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Shape Fixing via Salt Recrystallization: A Morphology-**Controlled Approach to Convert Nano-structured Polymer to** Carbon Nanomaterial as a High Active Catalyst for Oxygen **Reduction Reaction**

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ABSTRACT: Herein, we report a "shape fixing via salt recrystallization" method to efficiently synthesize nitrogen-doped carbon material with a large number of active sites exposed to the three-phase zones, for use as an ORR catalyst. Self-assembled polyaniline with a 3D network structure was fixed and fully sealed inside NaCl via recrystallization of NaCl solution. During pyrolysis, the NaCl crystal functions as a fully sealed nanoreactor, which facilitates nitrogen incorporation and graphitization. The gasification in such a closed nanoreactor creates a large number of pores in the resultant samples. The 3D network structure, which is conducive to mass transport and high utilization of active sites, was found to have been accurately transferred to the final N-doped carbon materials, after dissolution of the NaCl. Use of the invented cathode catalyst in a proton exchange membrane fuel cell produces a peak power of 600 mWcm⁻², making this among the best non-precious metal catalysts for the ORR reported so far. Furthermore, Ndoped carbon materials with a nanotube or nanoshell morphology can be realized by the invented method.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are electrochemical power generators, with potential applications in vehicle propulsion. To reduce their cost and encourage widespread use, research has focused on replacing the expensive Pt-based electrocatalyst with a lower-cost alternative for catalvsis of the oxygen reduction reaction (ORR) on the cathode side of the cells.¹ Great efforts have been undertaken to produce non-precious metal catalysts (NPMCs) by pyrolyzing nitrogen-containing precursors on a carbon support material. However, the power density of these NPMC-based cathodes have been low compared with Pt-based cathodes, due to fewer active-sites and poor mass-transport properties.³

One widely used strategy for the introduction of adequate active-sites is to increase the surface area of the NPMCs by using hard or soft template methods.⁴ However, the template methods frequently fail in increasing the number of ORR active-sites because the templates

hinder contact between the nitro-

gen-containing precursors and

metals, which are needed to in-

duce or catalyze the transfor-

mation of nitrogen-containing

precursors into materials that can

catalyze the ORR. To increase

precursors-metals contact in tem-

plate methods, an advanced template strategy has been developed

by using a low volatility precursor

to form more N-containing active

centers at the precursor's molten

state.⁵ The fuel cell with this tem-

of 420 mW cm⁻². Recently, by pyrolyzing well-defined metalligand coordinated metal-organic frameworks (MOFs) or porous organic polymer (POP), NPMCs were produced with surface areas of up to 903 m^2g^{-1} and an initial performance of close to the level reached by platinum-based catalysts.⁶ In addition to the number of active sites, the exposure of the active sites to the interface, where electrons, protons, oxygen and product water can flow in or exit out, is particularly important. Otherwise, the active sites cannot be utilized by the ORR.⁷ Therefore, it would be better if the NPMCs were porous enough or had an enough space to accommodate the linkage of various species-transport channels to their active sites: voids for O₂ and water, a polymer chain for protons, and a carbon framework for electrons. At this point, the traditional direct pyrolysis of the mixture of nitrogen-containing compounds, carbon, and transition metal precursors frequently fails in producing the necessary porous structure, leading to relatively poor transport properties and limited active sites that are ac-

plate synthesized catalyst catalyzed cathode produced a power

Scheme 1. Schematic of the "Shape Fixing via Salt Recrystallization" method.



cessible for the ORR.^{3, 8} Recently, we reported a spaceconfinement-induced method to selectively synthesize planar pyridinic and pyrrolic N -doped graphene.⁹ It exhibited a high yield of planar pyridinic and pyrrolic N-doped graphene and acceptable ORR catalysis. The density of the exposed sites activated by planar pyridinic and pyrrolic N, however, is still not high enough, as the exposed active sites only appear at the fringe of a large sheet of graphene.

