# Single-Iron Site Catalysts with Self-Assembled Dual-size Architecture and Hierarchical Porosity for Proton-Exchange Membrane Fuel Cells

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# **Graphical Abstract**



**Abstract:** Atomically dispersed and nitrogen coordinated single iron site (*i.e.*, FeN<sub>4</sub>) catalysts (Fe-N-C) are the most promising platinum group metal (PGM)-free cathode for the oxygen reduction reaction (ORR) in proton-exchange membrane fuel cells (PEMFCs). However, current Fe-N-C catalysts are limited by the inferior exposure of active FeN<sub>4</sub> sites due to the inevitable agglomeration of particles in cathodes. Herein, we report a self-assembled strategy to synthesize the atomically dispersed FeN<sub>4</sub> site catalysts with a hierarchically porous matrix derived from dual-size Fe-doped ZIF-8 crystal precursors. The tailored structure is effective in mitigating the particle migration, agglomeration, and spatial overlap, thereby exposing increased accessible active sites and facilitating mass transport. The best performing catalyst composed of 100 nm "nucleated seed" assembled by 30 nm "satellite" demonstrates exceptional ORR activity in acidic electrolyte and membrane electrode assembly. This work provides new concepts for designing hierarchically porous catalysts with single metal atom dispersion *via* self-assembly of ZIF-8 crystal precursors with tunable particle size and nanostructures.

**Keywords:** Single metal sites; oxygen reduction; self-assembly architecture; electrocatalysis; fuel cells

## 1. Introduction

The ever-growing energy demand and environmental issues have motivated the exploitation of technologies for sustainable and clean energy conversion [1, 2]. Proton-exchange membrane fuel cells (PEMFCs) have attracted extensive attention owing to environmental friendliness, zero-emission, energy conversion efficiency, and high energy density [3-7]. However, one of the main obstacles is the cathodic oxygen reduction reaction (ORR) that suffers from the inherently sluggish kinetics and requires significant platinum group metal (PGM) electrocatalysts [8-13]. Due to the scarce resource and prohibitive cost, current PGM catalysts must be substantially reduced or replaced by earth-abundant elements [14-19]. Among studied catalyst formulations, transition metal and nitrogen co-doped carbon catalysts (M-N-C, M: Fe, Co, or/and Mn) have been regarded as one of the most promising PGM-free candidates [20-27]. In particular, nitrogen-doped atomically dispersed Fe on carbon has demonstrated encouraging ORR activity and stability in acidic media, in which atomically dispersed FeN<sub>4</sub> sites are likely the active sites [28-34].

Recently, metal-organic frameworks (MOFs), in particular zeolitic imidazolate frameworks (ZIFs), composed of metal nodes and nitrogen-containing ligands, are considered as an ideal precursor for the synthesis of atomically dispersed and nitrogen coordinated metal site catalysts [33, 35, 36], including FeN<sub>4</sub> site-rich Fe-N-C catalysts [36]. The subsequent carbonization is necessary and can exclusively convert the Fe-N covalent bonds to FeN<sub>4</sub> active sites embedded into the porous carbon matrix [4, 37-39]. Also, most of the catalysts based on ZIFs exhibited porous carbon structures with dominant micropores [14, 21, 23]. The richness of micropores is critically significant in not only hosting FeN<sub>4</sub> active sites but also increasing specific surface

areas for the ORR [13, 28, 40, 41]. Unfortunately, excessive micropores would lead to the inaccessibility of ionomer to active sites and the significant limitation of mass transport, therefore reducing the catalyst performance in fuel cells [20-26, 42]. In contrast, meso- and macropores structures in catalysts not only remarkably promote mass transport of the reactants and products, but also facilitate the uniform dispersion of solid-state electrolyte (*i.e.*, Nafion) into catalyst particles to utilize more active sites. Unfortunately, most of the reported ZIF-8 dervied Fe-N-C catalysts failed to provide such favorable morphologies and nanostructures, due to dense particle agglomeration in cathodes.

