Supporting Information

Atomically Dispersed Pentacoordinated-Zirconium Catalyst with Axial Oxygen Ligand for Oxygen Reduction Reaction

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Experimental Procedures

**Chemicals.** Zirconium chloride, 2-methylimidazole, zinc chloride, silica colloid solution (12 nm, Ludox HS40, 40% in water), ammonium hydroxide, tetraethylorthosilicate and Nafion perfluorinated resin solution were purchased from Sigma Aldrich. Potassium hydroxide and zinc acetate were purchased from Fisher Scientific. All chemicals were used directly without any further purification.

**Synthesis of silica sphere.** The silica template with diameters of about 220 nm was prepared by the Stöber method. Specifically, 6 mL of tetraethylorthosilicate was dropped into 210 mL of ethanol under stirring. Afterwards, 7 mL of ammonium hydroxide (28 wt%) and 42 mL of water were added into the above solution slowly, respectively. The solution was kept at room temperature for 1 day under stirring. Next, the white precipitate was collected and washed with water and ethanol for 3 times. Finally, SiO₂ nanospheres were obtained by vacuum drying at 70 °C for 12 h.

**Synthesis of O-Zr-N-C, O-Zr-N-C-h, and N-C.** O-Zr-N-C was prepared by using the silica nanospheres as the template. 250 mg of SiO₂ nanospheres with diameters of 220 nm and 3.75 g of colloidal silica with diameters of 12 nm were first dispersed in 100 mL DI water by ultrasonication for 30 min. Then, 500 mg of 2-methylimidazole was added to the above suspension. Meanwhile, 0.5 mmol of zirconium chloride and 2 mmol of zinc chloride were dissolved into ethanol and subsequently dropwise added into the suspension under stirring. Afterwards, the solvent was removed by rotary evaporation, and the collected solid mixture was calcined at 950 °C for 2 hours in the Ar atmosphere. Finally, O-Zr-N-C was obtained by removing the silica template with 10% HF solution, followed by an activation process in the Ar atmosphere at 900 °C for 2 hours. N-C was synthesized in a similar process, except without adding zirconium chloride in the precursor. O-Zr-N-C-h was prepared in a similar process with O-Zr-N-C by using 4 mmol of zirconium chloride in the precursor.

**Material characterizations.** The morphologies of samples were investigated by scanning electron microscopy (SEM, Zeiss Gemini 500). Transmission electron microscopy (TEM, Carl Zeiss Libra 200 Cs MC STEM, FEI Titan Themis 60-300, probe-corrected) was performed at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed by a Scienta Omicron Multiprobe system using a monochromatic Al Kα X-ray source and an Argus CU electron analyzer with a spectral resolution of 0.6 eV. X-ray diffraction (XRD) was measured by a PANalytical X’Pert Pro diffractometer with Cu-Kα radiation. Inductively coupled plasma-optical emission spectroscopy analysis (ICP-OES, Optima 2000 DV, PerkinElmer Inc.) was used to determine the loading mass of Zr in O-Zr-N-C. Barrett-Emmett-Teller (BET) surface area was measured from nitrogen adsorption/desorption isotherms at 77 K on a Quantachrome volumetric analyzer (Quadrasorb EVO/Si). X-ray absorption spectroscopy (XAS) measurements were conducted at the 20-BM station of The Advanced Photon Source at Argonne National Laboratory and the beamline B18 at Diamond Light Source (Didcot, England). The Zr foil EXAFS was measured with a reference ion chamber for energy calibration for each sample scan. The edge energy was determined by the maximum of the first derivative of the first peak from XANES. Several scans were taken and averaged for each sample to gain a better signal-to-noise ratio.