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Herein, we report a "shape fixing via salt recrystallization" method to efficiently synthesize N-doped carbon material, with many active sites exposed to the three-phase zones, as a catalyst for the ORR. The procedure is shown in Scheme 1. A 3D PANI network was fabricated via a self-assembly process. (Unless otherwise stated, PANI refers to the 3D PANI network.) After adsorption of FeCl₃, an 80 °C, super-saturated NaCl solution was poured into a beaker containing PANI. The water was then evaporated so that the NaCl recrystallized around the PANI on the bottom of the beaker. This cycle of the addition of NaCl solution, water evaporation and NaCl recrystallization was repeated until the whole PANI was fully buried so that it appeared to be tightly sealed inside NaCl crystal. Thus, the original shape of the 3D PANI network would be fixed by NaCl crystal. After the NaCl crystal-sealed PANI was dehydrated at 120 °C, the temperature was raised to 900 °C at a heating rate of 6 K min⁻¹, held at 900 °C for 3 hours under flowing N₂, and finally cooled down to room temperature. The NaCl crystal and iron species were washed off in a hot 0.5 M H₂SO₄ solution. The resultant sample is referred to as CPANI-Fe-NaCl. For comparison, samples obtained from pyrolysis using NaCl crystal only, and those without either FeCl₃ or NaCl, were termed as CPANI-NaCl and CPANI, respectively. In this process, the NaCl crystal serves as a fully closed nanoreactor, which facilitates the N incorporation and graphitization. Moreover, when the temperature reaches 800.9 °C, i.e., the melting temperature of NaCl, the NaCl molten salt can facilitate the formation of active-sites. The original 3D structure of the PANI is well preserved and various pores, from micro- to meso- to macro-sized, are formed in large quantities in the high temperature pyrolysis, due to the gasification of various raw materials in a closed space. Electrochemical evaluations showed that the invented catalyst exhibits excellent conductivity, high ORR activity, and good stability in acidic electrolytes. In the present work the half-wave potential of the ORR on an electrode made of the invented catalyst was found to lag behind the state-of-the-art carbon-supported platinum by only 58 mV in acid electrolyte. The PEMFC, prepared with the invented catalyst as the cathode, achieved a maximum power density of 600 mW cm⁻². It is demonstrated that Ndoped carbon materials with 3D network morphology, nanotubes and nanoshells, can be realized by the "shape fixing via salt recrystallization" method. To our knowledge, this is the first report of such a method to efficiently construct carbon nanomaterials for catalysis of the ORR with controlled porous structure, active sits and morphology.

EXPERIMENTAL SECTION

Synthesis of PANI 3D Networks

Aniline monomer was distilled under reduced pressure before use. The PANI 3D network was synthesized by a slow chemical oxidation and self-assembly polymerization. In the typical synthesis, 3.728 g of aniline and 0.554 g of salicylic acid (SA) were dissolved in 200 ml deionized water with magnetic stirring at room temperature for 24 h. The stirring was then stopped. After 10 min, a 50 mL aqueous solution of 9.294 g ammonium persulfate (APS) was added at an addition rate of 0.8 ml/min, and the reaction was left for 48 h. The resulting PANI was washed with water, methanol, and ether several times. Finally, the product was dried under vacuum at room temperature for 24 h.

Synthesis of PANI Nanotubes and PANI Nanoshells

The PANI Nanotubes and PANI Nanoshells were synthesized by a severe chemical oxidation and self-assembly polymerization, similar to that reported previously ¹⁰. Aniline (3.725 g) and SA (1.379 g for nanotubes, 3.408 g for nanoshells) were dissolved in deionized water (200 ml). APS (9.320 g) was also dissolved in deionized water (20 ml) in a separate vial. The two solutions were vigorously mixed at room temperature. A brown precipitate appeared immediately, and the subsequent reaction was carried out at room temperature without any disturbance. After 7days, the precipitate was filtered and purified using a Buchner funnel with a water aspirator to wash the product several times with water, methanol, and ether. Finally, the product was dried in vacuum at room temperature for 24 h.

