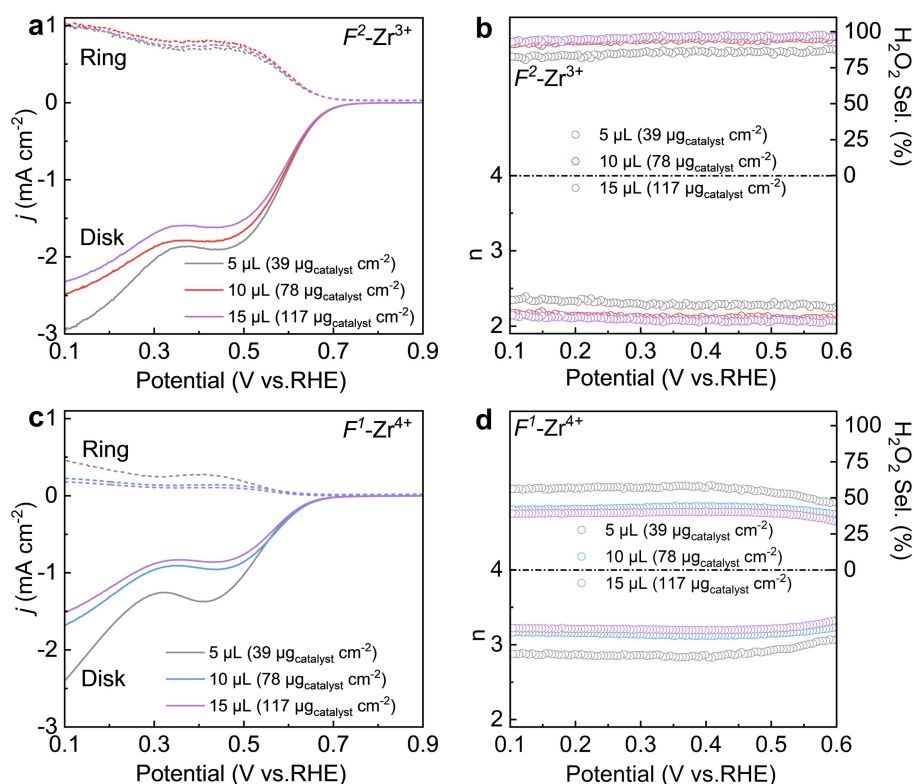


Supplementary Figure 20. (a) LSV curves and (b) corresponding H₂O₂ selectivity of O-CNTs.

To further clarify the contribution of surface carbon contamination, the LSV curve and ORR selectivity of O-CNTs were measured under the same catalyst loading and test conditions. O-CNTs exhibit a H₂O₂ selectivity of ~60%, which is clearly distinguishable from the 98% of F^2 -Zr³⁺ and the 44% of F^1 -Zr⁴⁺. This obvious difference effectively excludes the interference of adventitious carbon, verifying that the ORR performance is governed by the intrinsic properties of the as-prepared catalysts.

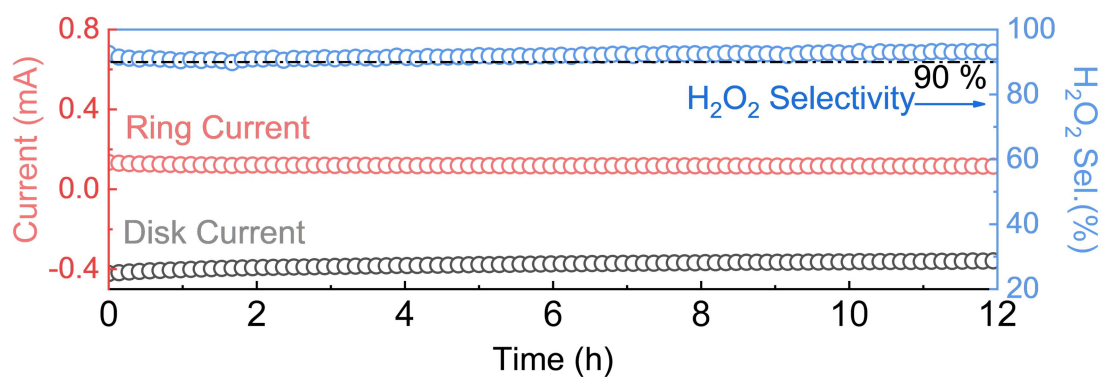


Supplementary Figure 21. Pressure-dependent electrical conductivity of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ powders measured by the four-probe method at room temperature. A fixed sample mass of 0.1 g was used for both measurements.

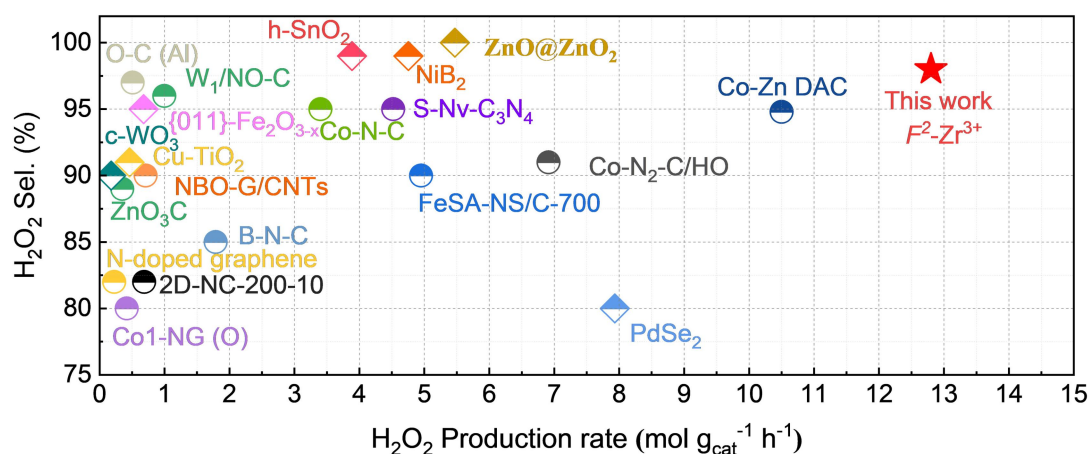


Supplementary Figure 22. LSV polarization curves, corresponding H₂O₂ selectivity and electron transfer numbers of (a, b) $F^2\text{-Zr}^{3+}$ and (c, d) $F^1\text{-Zr}^{4+}$ at different catalyst loadings for ORR in 0.1 M KOH.

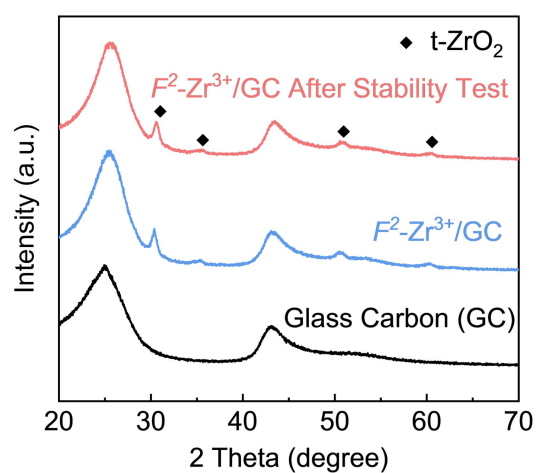
To optimize the catalyst loading, loading-dependent RRDE tests were performed on $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ using 5, 10, and 15 μL of catalyst ink (ink composition: 1.0 mg catalyst powder dispersed in 500 μL ethanol/water mixture (v/v=9/1), followed by addition of 20 μL 5 wt% Nafion solution). For $F^2\text{-Zr}^{3+}$, the lowest loading electrode (5 μL) exhibited a high disk current of -2.93 mA cm^{-2} at 0.1 V vs. RHE, but a low H₂O₂ selectivity of 82.7%, which arose from interference by the exposed bare glassy carbon substrate. In contrast, the highest loading (15 μL) improved the H₂O₂ selectivity to 92.9% yet caused a notable drop in disk current to -2.31 mA cm^{-2} , attributed to severe electron transport resistance in the overly thick catalyst layer. Therefore, the 10 μL loading was identified as the optimal condition for $F^2\text{-Zr}^{3+}$, achieving an ideal balance with a high H₂O₂ selectivity of 91.4% and a robust disk current of -2.48 mA cm^{-2} at 0.1 V vs. RHE. The same variation trend was observed for $F^1\text{-Zr}^{4+}$, confirming the general applicability of this optimal loading.