Hence, it is crucial to constructing ordered, tailored, and porous structures, especially hierarchical architecture, to facilitate mass transport, promote ionomer dispersion, and increase the exposure of active sites. In heterocatalysis processes, the catalysts with the hierarchically porous feature have exhibited apparent advantages compared to simple pore structures [43-45]. For example, Hycon *et al.* designed three types of N-doped carbon models with different pore size distributions and further synthesized corresponding Fe-N-C catalysts to investigate the effect of porous structures on the catalytic performance. They found that the catalyst with the trimodal pore size distribution shows the best performance towards the ORR. Overall, hierarchically porous structures with various morphologies can remarkably promote the mass transfer, increase the density of active sites, expose more available active sites, and regulate water management to maximize catalytic activity [46-51]. However, the preparation of hierarchically porous carbon materials was relatively complex by using templates coupled with tedious post-treatments such as acidic leaching, alkaline leaching, or second heating treatments [40, 41]. Hence, it is highly desirable to develop a simple process for the preparation of

hierarchically porous 3D architectures for the most promising Fe-N-C catalysts toward the ORR in fuel cells.

Herein, we developed a self-assembly approach to synthesizing a tailored ZIF-derived single Fe site electrocatalyst with dual-size architecture and hierarchical porosity. Through a two-step procedure, we deposited small-sized catalyst particles onto a large one, which aims to prevent the agglomeration of such small particles with increased exposure of active sites during the synthesis and long-term catalytic reaction. The small particles nucleated and grew on the presynthesized large ones as seeds through precise size control. Similar to traditional Fe-N-C catalysts with sole particle size [20, 52], the atomically dispersed FeN<sub>4</sub> sites successfully were generated in the dual-size Fe-N-C catalyst after one-step carbonization. Evidenced by the significantly improved MEA performance in fuel cells, the dual-size particles provided a more favorable pore structure and effectively addressed the issue of particle agglomeration in the PGM-free cathode.

#### 2. Experimental Section

## 2.1 Catalysts synthesis

The Fe-doped ZIF-8 crystal precursors were synthesized according to the previously reported chemical doping method with appropriate modifications [20]. The different sizes of Fe-doped ZIF can be accurately controlled by tuning the concentration of metal precursors in methanol solution. The synthesis of dual-size Fe-doped ZIF-derived catalysts using a self-assembled process, *i.e.*, "nucleated seed" of 100 nm assembled by "satellite" of 30 nm, is given here as an example.

To prepare the Fe-doped ZIF-8 precursor of 100 nm as a support, we prepared two following

solutions.  $Zn(NO_3)_2 \cdot 6H_2O$  (3.39 g) and  $Fe(NO_3)_3 \cdot 9H_2O$  (0.100 g) were dissolved in 300 mL methanol. The other 300 mL methanol solution contained 2-methylimidazole (3.94 g). Then both solutions were mixed together and heated at 60°C for 24 h. The precipitant was then collected, followed by centrifugation, washing with ethanol three times, and vacuum dried at 60°C for overnight.

To prepare the dual-size Fe-doped ZIF precursors, we developed the following procedures. The prepared 100 nm Fe-doped ZIF-8 precursor was dispersed again in methanol to form a 10 mg/mL suspension solution, as alleged "nucleated seed." During the preparation of 30 nm satellite Fe-doped ZIF-8 particles, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.70 g) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.050 g) were dissolved in 200 mL methanol. The other 200 mL methanol solution contained 2methylimidazole (1.97 g). Then both solutions were mixed. Next, the suspension mentioned above containing 100 nm Fe-doped ZIF-8 precursor was added into the mixed solutions immediately, followed by a thorough stirring for 15 min and heated at 60°C for 24 h. The precipitant was graduated generated, followed by washing with ethanol and dried at 60°C in a vacuum oven. To this end, the composite dual-size Fe-doped ZIF-8 precursor, consisting of self-assembled 30 nm particles onto a 100 nm large one, was heated at 1100°C under N<sub>2</sub> flow for one hour in a tube furnace to obtain the final catalyst. The samples were labeled as n% X@Y, where n% is the mass percent of large size precursor (X) against small size one (Y). For example, the 11%100@30 sample represents that 100 nm particles with 11 wt.% in the total mass of precursors were used for supporting 30 nm small particles with the rest fraction of 89 wt%.