Preparation of CPANI-Fe-NaCl by the "Saltcrystallization" method

Typically, 0.6 g of PANI and 0.6 g of FeCl₃.6H₂O were suspended in 10 ml deionized water, with magnetic stirring, at room temperature, for 12 h. After the adsorption of FeCl₃, 15 ml supersaturated NaCl solution was added to the suspension, and magnetic stirring was continued for 2 h. The suspension was raised to 60 °C to evaporate off water. During the evaporation, an 80°C over-saturated NaCl solution was continually and slowly added into the suspension, until the NaCl crystallized, encasing the PANI. To minimize the creation of air pockets during evaporation, the sample was repeatedly transferred to a vacuum chamber and held at a pressure of -0.1 MPa at 60°C for 1 hour after adding a small amount of 80°C supersaturated NaCl solution. The composite was then dried under vacuum at 60 °C for 24 h. The composite was then heated to 120 °C, after which the temperature was raised to 900°C at a heating rate of 6 K min⁻¹ and held at 900°C for 3 hours under flowing N₂. The NaCl crystal and iron species in the sample were finally washed off in 0.5 M H₂SO₄ solution at 80 °C.

Synthesis of CPANI and CPANI-NaCl

The CPANI-NaCl was prepared under conditions similar to those used for CPANI-Fe-NaCl. For CPANI-NaCl, Fe salt was not used, and NaCl was washed with room temperature water. For CPANI, PANI was directly pyrolyzed, without applying the NaCl crystallization procedure.

RESULTS AND DISCUSSION

The "shape fixing via salt recrystallization" procedure was monitored by nitrogen adsorption-desorption at 77 K. As shown in Figure 1, the adsorption hysteresis loop for PANI suggests a mesoporous structure, with a pore size distribution centered at 50.0 nm (via the Barrett-Joyner-Halenda method). After being encased in NaCl crystal, the PANI display a very small area by Brunauer-Emmett-Teller (BET) theory (0.7 m² g⁻¹) compared to the original value (30.7 m² g⁻¹). The pore volumes of the NaCl-buried PANI approach zero for all pore ra1 2

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59 60 dius, indicating that the PANI were fully encapsulated by the NaCl crystal. After pyrolysis at 900°C and removal of the NaCl crystal in a hot 0.5 M H_2SO_4 solution, the BET surface area of the final CPANI-Fe-NaCl increased to 265.7 m² g⁻¹. The BET surface increase is mainly due to the formation of micropores after pyrolysis. As shown in Figure 1a, the pore volumes for those radii ranging from 100 to 2.5 nm are unchanged by the transition from PANI to CPANI-Fe-NaCl, while pore volumes of less than 2.5 nm experience a substantial change. These results indicate that the 3D structure was well preserved and vast numbers of micropores were formed in the "shape fixing via salt recrystallization" method.



Figure 1. (a) Pore size distribution for PANI, PANI in NaCl, and CPANI-Fe-NaCl, assessed by BJH. (b) Nitrogen sorption isotherms for PANI, PANI in NaCl, and CPANI-Fe-NaCl.

Figure 2a show that the PANI 3D networks were comprised of PANI nanofibers with a diameter of ~100 nm. With the "shape fixing via salt recrystallization" method, as shown in Figure 2b, the PANI 3D network morphologies were faithfully transferred to the 3D carbon networks (see also Figure S1a-b). In contrast, the TEM and SEM images of CPANI synthesized by traditional pyrolysis reveal a large-scale, spherical or lumptype morphology (see Figure S2a and Figure S2b). Only one tiny difference can be observed between the morphology of the PANI 3D network and that of the carbon 3D network; that is, there are raised knots on the surface of the PANI but concavities on the CPANI-Fe-NaCl. This further demonstrated that a carbon nanotube with a diameter of~200 nm, length of~600 nm and thickness of ~50 nm (Figure S3a-b), as well as a carbon nanoshell, can be synthesized via the proposed method; all resultant samples accurately inherit their precursors' original structures (Figure 2c, 2d, 2e, and 2f; see also Figure S1c-f). These excellent conversions demonstrate the high efficiency of the "shape fixing via salt recrystallization" method in controlling morphology and pore structure. To investigate the role of Fe during the synthesis, we synthesized CPANI-Fe by pyrolyzing PANI absorbed FeCl₃. Our results show that Fe ions affect the graphitic structure during the synthesis but they cannot preserve the original sharp of PANI. As shown in Figure S4a and b, the original nano-fiber morphology of PANI transform into a lump-type and graphitic shellslike morphology. The graphitic shells-like morphology doesn't appear in the case of PANI pyrolysis without Fe participation, i.e., CPANI. The graphitic shells appearing in CPANI-Fe sample tells that the Fe species catalytically transform PANI into graphitic carbon. In contrast, the CPANI-NaCl preserves network morphology after pyrolysis (Figure S4c) indicating the original sharp of PANI can be preserved by NaCl alone.