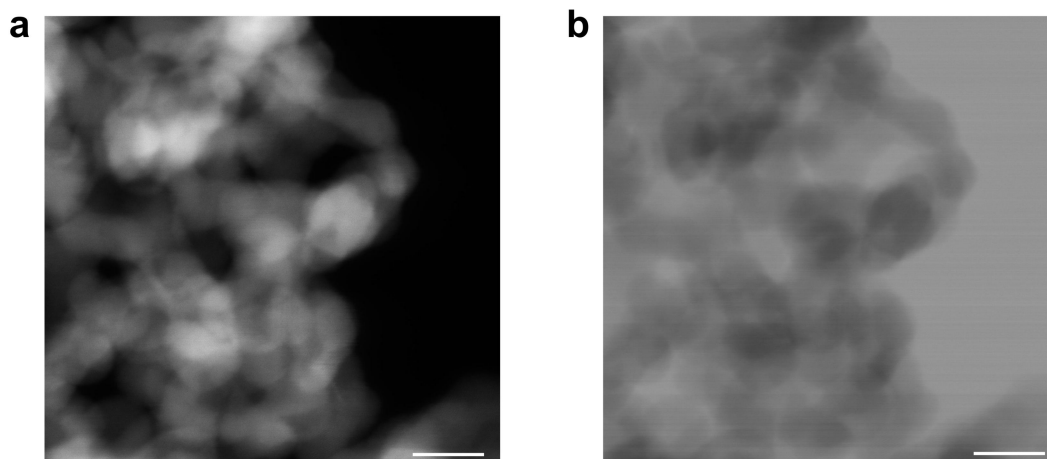
Supplementary Figure 23. Chronoamperometry measurement of F^2 -Zr³⁺ at 0.4 V (vs RHE).



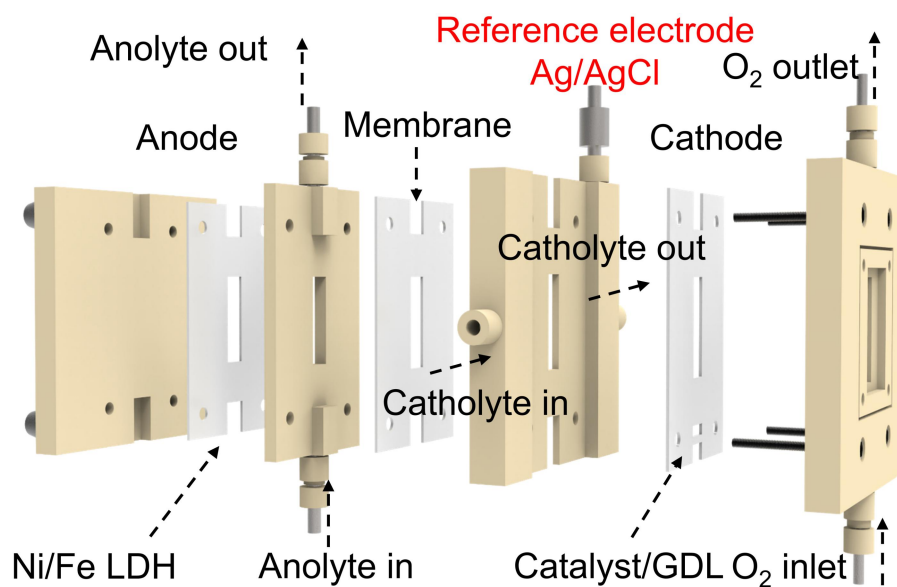
Supplementary Figure 24. Comparison of F^2 -Zr³⁺ H₂O₂ production rate and selectivity with previously reported catalysts (detailed information in Table 6).



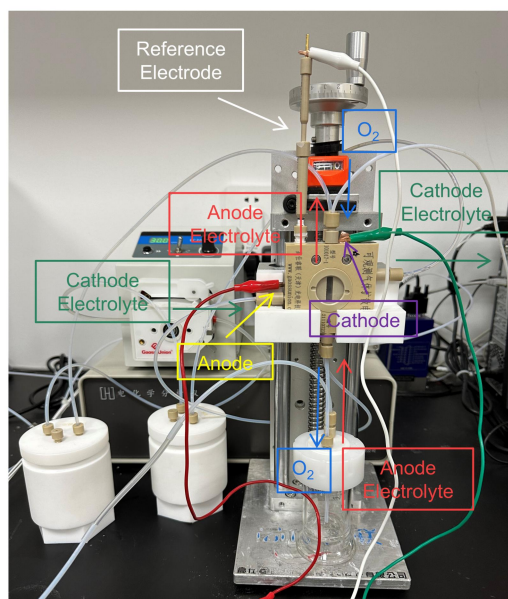
Supplementary Figure 25. The XRD patterns of the $F^2\text{-Zr}^{3+}$ loading on glassy carbon after stability test.



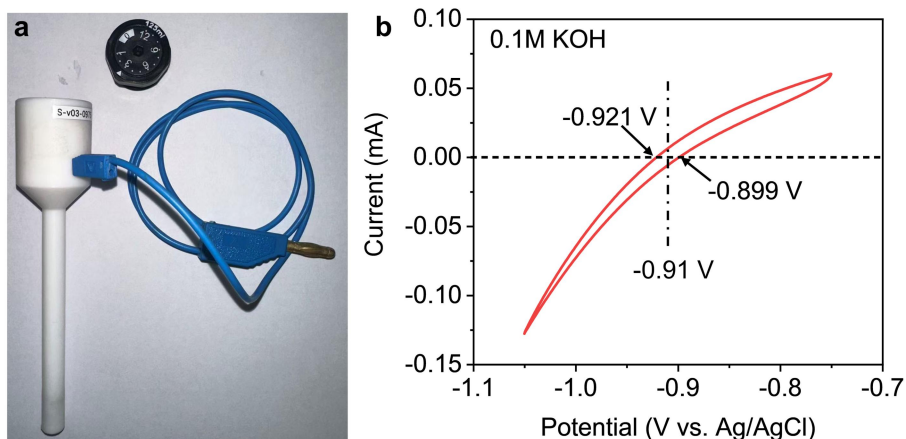
Supplementary Figure 26. (a) HAADF-STEM and (b) BF-STEM images of $F^2\text{-Zr}^{3+}$ after long-term ORR process (Scale bar = 10 nm).



Supplementary Figure 27. Schematic diagram of the flow cell for H_2O_2 production.



Supplementary Figure 28. Custom-made electrochemical Flow Cell.

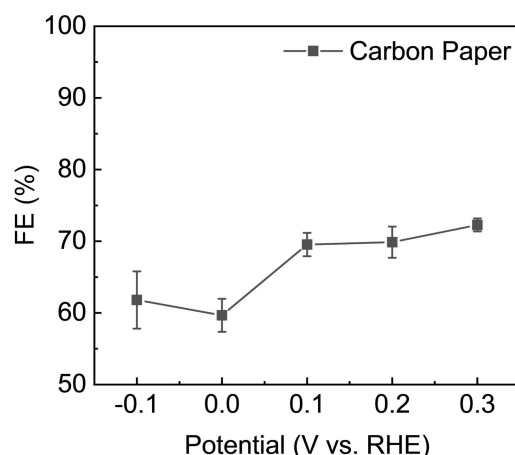


Supplementary Figure 29. (a) Photograph of the Standard Hydrogen Electrode (SHE) used for reference electrode potential calibration. (b) Single cycle CV curves of Ag/AgCl electrode calibration in 0.1 M KOH at room temperature.

To eliminate potential systematic errors (up to ~30 mV) derived from the simplified theoretical Nernst equation^[65], the Ag/AgCl reference electrode was calibrated experimentally. Before electrochemical measurements, the reference electrode was calibrated against a commercial standard hydrogen electrode (HydroFlex, Pine Research) in the working electrolyte, following the standard protocols recommended in the literature^[42]. The experimentally measured potential difference was determined to be 0.91 V, and all raw potentials were converted to the RHE scale using the following equation:

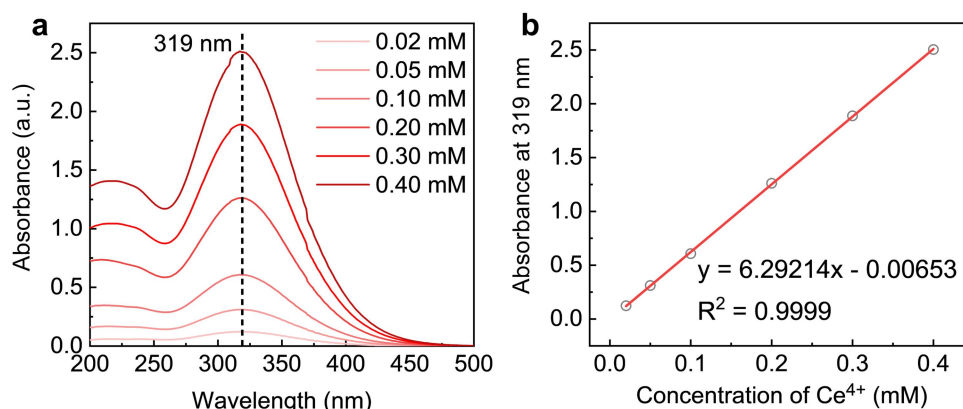
$$E_{RHE} = E_{Measured} + 0.91 \text{ V}$$

where E_{RHE} is the potential versus the reversible hydrogen electrode, and $E_{Measured}$ is the raw potential recorded against the Ag/AgCl reference electrode.