#### 2.2 Physical characterization

Catalyst morphology was studied using scanning electron microscopy (SEM) on a Hitachi SU 70 microscope at a working voltage of 5 kV. The crystal phases of studied samples were determined by using powder X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer with Cu K-α X-rays. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromatic Al K $\alpha$  source. The monochromatic Al K $\alpha$  source was operated at 15 keV and 150 W; pass energy was fixed at 40 eV for the high-resolution scans. The N<sub>2</sub> isothermal adsorption/desorption was recorded at 77 K on a Micromeritics TriStar II. Samples were degassed at 150°C for five hours under vacuum before nitrogen physisorption measurements. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), high angle annular dark-field scanning TEM (HAADF-STEM) were performed on a probe-corrected FEI Titan 80-300 S/TEM. Raman spectroscopy was performed using a Renishaw Raman system at 514 nm excitation. Fe K-edge X-ray absorption spectroscopy was measured at beamline 5BM, DND-CAT, Advanced Photon Source (APS), Argonne National Laboratory (ANL). Data reduction, data analysis, and EXAFS fitting were performed with the Athena, Artemis, and IFEFFIT software packages [53]. The metal content in the final catalyst was determined by using ICP (ICAP-6000, Thermo Fisher Scientific).

## 2.3 Electrochemical measurements

An electrochemical workstation (CHI760b) coupled with a rotating-ring disc electrode (RRDE, Pine, AFMSRCE 3005) in a three-electrode cell, was used for all electrochemical measurements. A graphite rod and a Hg/HgSO<sub>4</sub> (K<sub>2</sub>SO<sub>4</sub>-sat.) electrode were used as the counter and reference electrodes, respectively. The reference electrode was calibrated to a reversible

hydrogen electrode (RHE) in the same electrolyte before each measurement. A rotating disk electrode with a disk diameter of 5.6 mm covered by a thin film of the catalyst was used as the working electrode. Each catalyst was mixed with isopropanol and a 5 wt% Nafion solution to produce ink for depositing on the working electrode. Then the ink was drop-casted on the disk electrode with a designed loading of 0.6 mg cm<sup>-2</sup> and dried at room temperature to yield a thinfilm electrode. The catalyst-coated disk working electrode was subjected to cyclic voltammetry (CV) in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 20 mV s<sup>-1</sup> to activate the catalysts. The electrocatalytic activity for ORR was tested by steady-state measurement using potential staircase control with a step of 0.05 V at intervals of 30 s from 1.0 to 0 V vs. RHE in O<sub>2</sub>saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 25°C and a rotation rate of 900 rpm. Four-electron selectivity during the ORR was determined by measuring the ring current for calculating H<sub>2</sub>O<sub>2</sub> yield. The hydrogen peroxide yield was calculated from the recorded ring  $(I_r)$  and disk current  $(I_d)$  using the following equation where N = 0.36 is collection efficiency  $H_2O_2$  yield (%) =  $200I_r/(I_r + NI_d)$ [54]. Catalyst stability was studied by potential cycling (0.6 to 1.0 V, 50 mV s<sup>-1</sup>) and by holding at the constant potential at 0.85 V in O<sub>2</sub>-saturated 0.5 H<sub>2</sub>SO<sub>4</sub> during the ORR. Potential cycling was also conducted at high potentials from 1.0 to 1.5 V in N2-saturated 0.5 M H2SO4 at a scanning rate of 500 mV s<sup>-1</sup> to determine the carbon corrosion resistance of catalysts.

## 2.4 Fuel cell tests

To fabricate MEA for fuel cell tests, catalyst ink was made by ultrasonically mixing the Fe-N-C catalyst, isopropanol, de-ionized water, and 5% Nafion<sup>®</sup> suspension in alcohols for three hours. The inks were then manually brush-painted on one side of the membrane until the cathode catalyst loading reached ~4.0 mg cm<sup>-2</sup>. A commercial Pt-catalyzed gas diffusion

electrode (GDE, 0.2 mg Pt/cm<sup>2</sup>, IRD Fuel Cells) was used at the anode. Both cathode and anode were hot-pressed onto a Nafion<sup>®</sup> 212 membrane at 125°C for 5 min. Fuel cell testing was carried out in a single-cell fuel cell (Scribner) with single serpentine flow channels. Pure hydrogen and air/oxygen humidified at 80°C were supplied to the anode and cathode, respectively, at a flow rate of 200 ml min<sup>-1</sup>. The back pressures during the fuel cell tests are based on the U.S. Department of Energy protocols, which is 1.0 bar reactant gas. Fuel cell polarization plots were recorded in a voltage control mode.