**Electrochemical measurements.** All the electrocatalyst inks were prepared by thoroughly mixing 10 mg of catalysts in 980 μL of ethanol with 20 μL Nafion solution (5%). Subsequently, the homogeneous catalysts inks were drop-cast on the glassy carbon rotating disk electrode (RDE, 5 mm in diameter) with a loading of 0.25 mg cm⁻² for electrocatalytic tests. All the catalytic activities were measured on a PINE electrochemical workstation using a standard three-electrode configuration. RDE, Pt electrode, and a Hg/HgO electrode were used as the working electrode, counter electrode, and reference electrode, respectively. In detail, the ORR polarization was conducted in the O₂-saturated 0.1 M KOH solution with a scan rate of 5 mV s⁻¹. The accelerated durability test was performed by potential cycling from 0.60 to 1.00 V vs. RHE at a sweep rate of 100 mV s⁻¹. The Nernst equation (Equation 1) was used as the conversion formula for converting potentials from the Hg/HgO scale to the RHE scale.

\[ E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098 \] (1)
The rotating ring-disk electrode (RRDE) measurements were used to determine the hydrogen peroxide yield \( (H_2O_2(\%)) \) and electron transfer number \( (n) \) during the ORR process according to equation 2-3, where \( i_d \) is the disk current, \( i_r \) is the ring current, and \( N = 37\% \) is the collection efficiency of RRDE.

\[
H_2O_2(\%) = 200 \times \frac{i_r}{i_d + i_r} 
\]

(2)

\[
n = 4 \times \frac{i_r}{i_d + i_r} 
\]

(3)

Kinetic current density \( (J_k) \) was estimated from the steady-state polarization curves according to the Koutecky-Levich equation (equation 4), where \( J \) is the measured current density at various potentials on the steady-state polarization curve, and \( J_L \) is the limiting diffusion current density.

\[
J = \frac{1}{J_L} + \frac{1}{J_k} 
\]

(4)

**Assembly of zinc-air batteries (ZABs).** ZABs were assembled with a home-built electrochemical device. The electrocatalysts were drop-casted on the carbon cloth (with a geometric area of 0.5 cm\(^2\) and a loading amount of 1.0 mg cm\(^{-2}\)) attaching to the gas diffusion layer and used as air cathodes. Zn foil was used as the anode, while 6.0 M KOH with 0.2 M zinc acetate was used as the electrolyte. Ni foam was used as the current collector for both anode and cathode. Electrochemical measurements were carried out with a CHI660E electrochemical workstation and a LAND CT2001A multi-channel battery testing system.

**Computational methods.** All the calculations were carried out using Amsterdam Modeling Suite (AMS) package. Density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, and the valence triple-zeta polarized (TZP) basis sets composed of Slater-type and numerical orbitals were employed. London dispersion interactions were included, following Grimme’s-D3 approach. The geometries were fully optimized using 2D periodic models, scalar relativistic effects were employed for heavy elements Zr, and no frozen core was applied.

In alkaline media, the overall reduction of \( O_2 \) to \( OH^- \) can be described as equation 5.

\[
O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^- 
\]

(5)

This overall reaction is contributed by the following four elementary steps (equation 6-9), where * denotes the bare surface of (O)-Zr-N\(_{4x}\)-C\(_{a}\) \((n = 0, 2, \text{ and } 3)\), and OH\(^+\), O\(^-\), and OH\(^-\) are corresponding oxygen-containing intermediates.

\[
O_2(g) + H_2O(l) + e^- \rightarrow OOH^+ + OH^- 
\]

(6)

\[
OOH^+ + e^- \rightarrow O^+ + OH^- 
\]

(7)

\[
O^+ + H_2O(l) + e^- \rightarrow OH^+ + OH^- 
\]

(8)

\[
OH^+ + e^- \rightarrow OH^- + * 
\]

(9)

Taking the influence of the potential bias \( U \) and \( pH \) into consideration, the free energy change \( \Delta G \) for each step can be calculated as equation 10, where \( \Delta E \) is the reaction energy obtained from DFT calculations, \( \Delta ZPE \) and \( \Delta S \) are the change of zero-point energy and entropy, respectively, calculated from the vibrational frequencies using the DFT approach. \( \Delta G_U \) is the influence of external potential \( U \), \( \Delta G_{pH} = -\Delta U \). \( \Delta pH \) is the correction of \( pH \) dependence, \( \Delta G_{pH} = k_B T \times \ln 10 \times pH \) (\( k_B \) is the Boltzmann constant and \( T \) is temperature, and in this work \( T \) is set as 298.15 K).

\[
\Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_U + \Delta G_{pH} 
\]

(10)