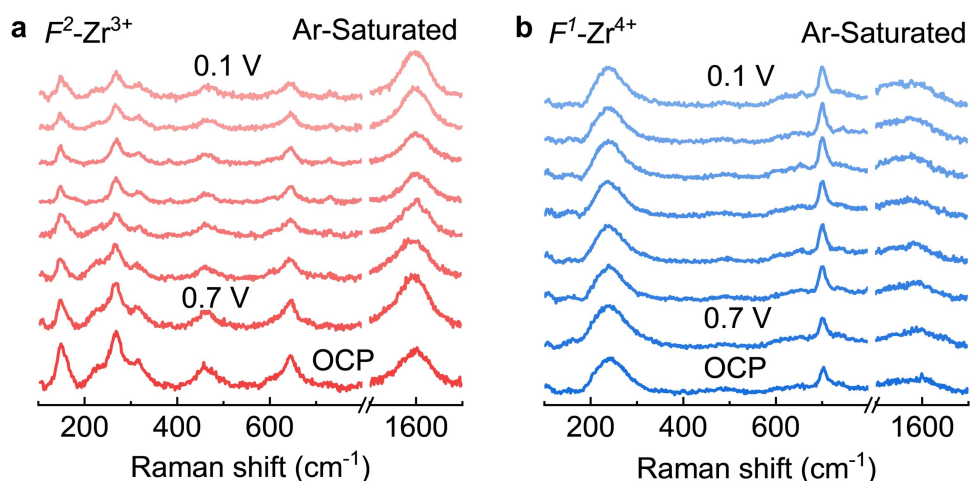


Supplementary Figure 30. Faradaic efficiencies of H₂O₂ on blank carbon paper at different potentials measured in a flow cell. Data are presented as mean values ± standard deviation from three independent measurements (n=3).

H₂O₂ faradaic efficiency (FE) of the bare carbon paper electrode was evaluated in a flow cell without catalyst loading, using bare carbon paper as the ORR cathode, commercial Ni/Fe-LDH as the OER anode, and a Nafion membrane as the separator. The bare carbon paper achieves a maximum H₂O₂ FE of only 72.3% within the potential range of -0.1 to 0.3 V vs. RHE, significantly lower than that of F²-Zr³⁺ (maximum FE of 94.5%, Main Text **Fig. 4f**). The obvious performance gap confirms that the high H₂O₂ production primarily stems from the intrinsic activity of F²-Zr³⁺ rather than the carbon paper substrate.

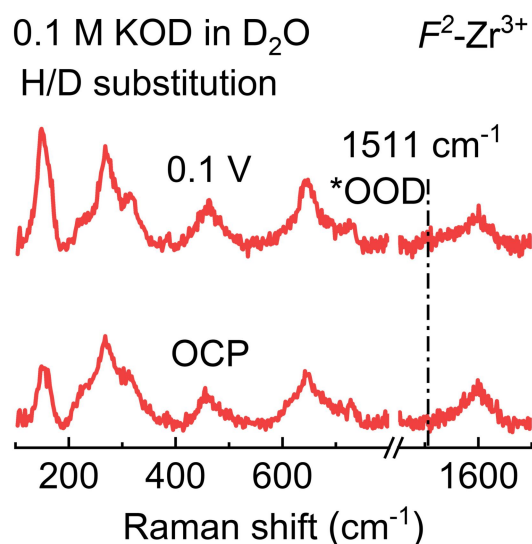


Supplementary Figure 31. The H_2O_2 concentrations in electrolytes were measured by titration using standard ceric sulfate solution. (a) The UV-Vis spectra of Ce^{4+} solutions with different concentrations. (b) The linear calibration relationship between the Ce^{4+} concentration and corresponding absorbance peak at 319 nm.



Supplementary Figure 32. In situ Raman of (a) $F^2\text{-Zr}^{3+}$ and (b) $F^1\text{-Zr}^{4+}$ under Ar-saturated electrolyte.

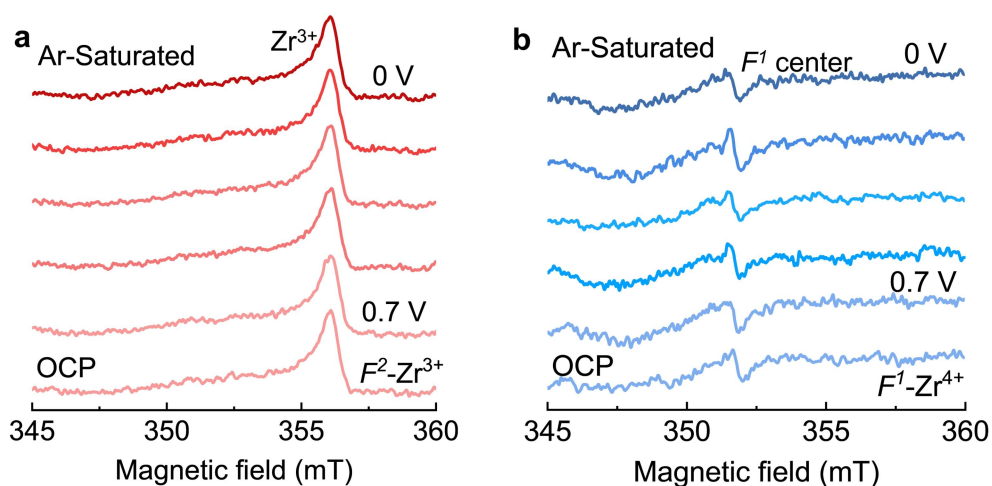
In situ Ar-atmosphere Raman measurements were performed under identical experimental conditions, with O_2 purging replaced by continuous Ar flow. No Raman feature assigned to ORR intermediates was detected under Ar, further proving that the $\sim 1537\text{ cm}^{-1}$ peak only emerges during O_2 reduction and is irrelevant to the bare catalyst or supporting electrolyte.



Supplementary Figure 33. Verification of the 1537 cm⁻¹ peak assignment to *OOH via in situ Raman spectroscopy. Deuterated experiments were performed by replacing KOH with KOD and H₂O with D₂O to validate the peak origin. To further verify the assignment of this Raman feature, deuterated in situ Raman measurements were conducted under otherwise identical conditions by replacing KOH/H₂O with KOD/D₂O.

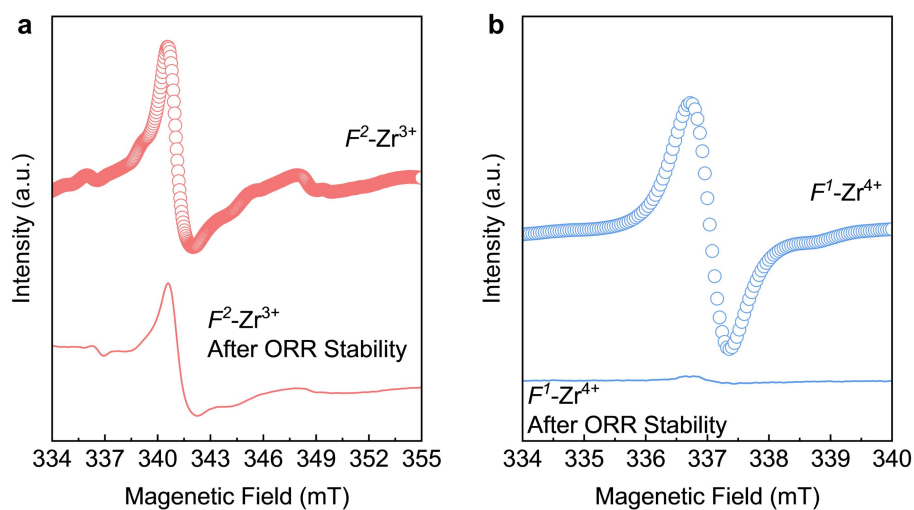


Supplementary Figure 34. Photograph of the in situ EPR setup for electrochemical ORR testing.

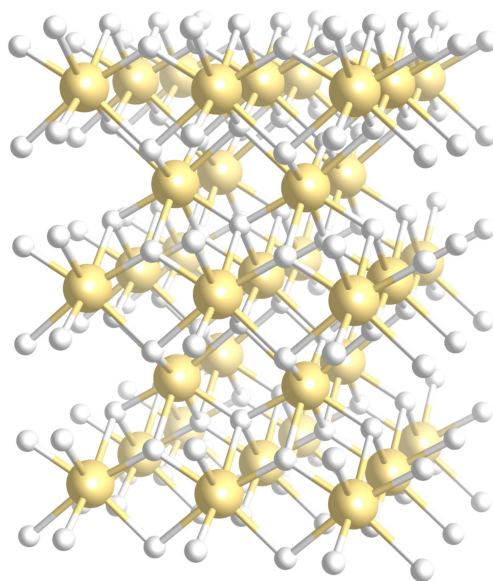


Supplementary Figure 35. In situ EPR of (a) $F^2\text{-Zr}^{3+}$ and (b) $F^1\text{-Zr}^{4+}$ under Ar-saturated electrolyte.