#### 3. Results and Discussion

### 3.1 Catalyst morphology and structures

Among studied catalyst particle sizes, our previous report manifested that 100 nm is the ideal size for significant MEA performance enhancement [55]. In principle, the smaller particle sizes, the more active sites exposed, which can yield enhanced mass activity. However, the grand challenge is that small particles tend to aggregate during the ink preparation and a long-term catalytic reaction. Here, we propose an innovative design to use large particles to support small particles and synthesize a composite structure. In this way, we can improve the MEA performance by simultaneously increasing active sites at the surface and providing favorable particle size morphologies. As schematically illustrated in **Fig. 1**, the dual-size Fe-doped ZIF-derived single Fe site catalyst was synthesized using a self-assembled process followed by one-step thermal activation. The synthetic procedure involves the initial synthesis of Fe-doped ZIF-8 precursors with a large size (*e.g.*, 100 nm) as "nucleated seeds." The subsequent self-assembly is to deposit smaller Fe-doped ZIF-8 particles (*e.g.*, 30 nm) as "satellites" onto the large one, followed by a one-step thermal activation.

After optimizing the ORR activity of catalysts with different sizes (Fig. S1 and S2), two ZIF-8 precursors with 100 nm and 30 nm were selected to be "nucleated seeds" and "satellites," respectively. The samples were labeled as n%X@Y, where n% is the mass percent of seeds against satellites, X is the size of seeds (large particles), and Y (small particles) is the size of satellites (for example, 11%100@30).



**Fig. 1.** Schematic illustration of the dual-size Fe-doped ZIF-derived single Fe site catalyst synthesis using a self-assembly process.

The morphologies of the precursor and catalyst after carbonization are shown in **Fig. 2a** and **Fig. 2b**, respectively. The 3D superstructure catalyst has been successfully realized, consisting of the large "nucleated seed" particles of 100 nm assembled by "satellite" particles of 30 nm. Most of the small satellites grow on the larger seeds, and the tailored structure restricts the particle migration, agglomeration, and spatial overlap, thereby exposing more accessible active sites and providing favorable porosity for mass transport. The self-assembly architectures can

be optimized by adjusting the mass ratio between "seed" and "satellite" in terms of the corresponding ORR activity. The best activity is obtained when the ratio of *n* reached 55%. The insufficient large particle "seeds" or excess small particle "satellites" with small size cause inevitable agglomeration (Fig. S3a, b), In contrast, the higher mass ratio of "seeds" leads to the declined ORR activity as the catalysts were dominated by the larger particles with fewer exposed active sites (Fig. S3c).

Furthermore, the catalyst in the aberration-corrected high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 2c, 2f) demonstrated a similar morphology in SEM images. It confirms that the two sizes of particles were interconnected to construct the 3D superstructures (Fig. S4a). The HAADF-STEM images in Fig. 2d and 2e indicate the atomic dispersion of single Fe sites uniformly dispersed in the porous carbon phase [20-23]. In particular, the bright spots in the HAADF-STEM images (Fig. 2e and Fig. S4b) show well-dispersed Fe atomic sites in the absence of Fe clusters or nanoparticles. Corresponding element mapping images (Fig. 2g, 2h) from Fig. 2f exhibit the homogeneous distribution of N and Fe elements in the optimal 55%100@30 catalyst. Our previous Mößbauer spectroscopy provides strong evidence of the existence of FeN4 active sites in similar Fe-N-C catalysts derived from the Fe-doped ZIF-8 precursors[20, 21]. Here, the Xray absorption spectroscopy (XAS) was carried out to confirm the well-dispersed Fe atomic sites and quantify the local coordination environment [23, 56]. The similarity of Fe K-edge Xray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) for our catalyst and FePc (Fig. 2i-k) suggests that Fe in the 55%100@30 catalyst has the very similar oxidization state and local structure to the standard FePc that contains the welldefined Fe-N<sub>4</sub> coordination structure. Also, when comparing the R-space EXAFS of our catalyst and standards (Fe and FePc) in **Fig. 2j**, the dominant Fe-N scattering peak (around 1.3 Å) in the absence of metallic Fe-Fe scattering peak (around 2.1Å) confirms the atomic dispersion of Fe sites in the 55%100@30 catalysts without Fe nanoclusters. We further performed the modeled-based EXAFS fitting (**Fig. 2k**) to quantify the local coordination. The Fe site is likely bonded with 4 N atoms as the well-defined FeN<sub>4</sub> active sites for the ORR (Table S1). In good agreement with the experimental characterization, our previous DFT calculations further suggest that the atomically dispersed and nitrogen coordinated FeN<sub>4</sub> site is the active site, which can thermodynamically and kinetically catalyze O<sub>2</sub> adsorption and subsequent O-O bond braking through a four-electron pathway [23, 57, 58].



