

The Semi-Closed Molten Salt-Assisted One-Step Synthesis of N-P-Fe Tridoped Porous Carbon Nanotubes for an Efficient Oxygen Reduction Reaction

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Abstract: Transition metal and heteroatom co-doped carbon nanomaterials (TM-H-C) are considered to be the most promising candidates to replace the expensive platinum-based catalysts for oxygen reduction reactions (ORR). Herein, we report a semi-closed molten salt-assisted one-step strategy for fabricating N-P-Fe-tridoped porous carbon nanotube (CNT) catalysts by using the evaporation of ZnCl_2 and the catalysis of iron ions to control the heteroatoms doping process and CNT formation. The resultant densely packed porous CNT structure imparts final catalysts with an enhanced mass transfer ability for electron and ORR-involved species, ensuring a high performance in catalyzing the ORR. Significantly, the optimal catalysts show a half-wave potential of 0.89 V (vs. RHE), which is better than commercial platinum-based catalysts and most reported TM-H-C ORR catalysts. Impressively, when applied to a primary inc-oxygen (Zn-O_2) battery, the synthesized catalyst comprehensively outperforms the state-of-the-art platinum-based catalyst in both its maximum power density and specific capacity.

Keywords: fuel cells; oxygen reduction reaction; non-noble metal catalysts; carbon nanotube



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1. Introduction

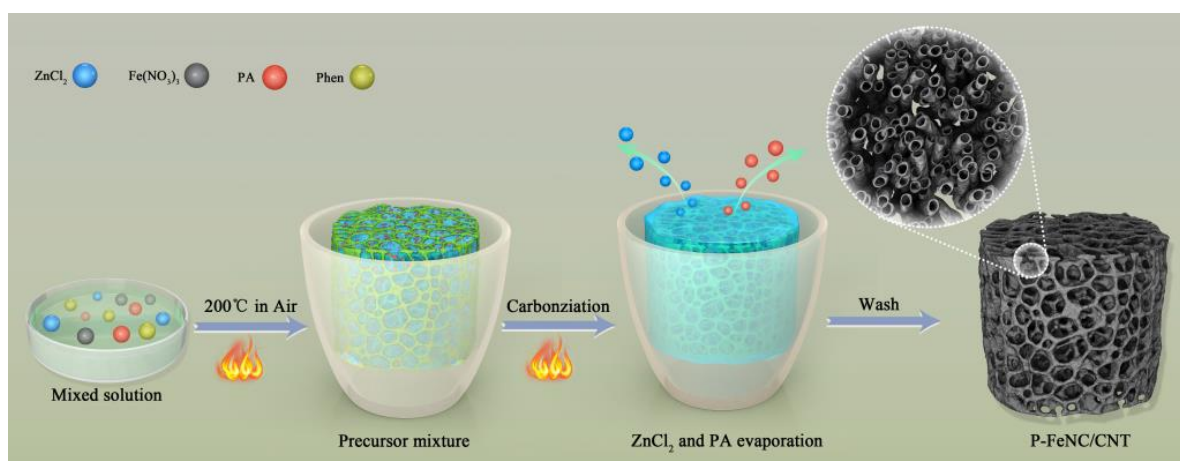
As clean and pollution-free power generation devices with a high energy conversion efficiency, fuel cells and metal–air batteries are of great significance for solving environmental pollution and energy problems [1–12]. However, the cathode ORR catalyst is highly dependent on the precious metal catalyst represented by platinum, which seriously restricts its large-scale commercial applications [13,14].

Transition metals (e.g., Fe, Co, and Ni) and heteroatoms (e.g., B, N, S, and P) co-doped carbon catalysts are regarded as very promising non-precious-metal-based catalysts (NPMCs) and electrocatalysts for the ORR [15–22], where transition metal and heteroatoms can change the charge distribution and introduce abundant active sites, thus enhancing the adsorption and reduction of oxygen. In addition to their doping properties, a large surface area, well-designed porosity, and excellent electrical conductivity are also important factors for improving the activity of these carbon-based catalysts.

Among the many NPMCs, heteroatom-doped CNTs have excellent electron conduction and matter transport capabilities [23]; hence, they are often used as catalysts for efficient oxygen reduction reactions. However, their low specific surface areas and complex preparation methods still limit their wide application. Recently, the template method has been regarded as an effective approach for fabricating efficient heteroatom-doped CNT catalysts, benefitted by its extendibility and ability to adjust aperture characteristics. CNTs with a porous structure and heteroatoms can be obtained by direct high temperatures to carbonize the mixture of carbon/heteroatom precursors with additive templates (e.g., silica and block copolymers) [24–26]. However, due to the weak wrapping property between the

CNT/templates and heteroatom precursors, the nano-sized precursors are easily aggregated, resulting in a limited specific surface area and unavailable active sites, leading to a poor catalytic performance. Furthermore, such a template-assisted pathway invariably needs complex processes to synthesize and remove templates, during which, it is easy to introduce toxic substances and poison the catalysts. Therefore, it is highly desired that a simple method for synthesizing heteroatomic-doped CNT catalysts with excellent doping properties and porous structures for oxygen reduction electrocatalysis is developed.