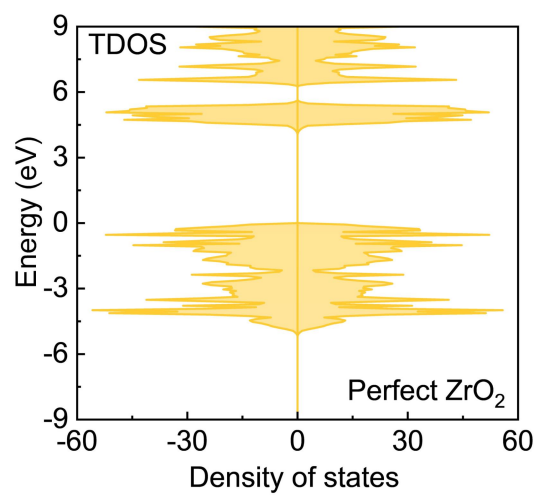
In situ EPR spectra collected under Ar-saturated electrolyte display stable F center signals in the absence of O_2 . This result confirms that the gradual transformation of EPR peaks observed under working ORR conditions is driven by successive catalytic redox cycles, not spontaneous material structural evolution in electrolyte.



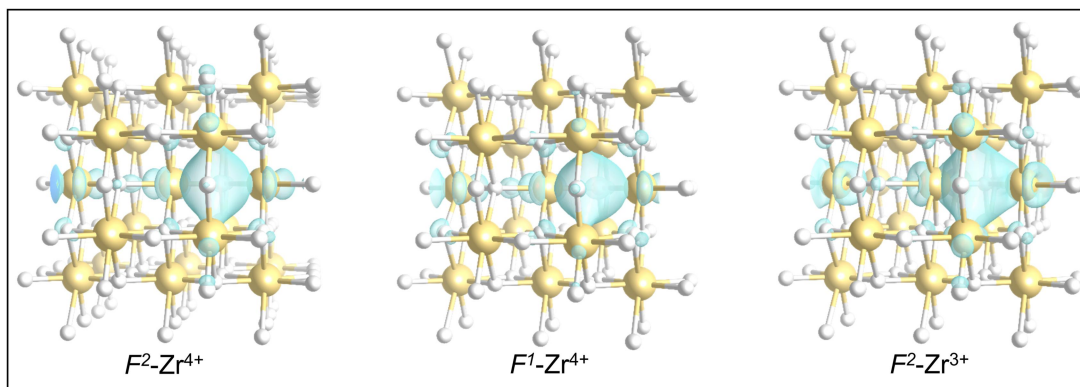
Supplementary Figure 36. EPR of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ at 100 K after long-term ORR process.



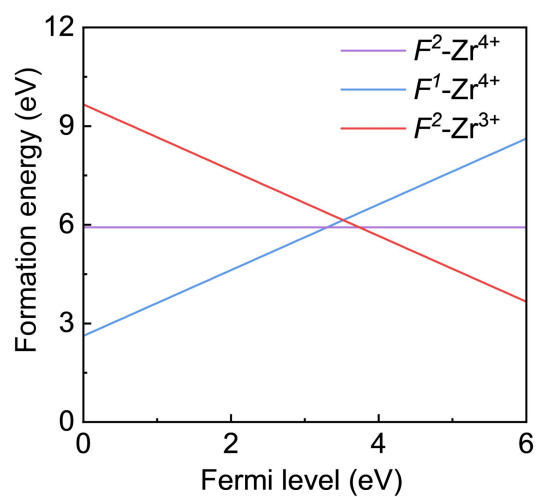
Supplementary Figure 37. Geometric model of the perfect tetragonal phase ZrO₂ bulk structure.



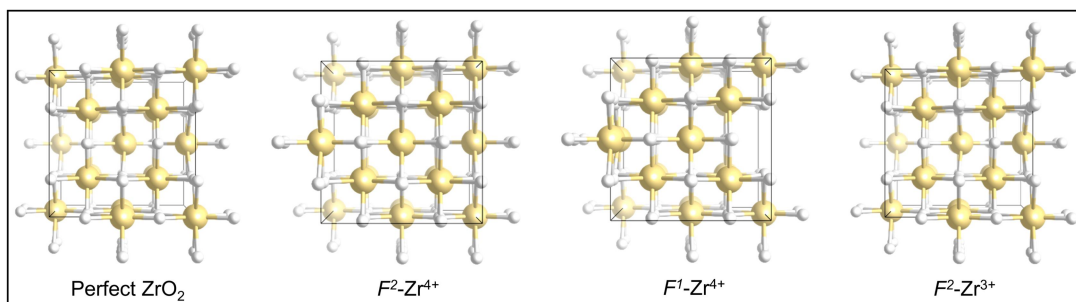
Supplementary Figure 38. Calculated total electronic density of states of perfect ZrO₂.



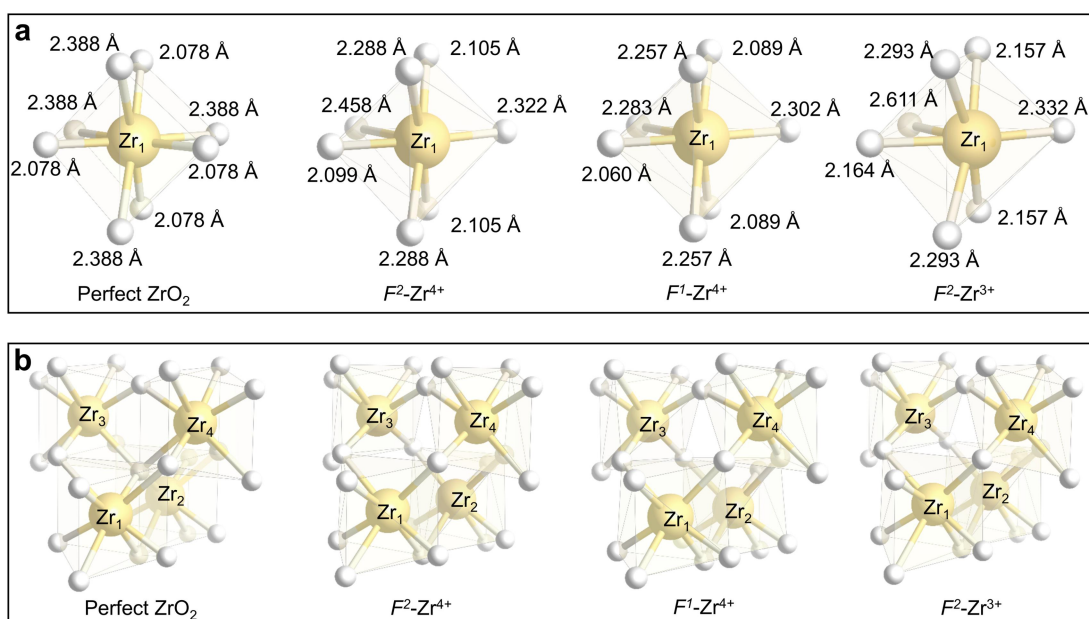
Supplementary Figure 39. The integrated local DOS of the highlighted occupied defect states of $F^2\text{-Zr}^{4+}$, $F^1\text{-Zr}^{4+}$ and $F^2\text{-Zr}^{3+}$. Zirconium atoms are shown in yellow and oxygen atoms in white.



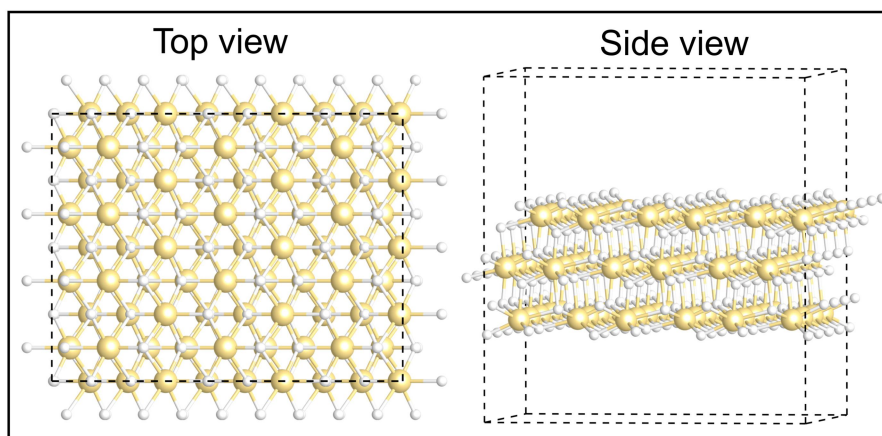
Supplementary Figure 40. Formation energy as a function of the Fermi energy for $F^2\text{-Zr}^{4+}$, $F^1\text{-Zr}^{4+}$ and $F^2\text{-Zr}^{3+}$.



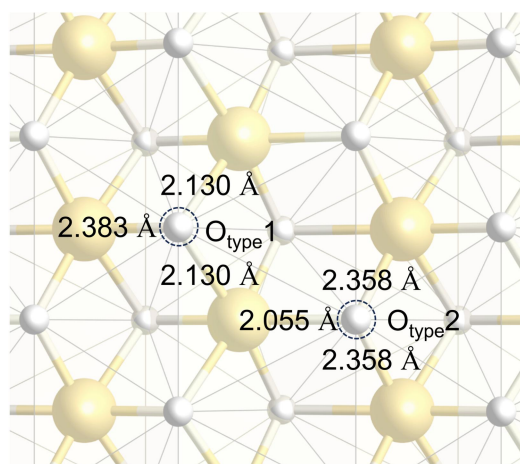
Supplementary Figure 41. Structural optimization of Perfect ZrO_2 , $F^2\text{-Zr}^{4+}$, $F^1\text{-Zr}^{4+}$ and $F^2\text{-Zr}^{3+}$.