High-resolution transmission electron microscopy (HRTEM), as shown in Figure 3, demonstrated the amorphous

carbon structure and lack of lattice fringe of the CPANI. Conversely, the CPANI-NaCl shows relatively clear graphitic fringes, suggesting an improved graphitic structure. This result is also supported by the Raman spectra (see Figure S5), which show the relative higher intensity ratio of G-band to D-band (I_G/I_D) for the CPANI-NaCl, implying that the graphitization degree of the CPANI-NaCl is higher than that of the CPANI. This is attributed to the effect of molten salts that promotes the degree of graphitization in the heat treatment process, which is consistent with the previous finding¹¹. The clearest lattice fringe and the highest I_G/I_D , corresponding to CPANI-Fe-NaCl (Figure 3c, 3f, and S5), indicate that the degree of graphitic structure can be further improved with the introduction of an Fe element.



Figure 2. TEM images of as-prepared 3D PANI network (a), PANI nanotubes (c), PANI nanoshell (e), and their corresponding carbonized products: CPANI-3D-Fe-NaCl (b), CPANI-NT-Fe-NaCl (d), and CPANI-NS-Fe-NaCl (f).



Figure 3. High-magnification TEM images showing the edges of CPANI (a, d), CPANI-NaCl (b, e) and CPANI-Fe-NaCl (c, f).

TGA/DTA at a heating rate of 6 K min⁻¹ in N₂ atmosphere was used to gauge how readily the precursors transform to carbon materials via the "shape fixing via salt recrystallization" method. As shown in Figure 4, PANI-NaCl exhibits excellent thermal stability, with weight loss starting at 443.8 °C. The PANI, however, shows poor thermal stability. Its decomposition started at temperatures as low as 199.8 °C. At 900 °C, only 4.1 % of the PANI residues remained, while 74.3 % and 67.1 % of the PANI-NaCl and PANI-Fe-NaCl residues re-10 mained, respectively. In addition, no obvious endothermic or 11 exothermic processes were found in the PANI. Because of the 12 uneven degree of the PANI polymerization, its decomposition 13 (exothermic), dehydrogenation (endothermic) and carboniza-14 tion (endothermic) may occur randomly and thus not occur at 15 a certain temperature range. This result indicates a random 16 transformation of PANI to carbon through direct pyrolysis. For PANI-NaCl, an endothermic process with weight loss was 17 found at 520.7 °C, followed by the occurrence of another en-18 dothermic process without weight loss at 577.1 °C. The two 19 endothermic processes are attributed to the dehydrogenation of 20 PANI at the lower temperature and the graphitization at the 21 higher. With the addition of FeCl₃, only one exothermic pro-22 cess at 337.6 °C exhibited weight loss. One possible explana-23 tion is the catalytic effect of iron species during pyrolysis. The 24 TGA/DTA plot of NaCl shows only one endothermic process 25 at 800.9 °C corresponding to the melting of NaCl crystal (Fig-26 ure S6). With the NaCl crystal melting at 800.9 °C, the graphi-27 tization of the pyrolyzed PANI was conducted in NaCl molten 28 salts. It should be noted that the difference in the specific 29 weights of NaCl molten salts (1.5 g cm⁻³) and pyrolyzed PANI 30 $(1.8 \sim 2.1 \text{ g cm}^{-3})$ is too small to overcome the high viscosity 31 of the NaCl molten salt, thereby avoiding phase separation. 32 Therefore, the graphitization of the pyrolyzed PNAI takes place inside the NaCl molten salts. As a matter of fact, as the 33 34 samples cooled down to room temperature, the final carbonbased products were still sealed inside the NaCl crystal, just as 35 shown in Scheme 1. The obvious weight loss after 800.9 °C in 36 the TGA curve of Figure 4 comes from the vaporization of 37 NaCl molten salts. As a result, the dehydrogenation, nitrogen 38 doping and graphitization of PANI, as well as the gasification 39 of various additives in the present method, are always con-40 ducted in a sealed system. This will, at most, prevent weight 41 loss and produce large quantities of pores in the final product, 42 due to the trapped gas. As mentioned above, the invented 43 method is conducive to increased active sites, induced by pla-44 nar pyridinic N and pyrrolic N. The substance interactions and 45 phase transitions may play important roles during the pyrolysis. 46 The polyaniline is in a doped form. Its backbone carries posi-47 tive charge.¹² Thus, during the absorption of FeCl₃, Cl⁻ ions will be preferentially adsorbed on the positive-charged PANI, 48 and then Fe³⁺ ions as shown in Figure 4. The outside of PANI-49 FeCl₃ was first covered by NaCl solution and then NaCl solids 50 with the recrystallization of NaCl. The thick NaCl solid layer 51 prevents the PANI from decomposition at a relatively lower 52 temperature. With decomposition temperature increasing, the 53 dedoping and dehydrogenation of PANI may finish before 54 PANI structure collapse. Nitrogen atoms with a lone pair elec-55 tron expose to the outside with the dedoping and dehydrogena-56 tion of PANI. The exposed N reacts with Fe³⁺ ions, and forms 57 FeNx/C complex. With the NaCl crystal melting at 800.9 °C, 58 the excess Fe species are dissolved in molten NaCl and flow 59