**Fig. 2.** SEM images of (a) 55%100@30 precursor and (b) 55%100@30 catalyst; (c, d, e, f) HAADF-STEM images of the 55%100@30 catalyst. Among them, (d) bright-field STEM image showing partially graphitized carbon fringes and (e) HAADF-STEM image of the same depicting the single Fe sites (bright dots) dispersed throughout the carbon phase in the 55%100@30 catalyst, (f) HAADF-STEM images and corresponding elemental images

showing the distribution of N (g), and Fe (h) elements in (f) for 55%100@30 catalyst; (i) Fe K-edge XANES spectrum of 55%100@30 catalysts and reference samples (Fe, FeO, Fe<sub>2</sub>O<sub>3</sub>, and FePc). Fourier transform (j) R-space and (k) K-space spectrum for the 55%100@30 catalysts (the solid red line are the simulation data).

X-ray diffraction (XRD) patterns shown in **Fig. 3a** and **3b** elucidate the crystalline structures of precursors and catalysts. The pattern of Fe-doped ZIF-8 precursor matched well with that of pristine ZIF-8 [20-23], implying that a similar zeolite-type structure was maintained after chemical Fe doping and dual-size self-assembly. After simple high-temperature carbonization at 1100°C under N<sub>2</sub> atmosphere, the catalysts exhibit two broad diffraction peaks at 25° and 44° for (002) and (101) planes of graphitic carbon, respectively. No Fe-containing crystalline phases or clusters are detected in all precursors or catalysts, indicating the Fe species were dispersed atomically in carbon phases. Besides, Raman spectra were confirmed further to analyze the carbon structure (Fig. 3c). There are the two prominent peaks, corresponding to D band (~1350<sup>-1</sup>) and G band (~1580<sup>-1</sup>), respectively [59, 60]. Generally,  $I_D/I_G$  ratios were conclusively established to verify the graphitization degree in carbon materials [61, 62]. All samples exhibited relatively low graphitized structure in carbon, containing significant defects and disordered structures. Compared to the pristine ZIF-8-derived catalyst,  $I_D/I_G$  value of the Fe-doped catalyst was slightly lower, indicating a higher graphitization degree, which may be beneficial for enhancing the ORR with increased electrical conductivity and improved resistance of carbon corrosion.



**Fig. 3.** Extensive materials characterization of the studied catalyst samples including XRD patterns of (a) precursors and (b) catalysts after the carbonization, (c) Raman spectroscopy, (d) N<sub>2</sub> adsorption-desorption curves, (e) pore-size distribution plots, and (f) the comparison of pore distribution and BET surface areas of the studied catalysts.

N<sub>2</sub> adsorption-desorption isotherms, as well as pore size distributions, are exhibited in **Fig. 3d-3f.** The catalyst with a size of 100 nm presents the type-I sorption isotherms, indicating the existence of only micropores, while the one with 30 nm achieves the highest percentage of mesopore volume of 74% (Table S2). In contrast, dual-size catalysts (*i.e.*, 55%100@30) exhibit the type-IV sorption isotherms with distinct hysteresis loops at high relative pressure, implying a hierarchically porous structure with various pore types (micropores and meso/macropores). The possible reason is that 3D superstructure carbon was interconnected *via* the self-assembly of dual-size nanoparticles with the effective evaporation of Zn at high temperatures [4]. Also, as the mass percent of 100 nm particles increases to 33%, the proportion of mesopores decreases while the proportion of micropores gradually increases. However, further increasing the ratio to 55%, the proportion of mesopores suddenly increases, which suggests that adjacent micropores merged into larger mesopores. Meanwhile, the highest BET surface area ( $651 \text{ m}^2/\text{g}$ ) was obtained at the ratio *n* of 55% with a balance of micropore and mesopore. Specifically, micropores in catalysts can host more active sites, and the meso/macropores facilitate O<sub>2</sub> transport and fast diffusion of the reactants along with uniform dispersion of ionomer in electrodes, which would be favorable for the MEA performance.