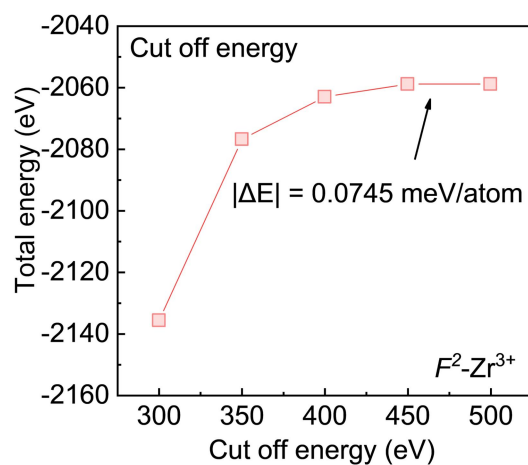
Supplementary Figure 42. (a) Optimized Zr–O bond lengths around the Zr_1 site. perfect ZrO_2 shows an eight-coordinated Zr–O environment, while the defective structures are seven-coordinated due to F center. (b) Schematic illustration of the four Zr sites neighboring the F centers.



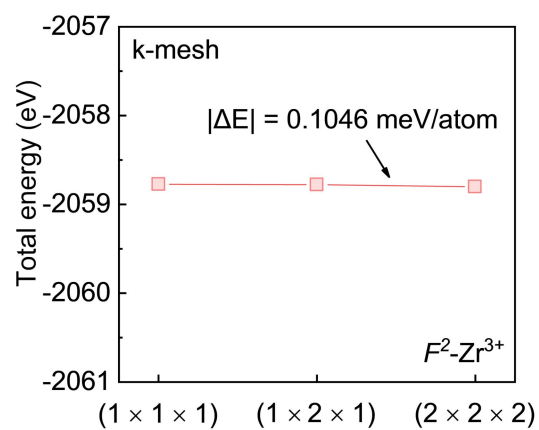
Supplementary Figure 43. Top-view and side-view structural models of the ZrO₂ (011) surface. The yellow and white spheres represent Zr and O atoms, respectively.



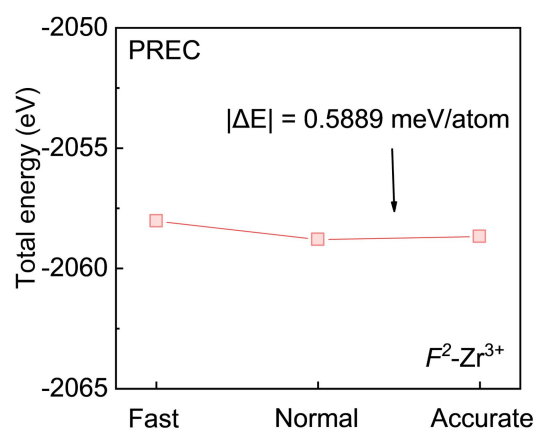
Supplementary Figure 44. Atomic structure of the tetragonal ZrO_2 (011) surface. Two inequivalent surface oxygen sites (O_{type1} and O_{type2}) are marked by dashed circles, along with the local Zr–O bond lengths labeled in Å. Yellow and white spheres represent Zr and O atoms, respectively. Two inequivalent surface oxygen sites, O_{type1} and O_{type2} , were considered for vacancy construction. Formation energy calculations show that $F^I\text{-Zr}^{4+}$ preferentially forms at O_{type1} (0.179 eV), while $F^2\text{-Zr}^{3+}$ is more stable at O_{type2} (0.029 eV). This energetic difference provides a solid basis for our defect model construction.



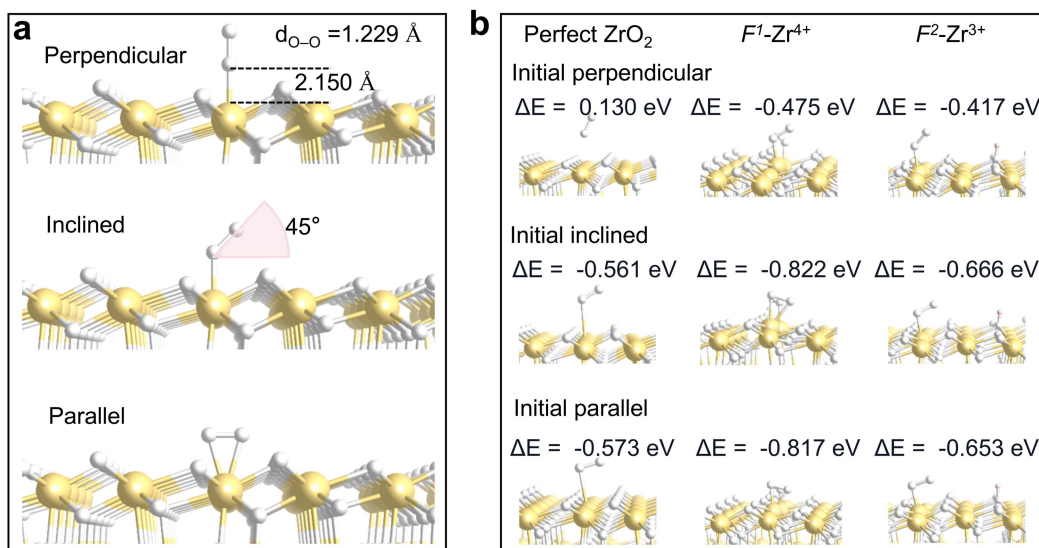
Supplementary Figure 45. Convergence test of the total energy with respect to the plane-wave cutoff energy for the $F^2\text{-Zr}^{3+}$ model.



Supplementary Figure 46. Convergence test of the total energy with respect to the k-point mesh density for the $F^2\text{-Zr}^{3+}$ model.

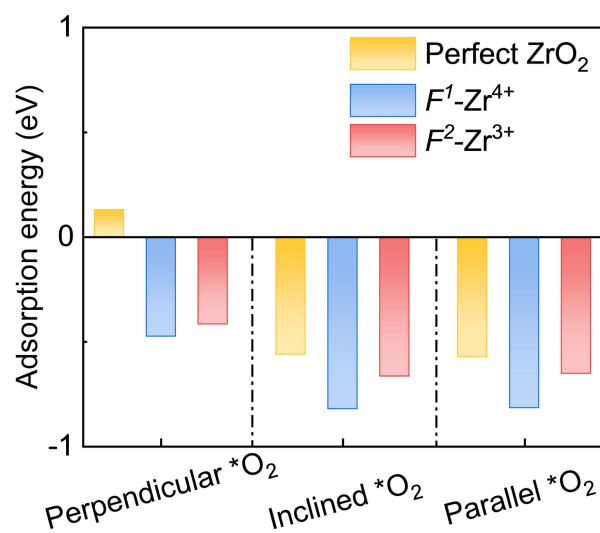


Supplementary Figure 47. Convergence test of the total energy with respect to the precision parameter (PREC) for the $F^2\text{-Zr}^{3+}$ model.

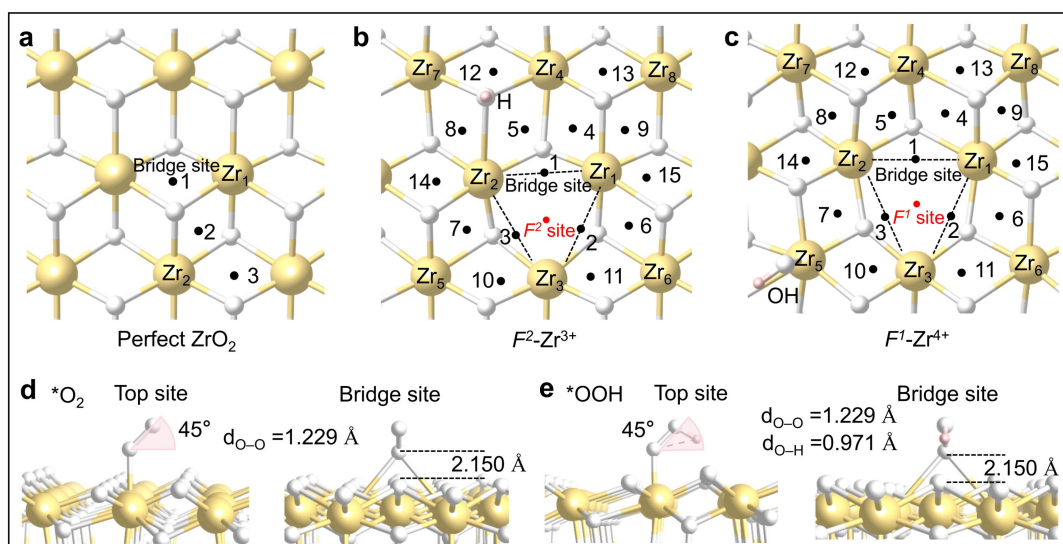


Supplementary Figure 48. (a) Initial geometric models of O_2 adsorption on the catalyst surface in perpendicular (90°), inclined (45°) and parallel (0°) configurations. The initial O–O bond length and the distance to the surface are uniformly set to 1.229 $\text{\AA}$ and 2.150 $\text{\AA}$, respectively. (b) Optimized adsorption structures and corresponding adsorption energies (ΔE) of O_2 on perfect ZrO_2 , $F^I\text{-Zr}^{4+}$, and $F^2\text{-Zr}^{3+}$ based on the initial configurations. Yellow and white spheres represent Zr and O atoms, respectively.