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away from the surface. This will be beneficial for the active sites because too much Fe species would destroy them at high temperature.13



Figure 4. TGA-DTA plot of PANI, PANI-NaCl, and PANI-Fe-NaCl; and schematic of substance interactions during the synthesis.

X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate the content and chemical state of the nitrogen on the surface of the prepared catalysts. The existence of C-N and C-C (graphite-type) bonds in the matrix confirms the N-doped carbon structure of the prepared catalysts (see Figure S7). The relative N/C ratio was only 3.04 % in CPANI but was 3.52 % and 5.85 % in CPANI-NaCl and CPANI-Fe-NaCl, respectively; indicating that nitrogen loss during pyrolysis at high temperatures was alleviated in the "shape fixing via salt recrystallization" method. The high resolution N1 s spectra for all catalysts were fitted with five different signals, having binding energies of 398.6, 399.2, 400.3, 401.4, and ~403 eV, corresponding to pyridinic N, nitrile N, pyrrolic N, quaternary N, and oxidized pyridinic N, respectively (Figure S8). Pyridinic N (most likely including Me-N) and pyrrolic N are generally believed to activate neighboring carbon atoms for catalysis of the ORR.^{9, 14} As shown in Figure S8, the content of

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pyridinic and pyrrolic N in the CPANI-NaCl and the CPANI-Fe-NaCl is higher than that in CPANI, indicating that the "shape fixing via salt recrystallization" method is more suitable for facilitating more active-site formation. Besides, 11 % of the N species in CPANI-NaCl are nitrile N, but no nitrile N is detected in CPANI-Fe-NaCl, indicating that the addition of iron species accelerates N incorporation into carbon-ring. The CPANI that have the highest content of quaternary N show the poorest activity for catalysis of the ORR in acidic medium. Figure S9 show that Fe presents in the CPANI-Fe-NaCl as Fe^{3+} (3.18 atm%), which may exist as a stable complex form rather than simple inorganic ions because the CPANI-Fe-NaCl was treated in a hot H₂SO₄ solution. Na and Cl were not detected in the CPANI-Fe-NaCl after hot H₂SO₄ solution washing. It means that NaCl has been washed off by a hot solution. For CPANI-NaCl, Na and Cl were detected as form of NaCl. This is because of the residual NaCl in sample after room temperature water washing.