Herein, N-P-Fe-tridoped CNT catalysts with a large surface area, considerable porosity, and heteroatomic doping characteristics were fabricated through an ingenious semi-closed molten salt-assisted one-step strategy. As shown in Scheme 1, the precursor mixture was adequately coated with excess ZnCl_2 through a 200°C low-temperature pre-carbonization. In the subsequent high-temperature carbonization process, the precursor could be induced to form a porous CNT structure. These porous CNT structures not only greatly increased the specific surface area of the catalyst and enabled the active sites to be fully exposed to the three interfaces, but also provided fast channels for electron conduction and material transport. Benefitting from its well-designed porous CNT structure and excellent doping properties, the N-P-Fe-tridoped catalyst exhibited superior oxygen reduction catalytic activity and stability compared to commercial Pt/C, making it a strong contender for applications in Zn- O_2 battery and fuel cells.



Scheme 1. Schematic illustration of the synthetic procedure for P-FeNC/CNT catalyst.

2. Results and Discussion

2.1. Morphology Analysis

The formation of porous carbon nanotubes induced by ZnCl_2 and Fe^{3+} was analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The final catalyst fabricated by carbonizing phen and phytic acid (PA) precursors with both ZnCl_2 and FeCl_3 was named as P-FeNC/CNT. The catalysts with only carbon precursors and ZnCl_2 or FeCl_3 were defined as P-NC and P-FeNC. Figure 1a shows the SEM image of the P-FeNC/CNT catalyst, which indicates that the P-FeNC/CNT is a densely arranged, open-ended CNT structure with a diameter of approximately 300 nm. During the reaction, these carbon nanotubes (CNTs) can provide a fast path for electrons, increasing the rate of the electron conduction inside the catalyst. The open structure allows for fast mass transfer channels both inside and outside of the CNTs for the ORR. In contrast, the P-FeNC catalysts without ZnCl_2 (Figure 1b) were heavily sintered and had a lumpy structure; the P-NC catalysts without the addition of FeCl_3 (Figure 1c) showed a stacked lamellar structure. This contrast illustrates that the formation of carbon nanotubes can only be induced by the combined effect of Fe and ZnCl_2 . During the high-temperature carbonization process, the molten ZnCl_2 will form a semi-closed nanoreactor and the precursor can be induced to form porous CNTs under the combined effect of iron catalysis and the volatilization of ZnCl_2 .