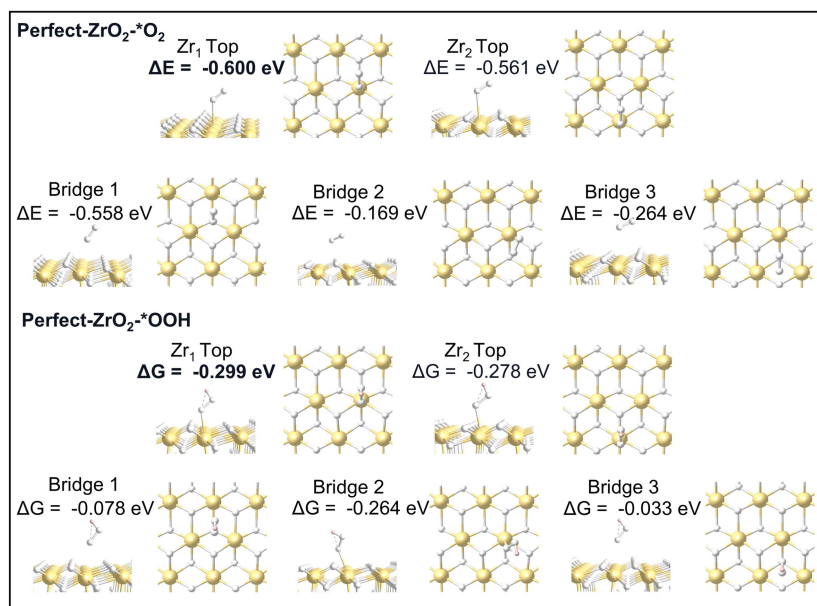
To avoid possible bias from a single preset adsorption geometry, we systematically screened three initial *O_2 orientations relative to the substrate plane, including parallel (0°), inclined (45°) and perpendicular (90°) configurations. The initial structures were generated using a Python script, in which the O–O bond length and the distance to the surface were uniformly set to 1.229 $\text{\AA}$ and 2.150 $\text{\AA}$, respectively, followed by full geometry relaxation to identify the equilibrium adsorption modes. Specifically, *O_2 on $F^I\text{-Zr}^{4+}$ tends to adopt a strong parallel side-on adsorption configuration, which favors O–O bond activation and possible cleavage. In contrast, *O_2 on $F^2\text{-Zr}^{3+}$ adopts a more moderate inclined or end-on adsorption mode, which enables electron transfer while better preserving the O–O bond for the $2e^-$ ORR pathway.



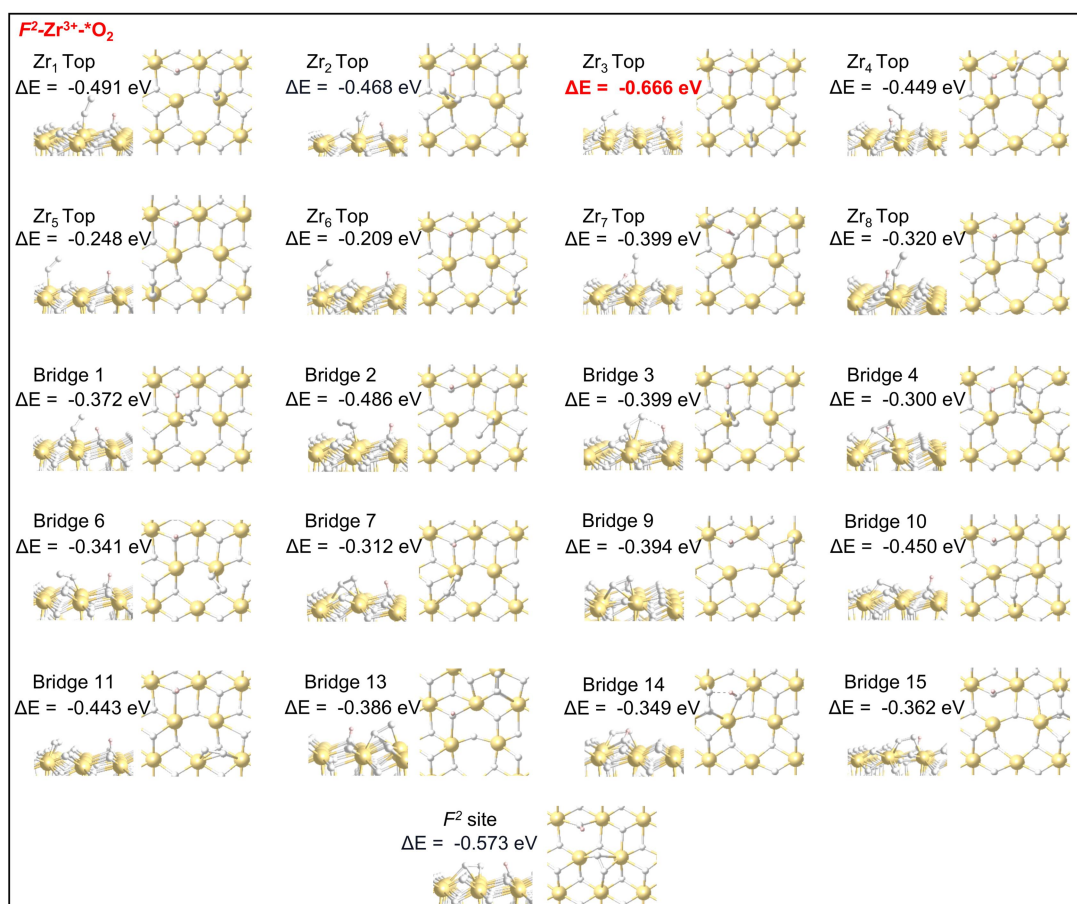
Supplementary Figure 49. Comparison of calculated oxygen adsorption energies on perfect ZrO₂, F¹-Zr⁴⁺ and F²-Zr³⁺ based on different initial adsorption configurations (perpendicular, inclined, and parallel).



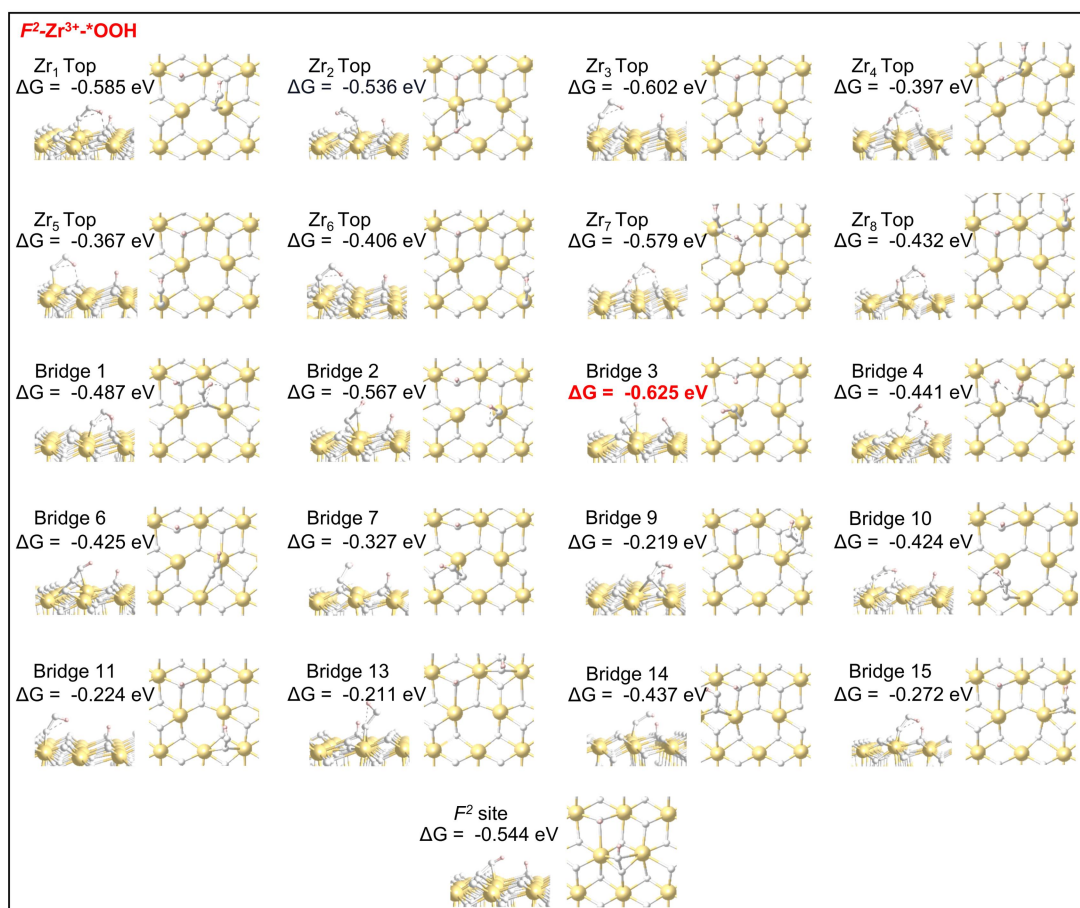
Supplementary Figure 50. Identified adsorption sites on the (a) perfect ZrO_2 , (b) $F^2\text{-Zr}^{3+}$, and (c) $F^1\text{-Zr}^{4+}$. Initial geometric parameters for adsorbed (d) O_2 and (e) OOH at the top and bridge sites.