The formation energy \( (\Delta E_i) \) is calculated according to equation 11, where \( E_{total} \) is the total energy of the Zr and N embedded graphene systems, here are Zr-N\(_{4x}\)-C\(_{a}\) and O-Zr-N\(_{4x}\)-C\(_{a}\) \((n = 0, 2, \text{ and } 3)\), \( \mu_C \), \( \mu_N \), \( \mu_Zr \), and \( \mu_O \) are the chemical potentials of carbon (derived from graphene), nitrogen (half N\(_2\) molecule), zirconium (in vacuum), and O (half O\(_2\) atoms, respectively.
Supporting Figures and Tables

Figure S1. (a) Low-magnification and (b) high-magnification SEM images of the SiO$_2$ spheres with an average diameter of 220 nm. (c) Low-magnification and (d) high-magnification SEM images of the SiO$_2$ spheres with an average diameter of 12 nm.
Figure S2. (a) N\textsubscript{2} adsorption-desorption isotherm curve and (b) pore-size distributions of O-Zr-N-C. (c) N\textsubscript{2} adsorption-desorption isotherm curve and (d) pore-size distributions of N-C.

From the pore-size distribution calculated by the density functional theory method, the main peak at ≈11 nm indicates the mesoporous structure of O-Zr-N-C and N-C. Besides, a peak at around 1.0 nm of pore-size distribution was calculated by the Horvath–Kawazoe method, indicating the microcellular structure of O-Zr-N-C and N-C. The micropore volume, mesopore volume, and specific surface area of O-Zr-N-C are 0.59 cm\textsuperscript{3} g\textsuperscript{−1}, 1.07 cm\textsuperscript{3} g\textsuperscript{−1}, and 1343 m\textsuperscript{2} g\textsuperscript{−1}, respectively. The micropore volume, mesopore volume, and specific surface area of N-C are 0.54 cm\textsuperscript{3} g\textsuperscript{−1}, 0.75 cm\textsuperscript{3} g\textsuperscript{−1}, and 1311 m\textsuperscript{2} g\textsuperscript{−1}, respectively.
No Zr-related XRD peaks were detected for O-Zr-N-C (Figure S3a). Only two broad peaks at 23.5 and 44.1° were found for both O-Zr-N-C and N-C, corresponding to the (002) and (101) planes of carbon, respectively. Zn-MIM@SiO₂ was prepared by the similar synthetic route of Zr-MIM@SiO₂ without adding zirconium chloride. Zn-MIM@SiO₂ shows a similar XRD pattern to the reported ZIF,[5] verifying its highly ordered structure. Meanwhile, Zr-MIM@SiO₂ shows multiple XRD peaks, which are obviously different from those of Zn-MIM@SiO₂. This XRD difference implies that the replacement of Zn by Zr changed the crystal structure of ZIF.

Raman spectra of O-Zr-N-C and N-C (Figure S3b) exhibit two broad peaks, designated as D band (≈1350 cm⁻¹) and G band (≈1587 cm⁻¹). The corresponding ratio of the relative intensity of the D band to the G band (I_D/I_G) for O-Zr-N-C was slightly lower than that of the N-C catalyst, thus suggesting that the presence of ZrCl₄ slightly enhanced the graphitization degree of the carbon matrix.
Figure S4. XPS spectrum of O-Zr-N-C.
**Figure S5.** Zr 3d XPS spectrum of O-Zr-N-C.

The high-resolution Zr 3d XPS spectrum can be deconvoluted into two typical signals of Zr 3d$_{5/2}$ peak (182.43 eV) and Zr 3d$_{3/2}$ peak (184.84 eV), respectively. Additionally, no Zr$^0$ (178.9 eV) are detected in the spectrum, indicating that no Zr-related nanoparticles or clusters in O-Zr-N-C.
**Figure S6.** Atomic structures of possible active sites in the O-Zr-N-C catalyst.