The X-ray photoelectron spectroscopy (XPS) was proved effective to elucidate the chemical bonding nature and identities of the atoms (C, N, and Fe species) in the surface layers of the porous Fe-N-C catalysts (**Fig. 4** and Table S3~S6). As a comparison, metal content in the bulk of the 55%100@30 catalyst was also further analyzed by using ICP as shown in Table S7. The survey spectra summarized the elemental quantifications of different catalysts, including pyridinic-N (398.6 eV), Fe-N<sub>x</sub> (399.4 eV), graphitic-N (401.1 eV) and oxidized graphitic-N (401.3 eV) (Table S4) [3]. Among studied catalysts, the 55%100@30 catalyst likely has the highest content associated with Fe-N coordination, which is responsible for the improved ORR activity. Generally, Fe atoms and pyridinic-N coordinated to form the Fe-N<sub>4</sub> active sites, while graphitic-N modified electron distribution and electronic structures of carbon, facilitating O<sub>2</sub> adsorption and dissociation, O=O bond breaking, and hosting Fe-N<sub>4</sub> active sites [63]. The high-resolution Fe 2p XPS spectra represent two major peaks around 724 and 711 eV for all studied catalysts (Table S5), corresponding to Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub> [64]. The adjacent peak at 711.4 eV in the Fe 2p<sub>3/2</sub> spectrum is likely related to the Fe-N<sub>x</sub> species [12, 65].



Fig. 4. XPS survey of (a) catalysts including 11%100@30, 33%100@30, 55%100@30, 77%100@30 catalysts and high-resolution spectra for (b) Fe 2p, (c) N 1s, and (d) C 1s in the corresponding catalysts.

## 3.2 Catalyst activity and stability

The electrocatalytic ORR activity and  $H_2O_2$  yields of various catalysts were measured using an RRDE in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The loading of all catalysts was controlled at 0.6 mg cm<sup>-2</sup> on the disk electrode. Pt/Vulcan XC-72 (20 wt% Pt) with a Pt loading of 20  $\mu$ g

cm<sup>-2</sup> was used as the Pt/C reference, which was tested in 0.1 M HClO<sub>4</sub> solution.



**Fig. 5.** (a) Steady-state ORR polarization plots and (b) H<sub>2</sub>O<sub>2</sub> yield plots on different catalysts, respectively, (c) ORR on the catalysts obtained by mechanical mixing 100 nm "seed" and 30 nm "satellite" precursors and (d) CV for different catalysts to determine electrochemical double-layer capacitance for calculating active surface areas.

The highest ORR activity of 55%100@30 catalyst exhibited an  $E_{\text{onset}}$  of 0.95 V and an  $E_{1/2}$  of 0.86 V vs. RHE, which is approaching to the values of the Pt/C catalyst (**Fig. 5a**) and the activity was repeated under different loadings to verify the optimal ratio (55%) (Fig. S5). The ORR performance of catalysts with dual-size particles is dependent mainly on the appropriate

ratio of these two sizes. The lack of large seeds with 100 nm causes the inevitable agglomeration of particles, thus resulting in the activity decline. As the ratio of large particles (i.e., 100 nm) increases to 55%,  $E_{1/2}$  gradually shifts in a positive direction, implying that a continuous increase in the number of active sites as micropores in the matrix gradually increases. Further increasing the ratio to 77% results in a decrease of catalytic activity due to the domination of more large particles with fewer numbers of active sites. Therefore, adjusting the ratio of dual-size particles to expose more effective active sites was of great significance for the development of innovative Fe-N-C catalysts with improved ORR activity. The H<sub>2</sub>O<sub>2</sub> yield of the best catalyst was less than 1%, indicating a four-electron reduction pathway (**Fig. 5b**).

Four control experiments were conducted to validate the optimal catalyst, including: (i) different sizes at various ratios, (ii) best two sizes, but through the direct physical mixture, (iii) Fe-free, and (iv) different thermal activation temperatures. Due to the promising catalytic activity of 50 nm particles [20], 50 nm particles were chosen as the seeds or the satellites, instead of 30 nm or 100 nm particles, to construct a 3D superstructure, and it also proved that the 55% was the optimal ratio (Fig. S6). Besides, other sizes with different ratios (Fig. S7) and the best sizes with directly mixed together (**Fig. 5c** and Fig. S8) have been studied. Their ORR activities, including the  $E_{1/2}$  and limiting current density, were far lower than the 55%100@30 catalyst. The Fe-free catalysts with similar size combinations were prepared using the same self-assembled method without Fe doping into ZIF-8 precursors (Fig. S9). The ORR activity of Fe-free 55%100@30 catalyst was slightly superior to single Fe-free 100 nm or 30 nm particles, further suggesting the advantages of using the unique dual-size configuration.