Supplementary Figure 51. Optimized geometric structures and corresponding calculated energies for *O₂ and *OOH intermediates adsorbed at different sites on the perfect ZrO₂.



Supplementary Figure 52. Optimized geometric structures and corresponding calculated energies for $*\text{O}_2$ intermediates adsorbed at different sites on the $F^2\text{-Zr}^{3+}$.



Supplementary Figure 53. Optimized geometric structures and corresponding calculated energies for *OOH intermediates adsorbed at different sites on the $F^2\text{-Zr}^{3+}$.



Supplementary Figure 54. Optimized geometric structures and corresponding calculated energies for $^*\text{O}_2$ intermediates adsorbed at different sites on the $F^I\text{-Zr}^{4+}$.



Supplementary Figure 55. Optimized geometric structures and corresponding calculated energies for *OOH intermediates adsorbed at different sites on the $F^I\text{-Zr}^{4+}$.

Supplementary Tables

Supplementary Table 1. The element analysis of F^2 -Zr³⁺ and F^I -Zr⁴⁺.

Catalyst	C (atom%)	Zr (atom%)	O (atom%)	O/Zr
F^2 -Zr ³⁺	12.04	30.58	57.38	1.876
F^I -Zr ⁴⁺	11.84	30.52	57.64	1.889

Note: Calculated from STEM-EDS.

Supplementary Table 2. Summary of simulation parameters for EPR spectra of F^2 -Zr³⁺ and F^I -Zr⁴⁺.

Sample	Adduct	<i>g</i> value	A/MHz	lw/mT
F^2 -Zr ³⁺	Zr ³⁺	[1.976, 1.923]	/	0.8, 1.7
F^I -Zr ⁴⁺	F^I center	[2.0023]	/	0.3, 0.8

Note: lw is the homogeneous Lorentzian linewidth; the linewidth defines the FWHM (full width at half height, in mT) of the absorption Gaussian (first number) and Lorentzian (second number) broadening of the lines in the spectrum.

513 **Supplementary Table 3.** The element analysis of $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$.

Catalyst	C (atom%)	Zr (atom%)	O (atom%)	O/Zr
$F^2\text{-Zr}^{3+}$	24.14	26.19	49.67	1.897
$F^1\text{-Zr}^{4+}$	23.31	26.41	50.28	1.904

514 Note: Calculated from XPS.

515

Supplementary Table 4. EXAFS fitting parameters at the Zr K-edge for F^2 -Zr³⁺ and F^1 -Zr⁴⁺.

Sample	Shell	CN ^a	R (Å) ^b	σ^2 (Å ²) ^c	ΔE_0 (eV) ^d	R factor
F^1 -Zr ⁴⁺	Zr-O ₁	4.5 ± 0.2	2.08 ± 0.01	0.0038	-2.00	0.0177
	Zr-O ₂	2.6 ± 0.2	2.27 ± 0.01	0.0088	-2.00	0.0177
	Zr-Zr	10.5 ± 0.3	3.63 ± 0.01	0.0080	-2.00	0.0177
F^2 -Zr ³⁺	Zr-O ₁	4.6 ± 0.2	2.11 ± 0.01	0.0030	-2.58	0.0186
	Zr-O ₂	2.4 ± 0.2	2.29 ± 0.01	0.0031	-2.58	0.0186
	Zr-Zr	10.1 ± 0.3	3.64 ± 0.01	0.0071	-2.58	0.0186

Note: (a) CN, coordination number; (b) R, distance between absorber and backscatter atoms; (c) σ^2 , Debye-Waller factor to account for both thermal and structural disorders; (d) ΔE_0 , inner potential correction; R factor indicates the goodness of the fit. S_0^2 was fixed to 0.77 for Zr. A reasonable range of EXAFS fitting parameters: 0.700 < S_0^2 < 1.000; CN > 0; σ^2 Å² > 0; $|\Delta E_0|$ < 15 eV; R factor < 0.02.

Supplementary Table 5. Effect of catalyst loading on H₂O₂ selectivity and disk current density for F^2 -Zr³⁺ and F^I -Zr⁴⁺ in RRDE measurements.

Catalyst	Loading (μL)	H ₂ O ₂ Sel. (%)	<i>j</i> (mA cm ⁻²)
F^2 -Zr ³⁺	5	82.7 @ 0.1 V	-2.93 @ 0.1 V
	10	91.4 @ 0.1 V	-2.48 @ 0.1 V
	15	92.9 @ 0.1 V	-2.31 @ 0.1 V
F^I -Zr ⁴⁺	5	56.2 @ 0.1 V	-2.40 @ 0.1 V
	10	41.9 @ 0.1 V	-1.68 @ 0.1 V
	15	39.0 @ 0.1 V	-1.51 @ 0.1 V

Supplementary Table 6. Comparison of the $F^2\text{-Zr}^{3+}$ electrocatalyst with representative literature results.

Catalyst	Electrolyte	Selectivity@Potential (% @V vs.RHE)	Productivity	Ref.
$F^2\text{-Zr}^{3+}$	0.1 M KOH	98@0.6 95@0.5	12.8 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	This work
S-Nv- C_3N_4	0.1 M KOH	95%	4.52 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[66]
PdSe ₂	0.5 M NaPi	80%	7.93 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[67]
FeSA-NS/C	0.1 M HCl	90%	4.95 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[68]
h-SnO ₂	1 M KOH	99%	3.19 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[69]
NiB ₂	0.1 M KOH	99%	4.75 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[70]
ZnO ₃ C	0.1 M KOH	89%	0.35 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[71]
NiO _x -C	0.1 M KOH	91%	/	[72]
c-WO ₃	0.1 M KOH	90%	0.179 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[73]
{001}-Fe ₂ O _{3-x}	0.1 M KOH	95%	0.454 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[74]
TiO _{2-x}	0.1 M KOH	94%	18.1 mmol $\text{L}^{-1} \text{h}^{-1}$	[75]
Cu-TiO ₂	0.1 M KOH	91%	0.461 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[76]
ZnO@ZnO ₂	0.1 M K ₂ SO ₄	100 %	5.47 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[77]
O-CNTs	0.1 M KOH	90%	0.112 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[78]
Co ₁ -NG(O)	0.1 M KOH	80%@0.4	~0.418 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[79]
Co-POC-O	0.1 M KOH	84%@0.8	/	[80]
Co-N SACDp	0.1 M HClO ₄	94%@0.5	26.7 mg $\text{cm}^{-2} \text{h}^{-1}$	[81]
Co-N ₂ -C/HO	0.1 M KOH	91.2%@0.7	6.91 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[82]
OCNS ₈₀₀	0.1 M KOH	91%	0.77 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[83]
N ₂ O-CNTs	0.1 M KOH	95%	0.265 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[84]
NiNb ₂ O ₆	0.1 M KOH	96%	0.996 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[85]
O-C(Al)	0.1 M NaOH	97%	0.51 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[86]
Fe-CNT	0.1 M KOH	97%	0.678 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[87]
Co-Zn DAC	0.1 M HClO ₄	94.8%	10.5 mol $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	[88]

Supplementary Table 7. Calculated initial Zr–O bond lengths (Å) of the local coordination polyhedra in the perfect ZrO₂.

Perfect ZrO ₂	Zr ₁ (Å)	Zr ₂ (Å)	Zr ₃ (Å)	Zr ₄ (Å)
Zr–O ₁	2.078	2.078	2.078	2.078
Zr–O ₂	2.078	2.078	2.078	2.078
Zr–O ₃	2.078	2.078	2.078	2.078
Zr–O ₄	2.078	2.078	2.078	2.078
Zr–O ₅	2.388	2.388	2.388	2.388
Zr–O ₆	2.388	2.388	2.388	2.388
Zr–O ₇	2.388	2.388	2.388	2.388
Zr–O ₈	2.388	2.388	2.388	2.388

Supplementary Table 8. Calculated Zr–O bond lengths (Å) of the local coordination polyhedra in the F^2 -Zr $^{4+}$.

F^2 -Zr $^{4+}$	Zr ₁ (Å)	Zr ₂ (Å)	Zr ₃ (Å)	Zr ₄ (Å)
Zr–O ₁	2.099	2.099	2.054	2.054
Zr–O ₂	2.105	2.105	2.061	2.061
Zr–O ₃	2.105	2.105	2.061	2.061
Zr–O ₄	2.288	2.288	2.079	2.079
Zr–O ₅	2.288	2.288	2.366	2.366
Zr–O ₆	2.322	2.322	2.377	2.377
Zr–O ₇	2.458	2.458	2.377	2.377

Supplementary Table 9. Calculated Zr–O bond lengths (Å) of the local coordination polyhedra in the F^I -Zr⁴⁺.