Electrical conductivity is a prominent concern for materials used in electrochemical applications. Electrochemical impedance spectroscopy (EIS) at high frequency (see the Supporting Information for details) revealed that the electrical resistance of the CAPNI-NaCl and the CPANI-Fe-NaCl are on the same order as that of commercial Vulcan XC-72R carbon (Figure S10). In other words, the electrical conductivity of the CAPNI-NaCl and CPANI-Fe-NaCl is as good as that of commercial Vulcan XC-72R carbon. Conversely, CPANI and PANI demonstrate very poor electrical conductivity, as illustrated in Figure S10. These physical analysis data combined with TEM results demonstrate that NaCl preserves the original morphology of precursors and promote the degree of graphitization; while iron species enhance both of graphitization and nitrogen incorporation during the synthesis.

The cyclic voltammograms (CVs) of CPANI and CPANI-NaCl in N₂-saturated H₂SO₄ solution are virtually featureless, while the CV of CPANI-Fe-NaCl reveals a pair of welldeveloped redox peaks at~0.63 V vs the reversible hydrogen electrode (RHE) (see in Figure S11). The peaks are expected for a reversible process involving surface Fe species (Fe³⁺ and Fe^{2+}). The Fe species are very stable. They cannot be removed by either acidic solution treatment at 80 °C or by long-term electrochemical cycling in acidic solution (see Figure S14). The double layer capacities of the CPANI-Fe-NaCl and the CPANI-NaCl are similar to each other, but they are twice larger than that of CPANI. However, active sites of a metal catalyst can but active sites of a nitrogen-doped carbon catalyst cannot be checked by the CVs. The CVs of the electrode made of nitrogen-doped carbon catalysts only tell the capacity of its electric double layer, which indicates the solid/electrolyte interface of the electrode but does nothing with the activity.

The activity of the catalysts was evaluated using a rotating ring–disk electrode (RRDE). All of the RRDE experiments were performed in 0.1 m HClO₄. The polarization curves and the Tafel slops for the catalysts are shown in Figure 5a and Figure S12, respectively. The CPANI-Fe-NaCl catalyst exhibited the highest activity, and the CPANI-NaCl metal-free catalyst also showed a good activity for the ORR. The ORR half-wave potentials measured on a CPANI-Fe-NaCl-catalyzed electrode and a CPANI-NaCl-catalyzed electrode were only 58 mV and 102 mV behind that on a state-of-the-art carbon-

supported platinum catalyst (Johnson Matthey, UK, 40 wt %, denoted as JM Pt/C) at a Pt loading of 50 μ gPt cm⁻². These results are comparable with those of the best NPMCs reported to date. ^{6b, 9, 15, 16} The H_2O_2 yield was as low as 1.5 % on a CPANI-Fe-NaCl-catalyzed electrode and 6.8% for a CPANI-NaCl-catalyzed electrode at the relative positive potential of 0.8 V (vs RHE). The H₂O₂ yield decreased with a negativeshifting potential. At 0.5 V (vs RHE), it was only 0.28% on the CPANI-Fe-NaCl-catalyzed electrode and was 0.85% on the CPANI-NaCl-catalyzed electrode, which is comparable with that on the JM Pt/C electrode (0.30%). In any respect, CPANI exhibited a poor activity for the ORR. The electron transfer number for the ORR on the CPANI-Fe-NaCl-catalyzed electrode was estimated according to the Koutecky-Levich plot. As shown in Figure S13, the electron transfer number is 3.9 \pm 0.1 on the CPANI-Fe-NaCl-catalyzed electrode in the potential range of 0.6-0.3 V, indicating a four-electron pathway for catalysis of the ORR and explaining the low H₂O₂ yield on the electrodes made of the prepared samples. The stability of the CPANI-Fe-NaCl- and CPANI-NaCl-catalyzed electrodes, together with the JM-Pt/C-catalyzed electrode, was assessed by cycling the electrodes in a potential range of 0-1.2 V in N_2 saturated 0.5 M H₂SO₄ (see Figure S14). No noticeable change in catalytic activity of the ORR was observed on the CPANI-Fe-NaCl-catalyzed electrode, but the ORR half-wave potentials on the electrodes catalyzed by CPANI-NaCl and by JM Pt/C were negatively shifted by 27 mV and by 73 mV, respectively, after CV cycling, indicating the excellent stability of CPANI-Fe-NaCl but relatively poor stability of CPANI-NaCl and JM-Pt/C. The relatively poor stability of CPANI-NaCl is attributed to the existence of large numbers of nitrile species in the CPANI-NaCl, which may accelerate destruction of the catalyst under harsh conditions.