The atomic structures in Figure S6 were employed to do the EXAFS spectra fitting and elucidate the local configuration (i.e., the first-shell coordination) of single-atom Zr sites in O-Zr-N-C. These atomic structures were proposed based on the early research experience on SACs, assuming a variable number (1-4) of N atoms in-plane coordinated with Zr.\(^6\) As the Zr-N coordination and the Zr-C coordination appear similarly in the EXAFS spectra,\(^7\) only the Zr-N coordination was considered in these atomic structures to simplify the calculation. A five-coordinated configuration was also established by bonding four-coordinated Zr with another N atom from a second carbon layer. Configurations with higher coordination numbers (\(> 5\)) were not considered as the valence state of Zr would not be realistic (\(> +4\)). Moreover, according to our synthetic route, a dangling O atom coordinated with Zr was expected. Thereby, the structures with a dangling O atom were further established.
Figure S7. The k space curve-fitting of O-Zr-N-C.

The mismatch between the fitting result and experimental data along with the increase of k is assigned to the scattering of the out-shell atoms and inevitable disordered structure. [8]
Figure S8. (a) SEM image and (b) N 1s XPS spectrum of N-C.
Figure S9. High-resolution HAADF-STEM image of O-Zr-N-C after the stability test. The distinct bright dots indicate that Zr is still atomically dispersed in the N-doped carbon matrix after the long-term stability test.
Figure S10. Chronoamperometric curves of a methanol crossover test with O-Zr-N-C and Pt/C at 0.70 V vs. RHE. Of note, the methanol crossover test conducted at such a low potential (not a real case for ORR) aims to prove the strong anti-poisoning effect of O-Zr-N-C towards methanol, which is desired for the ORR catalysts used in direct methanol fuel cells.
Figure S11. Free energy diagrams of (a) Zr-N$_4$, (b) Zr-N$_2$-C$_2$, and (c) Zr-N$_1$-C$_3$ models.
Figure S12. Atomic structures of O-Zr-N₄₋ₓ-Cₓ, n = 0, 2 and 3, the upper and bottom figures in each rectangular cell are the side- and top-view of each configuration. Dark grey, blue, magenta, and red spheres represent C, N, Zr, and O atoms, respectively.

According to coordination chemistry, the oxidation number in the macrocyclic ligand N₄ is −2. Therefore, the corresponding oxidation number of Zr in Zr-N₄ is +2. When the coordination number of N is less than 4, each N donates an electron and thus, has an oxidation number of −1. The -O has oxidation number of −2. As a result, the oxidation states of Zr varies from +2 to +4 in O-Zr-N₄₋ₓ-Cₓ, n = 0, 2 and 3. In this regard, O-Zr-N₃-C₁ was not considered realistic, as the valence state of Zr would be +5.
**Figure S13.** Free energy diagrams of O-Zr-N<sub>n</sub>-C<sub>n</sub>, n = 0, 2, and 3.
Figure S14. Projected density of states of Zr sites for (a) Zr-N$_4$ and O-Zr-N$_4$, and (b) Zr-N$_2$C$_2$ and O-Zr-N$_2$C$_2$. 

- **a:**
  - PDOS (a.u.)
  - Downshift of d-band center: -3.17 eV, -2.59 eV, -0.58 eV
  - E$_F$

- **b:**
  - PDOS (a.u.)
  - Downshift of d-band center: -2.15 eV, -0.52 eV, 1.63 eV
  - E$_F$
Figure S15. XRD pattern of O-Zr-N-C-h. The XRD pattern of O-Zr-N-C-h shows no Zr-related XRD peaks.
Figure S16. (a) SEM image of O-Zr-N-C-h. (b) HAADF-STEM and (c) High-resolution HAADF-STEM image of O-Zr-N-C-h. The distinct bright dots in (c) indicate that Zr atoms are atomically dispersed in the N-doped carbon matrix. (d) EELS mapping images of C, N, O, and Zr for O-Zr-N-C-h.