F^I -Zr ⁴⁺	Zr ₁ (Å)	Zr ₂ (Å)	Zr ₃ (Å)	Zr ₄ (Å)
Zr–O ₁	2.060	2.060	2.045	2.045
Zr–O ₂	2.089	2.089	2.054	2.054
Zr–O ₃	2.089	2.089	2.066	2.066
Zr–O ₄	2.257	2.257	2.066	2.066
Zr–O ₅	2.257	2.257	2.303	2.303
Zr–O ₆	2.283	2.283	2.309	2.309
Zr–O ₇	2.302	2.302	2.309	2.309

539 **Supplementary Table 10.** Calculated Zr–O bond lengths (Å) of the local
540 coordination polyhedra in the F^2 -Zr³⁺.

F^2 -Zr ³⁺	Zr ₁ (Å)	Zr ₂ (Å)	Zr ₃ (Å)	Zr ₄ (Å)
Zr–O ₁	2.157	2.157	2.061	2.061
Zr–O ₂	2.157	2.157	2.064	2.064
Zr–O ₃	2.164	2.164	2.064	2.064
Zr–O ₄	2.293	2.293	2.093	2.093
Zr–O ₅	2.293	2.293	2.403	2.403
Zr–O ₆	2.332	2.332	2.440	2.440
Zr–O ₇	2.611	2.611	2.440	2.440

541

Supplementary Table 11. Calculated Jahn-Teller distortions and the average distortion of the four Zr sites adjacent to the F center of $F^2\text{-Zr}^{4+}$, $F^1\text{-Zr}^{4+}$ and $F^2\text{-Zr}^{3+}$.

Model	Zr ₁	Zr ₂	Zr ₃	Zr ₄	Average
$F^2\text{-Zr}^{4+}$	0.0517	0.0517	0.0690	0.0690	0.0600
$F^1\text{-Zr}^{4+}$	0.0437	0.0437	0.0564	0.0564	0.0501
$F^2\text{-Zr}^{3+}$	0.0477	0.0477	0.0787	0.0787	0.0632

Note: The corresponding distortion parameters ε_I were calculated according to equation^[89]:

$$\varepsilon_I = \frac{I}{7} \sum \frac{|R_i - R_a|}{R_a}$$

where R_i represents the length of each bond, and R_a denotes the average bond length of each system.

Supplementary Table 12. Lattice parameters of perfect ZrO₂, F^2 -Zr⁴⁺, F^I -Zr⁴⁺ and F^2 -Zr³⁺.

Model	$a/\text{\AA}, \alpha/^\circ$	$b/\text{\AA}, \beta/^\circ$	$c/\text{\AA}, \gamma/^\circ$
Perfect ZrO ₂	7.1986, 90	7.1986, 90	10.4288, 90
F^2 -Zr ⁴⁺	7.1788, 90	7.2065, 90	10.4010, 90
F^I -Zr ⁴⁺	7.1637, 90	7.1937, 90	10.3958, 90
F^2 -Zr ³⁺	7.2286, 90	7.2408, 90	10.5031, 90

Note: The uniaxial strain (ε_2) formula to calculate the average absolute distortion degree across the three crystallographic axes for the different defect models compared to the perfect cell^[90].

$$\varepsilon_2 = \frac{\frac{|a_{\text{perfect}} - a_{\text{defect}}|}{a_{\text{perfect}}} + \frac{|b_{\text{perfect}} - b_{\text{defect}}|}{b_{\text{perfect}}} + \frac{|c_{\text{perfect}} - c_{\text{defect}}|}{c_{\text{perfect}}}}{3} \times 100 \%$$

The variables a_{perfect} , b_{perfect} and c_{perfect} represent the lattice constants of the perfect ZrO₂. a_{defect} , b_{defect} and c_{defect} denote the respective lattice parameters of the defective ZrO₂ containing different F centers.

559 **Supplementary Table 13.** Convergence test of the total energy and energy difference
560 ($|\Delta E|$) with respect to the plane-wave cutoff energy for the F^2 -Zr $^{3+}$ model.

Cut off energy	E_{total} (eV)	Atom number	$ \Delta E $ (meV/atom)
300 eV	-2135.6967	216	/
350 eV	-2076.7217	216	273.03
400 eV	-2062.9488	216	63.763
450 eV	-2058.8014	216	19.201
500 eV	-2058.8175	216	0.0745

561

562 **Supplementary Table 14.** Convergence test of the total energy and energy difference
563 ($|\Delta E|$) with respect to the k-point mesh density for the F^2 -Zr³⁺ model.

k-mesh	E_{total} (eV)	Atom number	ΔE (meV/atom)
(1 × 1 × 1)	-2058.7731	216	/
(1 × 2 × 1)	-2058.7788	216	0.0264
(2 × 2 × 1)	-2058.8014	216	0.1046

564

565 **Supplementary Table 15.** Convergence test of the total energy and energy difference
 566 ($|\Delta E|$) with respect to the precision parameter (PREC) for the F^2 -Zr³⁺ model.

PREC	E _{total} (eV)	Atom number	$ \Delta E $ (meV/atom)
Fast	-2058.0330	216	/
Normal	-2058.8014	216	3.5574
Accurate	-2058.6742	216	0.5889

567

Supplementary Table 16. Entropies, zero-point energies, and solvation correction energies of the intermediates.

Intermediate	TS (eV)	E _{ZPE} (eV)	E _w (eV)
*O ₂	0.000 ^[60]	0.111 ^[60]	-0.32 ^[92]
*OOH	0.000 ^[60]	0.448 ^[60]	-0.54 ^[92]
H ₂	0.410 ^[60]	0.293 ^[60]	/
H ₂ O	0.670 ^[60]	0.607 ^[60]	/
O ₂	0.634 ^[91]	0.096 ^[61]	/

Note: E_{ZPE} is the zero-point energy correction, TS is the entropy contribution at 298.15 K, and E_w represents the aqueous solvation correction.

Supplementary Table 17. Calculated free energy change of each reaction step on the Perfect ZrO_2 , $F^2\text{-Zr}^{3+}$ and $F^1\text{-Zr}^{4+}$ at 0 V.

Surface	$\Delta G_1(*\text{O}_2)_{U=0}$	$\Delta G_2(*\text{OOH})_{U=0}$
Perfect- ZrO_2 (011)	-0.271	-0.299
$F^2\text{-Zr}^{3+}$	-0.337	-0.625
$F^1\text{-Zr}^{4+}$	-0.634	-1.092

Supplementary Table 18. Comparison of the calculated free energy change of each reaction step on perfect ZrO₂ between this work and previous literature.

Surface	$\Delta G_1(*O_2)_{U=0}$	$\Delta G_2(*OOH)_{U=0}$
This work		
Perfect-ZrO₂ (011)	-0.271	-0.299
m-ZrO ₂ (-111) ^[60]	-0.250	-0.246
m-ZrO ₂ (-101) ^[60]	-0.292	-0.434
m-ZrO ₂ (110) ^[60]	-0.382	-0.526

Note: The calculated adsorption free energies of *O₂ and *OOH on perfect ZrO₂ are -0.271 and -0.299 eV, respectively, which are close to the reported ranges for monoclinic ZrO₂ facets (-0.250 to -0.382 eV for *O₂ and -0.246 to -0.526 eV for *OOH). This agreement supports the reliability of our computational setup.

Supplementary Table 19. Comparison of the calculated free energy change of each reaction step on defective ZrO₂ between this work and previous literature.

Surface	$\Delta G_1(*O_2)_{U=0}$	$\Delta G_2(*OOH)_{U=0}$
$F^2\text{-Zr}^{3+}$	-0.337	-0.625
$F^I\text{-Zr}^{4+}$	-0.634	-1.092
t-ZrO ₂ (101) V _{O2} path1 ^[61]	-0.328	-1.616
t-ZrO ₂ (101) V _{O2} path2 ^[61]	-0.328	-1.616
t-ZrO ₂ (101) V _{O2} path3 ^[61]	-0.328	-1.329
t-ZrO ₂ (101) V _{O2} path4 ^[61]	-0.328	-1.329
t-ZrO ₂ (101) V _{O3} path1 ^[61]	-0.229	-1.383
t-ZrO ₂ (101) V _{O3} path2 ^[61]	-0.229	-1.383

Note: Compared with conventional neutral oxygen vacancies in ZrO₂ reported by Muhammady et al., the charged F -center models show distinct adsorption behavior. For $*O_2$, $F^2\text{-Zr}^{3+}$ gives a comparable adsorption free energy (-0.337 vs. -0.229 to -0.328 eV), while $F^I\text{-Zr}^{4+}$ binds $*O_2$ more strongly (-0.634 eV). In contrast, the $*OOH$ adsorption on $F^2\text{-Zr}^{3+}$ and $F^I\text{-Zr}^{4+}$ (-0.625 and -1.092 eV) is weaker than that on neutral oxygen vacancies (-1.329 to -1.616 eV). These differences reflect the influence of the explicit charge states of F centers on the surface electronic structure and intermediate binding strength.

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