Figure 5. (a) Steady-state plots of ORR polarization (bottom) and H_2O_2 yield (top) for different catalysts in O_2 -saturated 0.1 m HCIO₄. The loading is 50 µgPt cm⁻² for Pt/C (40%) and is 0.6 mg cm⁻² for non-Pt catalyst. (b) Polarization curves and corresponding power densities of membrane electrode assemblies fabricated with the CPANI-Fe-NaCl, CPANI-NaCl and CPANI cathode catalysts. (c) Schematic of active sites on edges and in pores.

To investigate whether the remained NaCl in CPANI-NaCl involve the ORR, the ORR activity of CPANI-NaCl was evaluated after repeatedly washing with hot water until no Cl⁻ was detected. As shown in Figure S15, the activities show unchanged after removal of NaCl, indicating that NaCl do not involve the catalysis of the ORR. As mentioned above, Fe species are hardly removed from the CPANI-Fe-NaCl, even by being treated in a hot acidic solution or by being long-term cycled in acidic solution (Figure S14a). It suggests that Fe elements may exist in a very stable complex rather than simple inorganic ions, otherwise, Fe would be leached off from the catalysts. According to recent studies relied on Mössbauer spectroscopy and X-ray absorption spectroscopy about Fe state after pyrolysis of the mixture of PANI and iron-

containing species, Fe elements exist in FeNx/C complex, of which FeN_4/C and N-FeN₂₊₂/C are highly active for the ORR in acid medium.¹⁷ In contrast, some argued that Fe only promotes key properties of catalyst, such as electronic conductivity, morphology, and nitrogen-doping level, but it does not directly participate in active site.¹⁸ We made a comparative investigation between Fe-free and Fe-doping catalyst, that is, CPANI-NaCl and CPANI-Fe-NaCl. Our results show that their electronic conductivity, morphology, and nitrogendoping level are quite similar to each other but their ORR activities are different. As shown in Figure 5a, the electrode made of the CPANI-NaCl catalysts (Fe-free) shows an excellent ORR activity, indicating the nitrogen-doped carbon without Fe also catalyzes the ORR. This is ascribed to numerous inner pores formed in the present method. The sites activated by planar pyridinic and pyrrolic N atoms with sp² hybrid orbitals, which appear at the fringes of a graphene sheet and the fringes of graphene inner pores, are active for the ORR. The present method makes such active sites increase obviously, for instance, 68% for the given graphene sheet as shown in Figure 5c. On the other hand, the electrode made of the CPANI-Fe-NaCl catalysts (Fe-doping) shows much better ORR activity. The catalytic role of Fe complex for the ORR is obvious, which is in accordance with previous studies based on Möss-bauer spectroscopy.^{15a, 19} According to Frédéric Jaouen's research result, the Fe/N/C-catalyst contains two types of FeN_x sites assigned to micropore-hosted sites in edges and graphene-defect-hosted sites in inner plane, while the later are more stable than the former one during the carbon corrosion.¹⁹ The present method might benefit more FeN_x sites formation owing to the existence of numerous inner pores, as shown in Figure S19. At this stage, we cannot exclude another role of Fe species in bettering graphitic structure, which is well known to be conducive for the catalysis of the ORR as reported before.9, 15, 19

The performance of the single cell with these catalyst-based cathodes and Pt/C anodes is shown in Figure 5b. An opencircuit voltage (OCV) of 0.85 V was observed and the current density reached as high as 2.1 A cm⁻² at 0.28 V. A higher OCV of 0.9 V was observed when the MEA was prepared using Nafion 117 to substitute Nafion 112 to reduce the crossover current (see in Figure S16). A maximum power output of 600 mW cm⁻² was achieved with the CPANI-Fe-NaClcatalyzed cathode, with 300 mW cm⁻² for the metal-free, CPANI-NaCl-catalyzed cathode. In contrast, the maximum power output is only 180 mW cm⁻² for the CPANI-catalyzed cathode, which is consistence with previous report about the single cell performance of a NC-catalyzed cathode obtained from direct pyrolyzed PANI.¹⁶ The CPANI-Fe catalyst produced without NaCl, also show a poor performance with the maximum power output of only 284 mW cm⁻² (Figure S17). It tells that NaCl participation is very important in synthesis of high active nitrogen-doped carbon catalysts.