Furthermore, compared to the complete Fe-free one, the 55%100(Fe-free)@30 catalyst (100 nm Fe-free precursors against 30 nm Fe-doped particles) and 55%100@30(Fe-free) catalyst (100 nm Fe-doped precursors against 30 nm Fe-free particles) demonstrated much improved ORR activity with the partial addition of Fe. The atomically dispersed Fe sites, regardless of the "seed" or "satellite," can dramatically enhance catalytic performance, which was related to the formation of FeN4 active sites [20]. Moreover, the influence of the thermal activation temperatures on ORR activity of the dual-size 55%100@30 Fe-N-C catalyst was further investigated (Fig. S10). It exhibits relatively high activity at 800°C after the thermal activation, suggesting the formation of active catalytic sites at the critical temperature. Further increasing the temperature up to 1100°C results in improved performance, linked to the increase in graphitic N and the number of FeN4 sites, which is in agreement with XAS, DFT, and Mössbauer spectrum in our previous studies.

The electrochemically active surface area (EASA) was determined by measuring the doublelayer capacitance (**Fig. 5d**) to verify the optimal ratio of the self-assembled dual-size particles. Among the various ratios of catalysts, the 55%100@30 catalyst exhibited the largest EASA, likely due to the abundant porosity and prominent accessibility to the electrolyte (Table S8). Importantly, catalysts exhibited larger CV capacitance than similar Fe-N-C catalysts we reported previously [20, 23], indicating the dual-size assembly can provide increased EASA and accessible active sites for the ORR. Therefore, the excellent ORR activity of the 55%100@30 catalyst can be attributed to the optimal size-control, hierarchical porosity, and abundant EASA. Thus, the integration of tailored dual-size architecture and compositional advantages endows the 55%100@30 catalysts to achieve an outstanding catalytic activity.



**Fig. 6.** Stability tests for the 55%100@30 catalyst. (a) ORR polarization plots before and after potential (0.6~1.0 V, 30,000 cycles) and (b) the corresponding carbon particle morphology after potential cycling, (c) 100 h chronoamperometry tests at constant potentials of 0.8 V, (d) ORR polarization plots before and after 100 h chronoamperometry tests and (e) the corresponding CV curves, (f) HAADF-STEM image and (g) EELS point spectra after 100 h chronoamperometry test, (h) ORR polarization plots before and after 200 h curves.

In addition to ORR activity, stability is more crucial for the possible applications of Fe-N-C

catalysts in fuel cells. U.S. DOE protocols indicated that potential cycling durability tests and holding at constant potentials were more relevant to the actual dynamic operating conditions in fuel cells. The accelerated stress tests (ASTs) were proposed by cycling the potential from 0.6 to 1.0 V in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> (**Fig. 6a**). The best catalyst after 30,000 cycles exhibited excellent stability with only a 24.5 mV loss of  $E_{1/2}$ , no evident change of  $E_{onset}$ , similar to the most stable M-N-C catalyst [26]. Also, the microstructure and morphology of catalysts were maintained after the potential cycling tests (**Fig. 6b**), confirming the remarkable stability of the catalyst structure.

Furthermore, under a harsher condition, the 55%100@30 catalyst was tested by holding at a relatively high potential of 0.85 V for 100 h in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (**Fig. 6c**). The encouraging stability retained 50.6% of the initial current density and only 30.8 mV loss of  $E_{1/2}$  after the 100- hour test (**Fig. 6d**, **6e**), which are comparable to the record performance of catalysts (Table S9). To further elucidate the possible degradation mechanisms, the catalyst after 100 h was studied by using STEM images (**Fig. 6f**). The microstructure was damaged. The edges of polyhedral particles became obscure, and Fe sites eventually agglomerated and formed small clusters. Also, EELS shows that Fe no longer coordinated with N, but with O (**Fig. 6g**). Generally, the most likely degradation mechanisms involve the Fe-N coordination cleavage and carbon oxidation, which can also affect each other [36, 66]. Specifically, carbon oxidation can accelerate the demetalation process by corroding the carbon structure and decreasing the number of active sites. The degradation of active surface sites on 55%100@30 catalyst was supposed to account for the decrease of the ORR activity. Besides, the high potential cycling was performed from 1.0 to 1.5 V in an N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution to

evaluate the resistance of carbon corrosion (**Fig. 6h**, **6i**, and Fig. S11). After 5,000 cycles, the capacitance of the 55%100@30 catalyst increased by 42%, indicating severe carbon oxidation in the catalyst, responsible for the noticeable activity loss (**Fig. 6h**).