SEM and HAADF-STEM images of O-Zr-N-C-h were collected to evaluate the morphology of O-Zr-N-C-h. The hierarchical porous structure of O-Zr-N-C-h with abundant mesopores and macropores is apparently revealed by the SEM image (Figure S16a). No metal-related particles are found in the HAADF-STEM image of O-Zr-N-C-h (Figure S16b). Figure S16c shows uniformly dispersed single Zr sites with higher density in the O-Zr-N-C-h compared with O-Zr-N-C catalyst. Furthermore, EELS mapping images of O-Zr-N-C-h (Figure S16d) demonstrate the uniform distribution of C, N, O, and Zr, without the detection of impurities like Cl and Zn.
Zr K-edge X-ray absorption spectra were collected to analyse the local coordination structure of Zr in O-Zr-N-C-h. In the Zr K-edge XANES spectra, O-Zr-N-C-h depicts the threshold energy situated between those of ZrN and ZrO$_2$ (Figure S17a), which is in good line with O-Zr-N-C. The k$^3$-weighted Fourier transform of the O-Zr-N-C-h EXAFS spectrum (Figure S17b) shows the dominant contribution of a first-shell peak at 1.59 Å associated with the coordination with light atoms. No strong contribution related to the Zr metal or ZrO$_2$ was detected. The Zr K-edge EXAFS spectrum of O-Zr-N-C-h was then fitted with the established atomic structures shown in Figure S6, which identifies four in-plane first-shell N/C atoms at 2.10 Å and one axial oxygen atom at 2.20 Å (Figure S17c, Table S2).
Figure S18. Nyquist plots of O-Zr-N-C-h and O-Zr-N-C.
Figure S19. (a) N\textsubscript{2} adsorption-desorption isotherm curves of O-Zr-N-C and O-Zr-N-C-h. (b) Pore size distribution of O-Zr-N-C-h.

The mesopores (2–20 nm) of O-Zr-N-C-h were calculated by the density functional theory method, while the micropores (0.4–2.0 nm) were calculated by the Horvath–Kawazoe method, indicating the microcellular structure of O-Zr-N-C-h. The micropore volume, mesopore volume, and specific surface area of O-Zr-N-C-h are 0.58 cm\textsuperscript{3} g\textsuperscript{-1}, 1.73 cm\textsuperscript{3} g\textsuperscript{-1}, and 1377 m\textsuperscript{2} g\textsuperscript{-1}, respectively.
Figure S20. Tafel plots of O-Zr-N-C and O-Zr-N-C-h.
Figure S21. The open circuit voltages of O-Zr-N-C-h-, O-Zr-N-C-, and Pt/C-based ZABs.
Table S1. Element atomic contents (at.%) of O-Zr-N-C and N-C catalysts based on XPS analysis.

| Samples | Zr  | N   | O   | C   |
|---------|-----|-----|-----|-----|
| O-Zr-N-C| 0.48| 6.38| 4.11| 88.96|
| N-C    | 0   | 7.43| 4.81| 87.76|
**SUPPORTING INFORMATION**

| Samples     | Path | CNs  | R (Å)      | $\sigma^2$ (10$^{-3}$ Å$^2$) | $\Delta E_0$ (eV) |
|-------------|------|------|------------|-----------------------------|------------------|
| O-Zr-N-C    | Zr-N | 3.82 (0.4) | 2.05 (0.016) | 0.1 (0)                  | -9.9 (0)        |
|             | Zr-O | 1.40 (0)  | 2.20 (0.095) | 0 (0)                   |                  |
| O-Zr-N-C-h  | Zr-N | 4.30 (0.1) | 2.10 (0.032) | 3.9 (2.9)               | -5 (0)          |
|             | Zr-O | 1.40 (0)  | 2.20 (0.098) | 0 (0)                   |                  |
| Zr foil     | Zr-Zr | 12   | 3.22 (0.03) | 9.0 (5.0)              | -4.84 (0.46)    |

(CN: coordination number; R: distance; $\sigma^2$: mean-square disorder; $\Delta E_0$: energy shift. Zr-N scattering is the single scattering from the neighbour Zr to N. The value in the bracket is the error.)
Table S3. ORR performance of recently developed SACs in alkaline solution.