In the present work, the loading of nitrogen-doped carbon catalysts in the catalyst layer is much higher than that of Pt catalysts, 4.0 mg cm⁻² vs 0.1 or 0.3 mg cm⁻². Thus the ohmic voltage loss in the catalyst layer is not negligible owing to the thick catalyst layer but negligible in the case of Pt/C catalysts owing to its ultrathin catalyst layer. The ohmic resistance would affect the I-V slope. As shown in Figure 5b, the I-V slopes of the three types of catalysts are different from each



60

other. The I-V slopes indicate the electric resistance of the three types of cathodes, that is, $R_{CPANI-Fe-NaCl} \approx R_{CPANI-NaCl} \ll R_{CPANI}$. This is consistence with the EIS result illustrated in Figure S10.

An internal comparison has been made with the commercial Pt/C catalyst. As shown Figure S17, with the JM Pt/Ccatalyzed cathodes, the maximum power output is 450 mW cm^{-2} at Pt loading of 0.1 mg cm⁻² and is 820 mW cm⁻² at 0.3 mg Pt cm⁻². The CPANI-Fe-NaCl with the maximum power output of 600 mW cm⁻² show a comparable performance to that of the commercial Pt/C. In addition, the single cell performances of the different morphology CPANI-Fe-NaCl catalyzed cathodes are evaluated as shown in Figure S18. The maximum power output is 530 mW cm⁻² with the nanotube CPANI-Fe-NaCl-catalyzed cathode, and is 490 mW cm⁻² with the nanoshell CPANI-Fe-NaCl-catalyzed cathode. The cell performances observed in these tests are among the best reported world-wide, to date.⁶ In contrast to efforts that focus on improving the surface area, the best catalyst found in the present work has a BET surface area of only 265.7 m² g⁻¹, but exhibits excellent cell performance despite this. This is attributed to the unique advantages of the "shape fixing via salt recrystallization" method, by which a high microporosity is achieved, with a high density of ORR active sites located along the efficient, mass transport pathway (composed of meso- and macropores), leading to a high utilization of active sites.

CONCLUSION

In summary, we have demonstrated a "shape fixing via salt recrystallization" method to efficiently synthesize N-doped carbon nanomaterials with a high density of active sites, as an ORR catalyst. In this method, the NaCl crystal functions as a fully sealed nanoreactor, facilitating the N incorporation and graphitization. The gas from gasification in such a closed nanoreactor produces a large quantity of pores in resultant samples. As for an Fe-free catalyst, this method makes it possible for the active sites (activated by planar pyridinic and pyrrolic N atoms with sp^2 hybrid orbitals, which only appear at the outside fringe of a graphene sheet) to appear in large quantities on the edges of numerous pores, as shown in Figure 5c. As for an Fe-doping catalyst, the present method benefits formation of more FeN_x sites in inner pores and graphitic structure. A favorable catalyst structure leads to the availability of efficient mass transport pathways and a high utilization of the active sites. It results in an excellent ORR activity with a halfwave potential only 58 mV behind that of Pt/C in an acidic medium. The PEMFC with the CPANI-Fe-NaCl-catalyzed cathode outputs a peak power of 600 mW cm⁻², which is among the best for non-precious metal catalysts reported so far for the ORR. Additionally, no other method is comparable to this invention, in terms of its high yield per batch of N-doped carbon catalysts. The "shape fixing via salt recrystallization" method represents a powerful approach for the preparation of high-performance carbon nanostructures by confined pyrolysis of nanopolymers and, more importantly, provides insight into the design of advanced PEMFC cathode catalysts.

Supporting Information

Experimental details and more characterization and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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