## 3.3 Fuel cell studies

After the half-cell test, three representative catalysts were further evaluated as practical PGMfree cathodes in MEAs for fuel cell performance evaluation (**Fig. 7**). As expected, the corresponding MEA with the best performing 55%100@30 cathode exhibited an open-circuit voltage (OCV) up to 0.97 V and generated the most significant current density of 0.035 A cm<sup>2</sup> at 0.9 V<sub>iR-free</sub> and the highest power density of 0.75 W cm<sup>2</sup> (**Fig. 7c**) under 1.0 bar H<sub>2</sub>-O<sub>2</sub> conditions compared to other catalysts (**Fig. 7a** and **7e**). Additionally, the MEA yielded a current activity of 0.064 A cm<sup>2</sup> at 0.8 V<sub>iR-free</sub> and power density of 0.34 W cm<sup>2</sup> under H<sub>2</sub>-air at 1.0 bar (**Fig. 7d**), which are superior to other studied catalysts (**Fig. 7b, 7f**). More interestingly, when a low RH (60%) was applied (Fig. S12), the fuel cell performance of the 55%100@30 catalyst was inferior to that of the one at 100% likely due to insufficient proton conductivity. Overall, the best performing dual-size assembled Fe-N-C catalyst provides beneficial size diversity and porosity, which is favorable for ionomer dispersion and active site utilization. This work further emphasizes the significant role of hierarchical porosity in boosting MEA performance for Fe-N-C catalysts.



**Fig. 7.** H<sub>2</sub>-O<sub>2</sub> and H<sub>2</sub>-air fuel cell performance of the (a, b) 33%100@30 catalyst, (c, d) 55%100@30 catalyst and (e, f) 77%100@30 catalyst, respectively. Test conditions: Anode: 0.2 mg<sub>Pt</sub> cm<sup>2</sup> Pt/C; H<sub>2</sub> flow rate 200 sccm, 1.0 bar H<sub>2</sub> partial pressure; cathode: ca. 4.0 mg cm<sup>2</sup>, 200 sccm gas flow rate, 1.0 bar total partial pressure of gas flow; membrane: Nafion<sup>®</sup> 211; cell: 80°C, 100% RH, 5.0 cm<sup>2</sup> MEA electrode area.

### 4 Conclusion

In summary, we developed a new self-assembly strategy to design dual-size particle architecture morphology for the promising Fe-N-C catalysts. Ideally, the catalyst with small particles can expose more active sites at the surface, which can exhibit improved catalytic performance. However, the challenge is that small particles tend to aggregate during the synthesis process and long-term catalytic reaction. In this work, the small particles were nucleated and grew on the pre-synthesized large particles as a seed through a fine-control in size during the synthesis by using Fe-doped ZIF-8 as precursors in methanol solution. The unique catalyst design is effective to prevent the agglomeration of highly active small-sized catalysts. We have investigated the effect of various sizes' ratios in the precursor on the morphology and structure of the assembled catalyst (e.g., porosity, BET, nitrogen dopant, and carbon structure). The dual-sized catalyst exhibits a hierarchically porous structure with various pore types (micropores and meso/macropores) compared with the simple pore structure of single-size catalyst particles. Through precise tuning and optimizing the ratio of two sizes (100 and 30 nm), we prepared an atomically dispersed Fe-N-C catalyst after one-step carbonization, free of any Fe clusters or nanoparticles. This 3D superstructure avoided the agglomeration of particles, exposed more accessible active sites, enhanced the mass transfer, and facilitated the water management, thus maximizing the catalytic performances for the ORR.

The best performing catalyst with optimal dual-size and ratio of particles as well as thermal activation temperature showed encouraging ORR activity and stability in both acid electrolytes and MEAs. Importantly, the 55%100@30 catalyst demonstrated the highest EASA and larger capacitance than Fe-N-C catalysts with a single-size distribution, due to the hierarchical

porosity and prominent accessibility to the electrolyte. Therefore, likely due to the perfect size combination, abundant EASA, hierarchical porosity, and accessible active sites, the excellent ORR activity of the dual-sized Fe-N-C catalyst can be further transferred into MEAs with encouraging fuel cell performance. This work provided a novel approach to engineering 3D superstructure single metal site catalysts tailored through appropriately size-control and self-assembly for the ORR and other critical reactions.

#### **Declaration of interests**

The authors declare that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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