| ORR catalysts     | Metal weight ratio (wt %) | $E_{1/2}$ (V vs. RHE) | Stability                          | $i_0$ (mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | Ref |
|-------------------|---------------------------|------------------------|------------------------------------|----------------------|----------------------------|-----|
| Co-ISAS/p-CN      | 0.4 wt%                   | 0.838                  | 6 mV delay after 5000 cycles       | ≈5.2 at 0.83 V       | 61                         | [9] |
| Cu-N-C            | 20.9 wt%                  | 0.869                  | 0.2% loss after 10000 s            | 11.8 at 0.85 V       | /                          | [10]|
| g-SA-Mn-900       | 2.9 wt%                   | 0.90                   | 9 mV delay after 5000 cycle        | /                    | /                          | [11]|
| Co SAs/N-C        | /                         | 0.881                  | No delay after 5000 cycle          | 21.2 at 0.80 V       | 75                         | [12]|
| Fe-ISAs/CN        | 2.16 wt%                  | 0.90                   | 2 mV delay after 5000 cycle        | 37.85 at 0.85 V      | /                          | [13]|
| Fe,Mn/N-C         | 2.3 wt% for Fe and 1.6 wt% for Mn | 0.928              | No delay after 40000 cycle         | ≈7                   | /                          | [14]|
| Fe/N-G-SAC        | 0.67 wt%                  | 0.89                   | /                                  | 3.837 at 0.9 V       | 50                         | [15]|
| Zn-B/N-C          | 2.4 wt%                   | 0.886                  | 3% loss after 36000 s              | /                    | 50                         | [16]|
| CANPc (Co)-p      | /                         | 0.85                   | 12.4% loss after 12000 s           | 43.73 at 0.9 V       | 45                         | [17]|
| Fe-SAs/NSC        | 0.87 wt%                  | 0.87                   | No delay 5000 cycles               | 35.9 at 0.80 V       | 60                         | [18]|
| Fe/OES            | 0.11 wt%                  | 0.85                   | 13.3% loss after 36000 s           | ≈6                   | /                          | [19]|
| 10Co-N@DCNF       | 0.108 wt%                 | 0.83                   | 10 mV delay after 5000 cycles      | /                    | 56                         | [20]|
| Fe-N/P-C-700      | 4.5 wt%                   | 0.867                  | No delay after 36000 s             | 24.49                | /                          | [21]|
| CoNi-SAs/NC       | /                         | 0.76                   | 10% loss after 16 h                | /                    | 58.7                       | [22]|
| Cu SAs/NC-900     | 2.1 wt%                   | 0.87                   | 7% loss after 10 000 s             | 2.72 at 0.9 V        | 79                         | [23]|
| Mn-NC/CNT         | /                         | 0.83                   | No delay after 10 000 cycles       | /                    | 56                         | [24]|
| Cu/Zn@NC          | 0.42 wt%                  | 0.83                   | No delay after 10 000 cycles       | /                    | 54.8                       | [25]|
| O-Zr-N-C          | 3.1 wt%                   | 0.91                   | No delay after 10000 cycles, 8% loss after 130 h | 76.0 at 0.8 V       | 66                         | This Work |
| O-Zr-N-C-h        | 9.1 wt%                   | 0.92                   | 6.4% loss after 130 h              | 103.8 at 0.8 V       | 58.3                       | This Work |
Table S4. BET surface area and pore volume of O-Zr-N-C-h and O-Zr-N-C.

| Samples  | Micropore volume (cm³ g⁻¹) | Mesopore volume (cm³ g⁻¹) | Specific surface area (m² g⁻¹) |
|----------|-----------------------------|---------------------------|-------------------------------|
| O-Zr-N-C | 0.59                        | 1.07                      | 1343                          |
| O-Zr-N-C-h | 0.58                     | 1.73                      | 1377                          |
Table S5. Performance comparison of recently developed ZABs.

| Samples                  | Peak powder density (mW cm\(^{-2}\)) | Stability          | Open circuit voltage (V) | Ref. |
|--------------------------|--------------------------------------|--------------------|--------------------------|------|
| Co\(_2\)-N/PS/HC         | 176                                  | 50 h               | 1.47                     | [26] |
| Fe-N/P-C-700             | 133.2                                | 40 h at 10 mA cm\(^{-2}\) | 1.42                     | [21] |
| Zn-N-C-1                 | 179                                  | /                  | /                        | [27] |
| Mn/C-NO                  | 120                                  | 5.56 h at 20 mA cm\(^{-2}\) | /                        | [28] |
| SA-Fe/NG                 | 91                                   | 20 h               | /                        | [29] |
| Fe,Mn/N-C                | 160.8                                | 81 h at 5.0 mA cm\(^{-2}\) | 1.33                     | [14] |
| Fe/N-G-SAC               | 120                                  | 240 cycles         | /                        | [15] |
| CAN-Pc(Co)jp             | 137                                  | 60 h               | 1.46                     | [17] |
| Fe/OES                   | 186.8                                | >130 h             | 1.51                     | [19] |
| CoNi-SAs/NC              | 101.4                                | 31.7 h             | 1.45                     | [22] |
| C-MOF-C2-900             | 105                                  | 40 h               | 1.46                     | [20] |
| Co/Co\(_3\)O@PGS         | 118.3                                | 800 h              | 1.45                     | [31] |
| N-GCNT/FeCo              | 89                                   | 9 h                | 1.48                     | [32] |
| NPMc-1000                | 55                                   | 240 h              | 1.48                     | [33] |
| NGM-Co                   | 152                                  | /                  | 1.44                     | [34] |
| Fe\(_{0.6}\)Co\(_{0.4}\)O\(_x\) | 86                                  | 120 h at 10 mA cm\(^{-2}\) | 1.44                     | [35] |
| Co–N/C NRA               | 193                                  | 80 h               | 1.42                     | [26] |
| CuS/NS\(_2\)            | 172.4                                | 83 h               | 1.44                     | [33] |
| Meso-CoNC@GF             | 154.4                                | 105 h              | 1.51                     | [38] |
| Co\(_2\)Fe@NC            | 423.7                                | 250h               | 1.454                    | [39] |
| Ni-doped CoO NSs         | 377                                  | 400 h              | 1.45                     | [40] |
| Co@NG-acid               | 350                                  | 14h                | 1.4                      | [41] |
| O-Zr-N-C                 | 289                                  | 312 h at 10 mA cm\(^{-2}\) | 1.50                     | This work |
| O-Zr-N-C-h               | 324                                  | 312 h at 10 mA cm\(^{-2}\) | 1.48                     | This work |

This work
In the C K-edge spectrum, the sharp peak at about 284 eV is due to transitions from the 1s core level to the n* band, while the broad peak around 296 eV corresponds to transitions to the p-orbital projected part of the o^* band. Moreover, the N K-edge spectrum exhibits two splitting peaks at ~399 eV and ~406 eV, attributing to the n* state of the pyridine-like and the graphic-like arrangement, respectively. Particularly, the pyridine-like N atoms have rich electron lone pairs to capture metal ions, showing a strong tendency to coordinate with Zr atoms. The main peak of the O K-edge located at 539 eV can be ascribed to the bond formation with neighboring Zr 3d orbitals. Besides, the co-existence of C, N, O, and Zr within an Ångström-scale region implies that Zr atoms are fixed in the carbon matrix by coordinating with C, N, and O atoms.
SUPPORTING INFORMATION

[42] K. Suenaga, M. Koshino, *Nature* **2010**, *468*, 1088-1090.
[43] H. Lin, R. Arenal, S. Enouz-Vedrenne, O. Stephan, A. Loiseau, *J. Phys. Chem. C* **2009**, *113*, 9509-9511.
[44] a) Y. Zheng, Y. Jiao, Y. Zhu, Q. Cai, A. Vasileff, L. H. Li, Y. Han, Y. Chen, S.-Z. Qiao, *J. Am. Chem. Soc.* **2017**, *139*, 3336-3339; b) H. Xu, D. Cheng, D. Cao, X. C. Zeng, *Nat. Catal.* **2018**, *1*, 339-348.
[45] D. Qian, B. Xu, M. Chi, Y. S. Meng, *Phys. Chem. Chem. Phys.* **2014**, *16*, 14665-14668.

**Author Contributions**

X.F., M.Y., and X.W. conceived and designed this work. X.W. performed the experiments and wrote the manuscript under the supervision of X.F. and M.Y. Y.A. conducted the DFT calculations under the supervision of K.A. T.H. And L.L. conducted the STEM characterizations. L.F. conducted the XAS characterizations under the supervision of T.L. Y.L., J.Z., and H.Q. discussed the results and participated in the preparation of the manuscript.