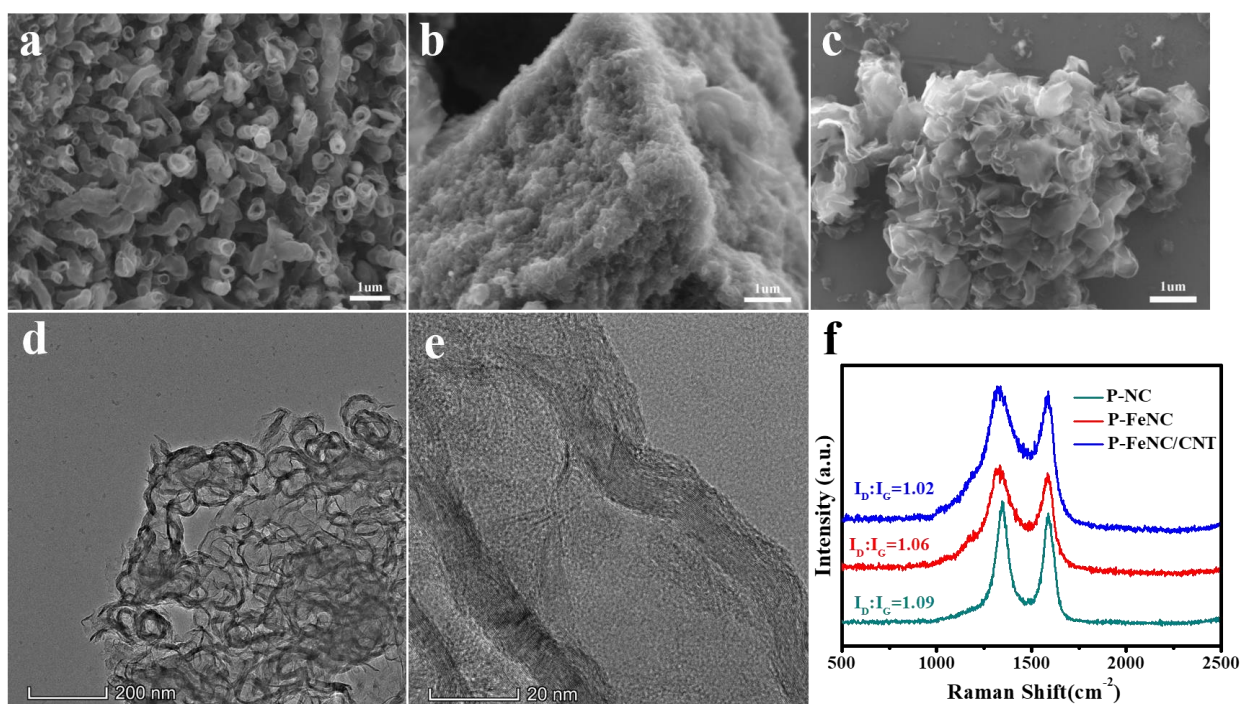


Figure 1. SEM images of (a) P-FeNC/CNT, (b) P-FeNC, and (c) P-NC catalysts. (d) TEM image and (e) HRTEM image of P-FeNC/CNT. (f) Raman spectra of P-FeNC/CNT, P-NC, and P-FeNC catalysts.

The TEM image (Figure 1d) shows that P-FeNC/CNT has a cross-linked porous CNT structure and the high-resolution TEM (HRTEM) image (Figure 1e) reveals that CNT walls have a highly crystalline graphite structure, again indicating its excellent mass transport properties and electrical conductivity. The Raman spectroscopy analysis (Figure 1f) displays that the D-band (1327 cm^{-1}) and G-band (1579 cm^{-1}) ratios (ID:IG) of P-FeNC/CNT and P-FeNC are 1.02 and 1.06, respectively, which are smaller than that of P-NC at 1.09, indicating that iron doping can not only catalyze the formation of CNT structures, but also enhance the degree of the graphitization of catalysts. The X-ray diffraction (XRD) pattern (Figure S1) also confirms this conclusion. Compared to P-NC, P-FeNC/CNT and P-FeNC have strong peaks at 25.2° and 43.7° , respectively, corresponding to the (002) and (101) peaks of graphitic carbon, indicating that the iron-doped catalyst has a higher degree of graphitization.

2.2. Pore Structure and Surface Area Analysis

For further studying the effect of ZnCl_2 and iron on the BET surface area (SBET), N_2 adsorption–desorption isotherms were measured (Figure 2a). The type I curve and obvious hysteresis loop of P-FeNC/CNT indicate its micropores and mesoporous pores structure. Both the specific surface areas (Figure 2b) of P-FeNC/CNT ($1849\text{ m}^2\text{g}^{-1}$) and P-NC ($1420\text{ m}^2\text{g}^{-1}$) are higher than that of P-FeNC ($829\text{ m}^2\text{g}^{-1}$), revealing that the volatilization of ZnCl_2 can lead to the formation of a large number of pore structures during high-temperature annealing. The pore size distribution diagram (Figure 2c) demonstrates that P-FeNC/CNT has a large number of micropores (Figure 2c inset) and mesoporous pores with pore sizes smaller than 10 nm, which further indicates the pore-making ability of ZnCl_2 . The large surface areas and excellent pore structures of P-FeNC/CNT catalysts can host plentiful active sites and facilitate their full exposure. In addition, the well-constructed porous structures of CNTs can supply fast mass transfer channels for the substances associated with the ORR, thus enhancing the electrocatalytic activity.

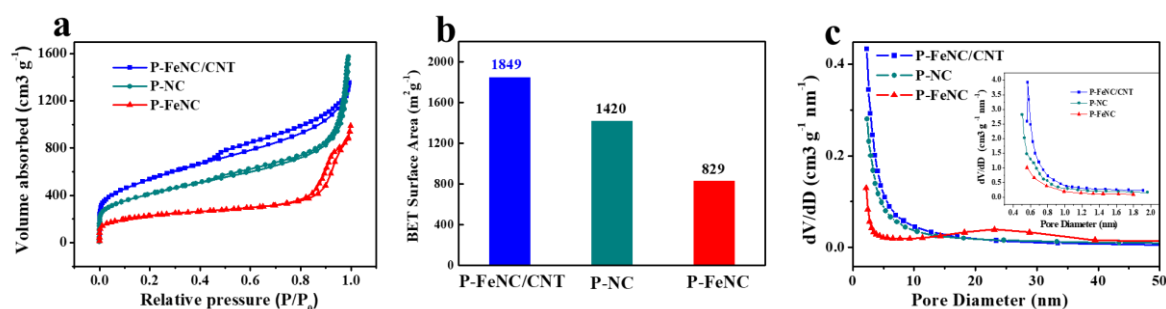


Figure 2. (a) Nitrogen adsorption–desorption isotherms, (b) BET surface area, and (c) the pore size distribution of P-FeNC/CNT, P-NC, and P-FeNC catalysts.

2.3. Chemical States and Surface Element Analysis

The surface elemental composition and chemical valence of P-Fe-NC/CNT were investigated using X-ray photoelectron spectroscopy (XPS). The full spectrum of P-FeNC/CNT (Figure 3a) shows that N, P, and Fe were successfully doped into P-Fe-NC at 1.88 at%, 1.76 at%, and 0.30 at%, respectively (Table S1).

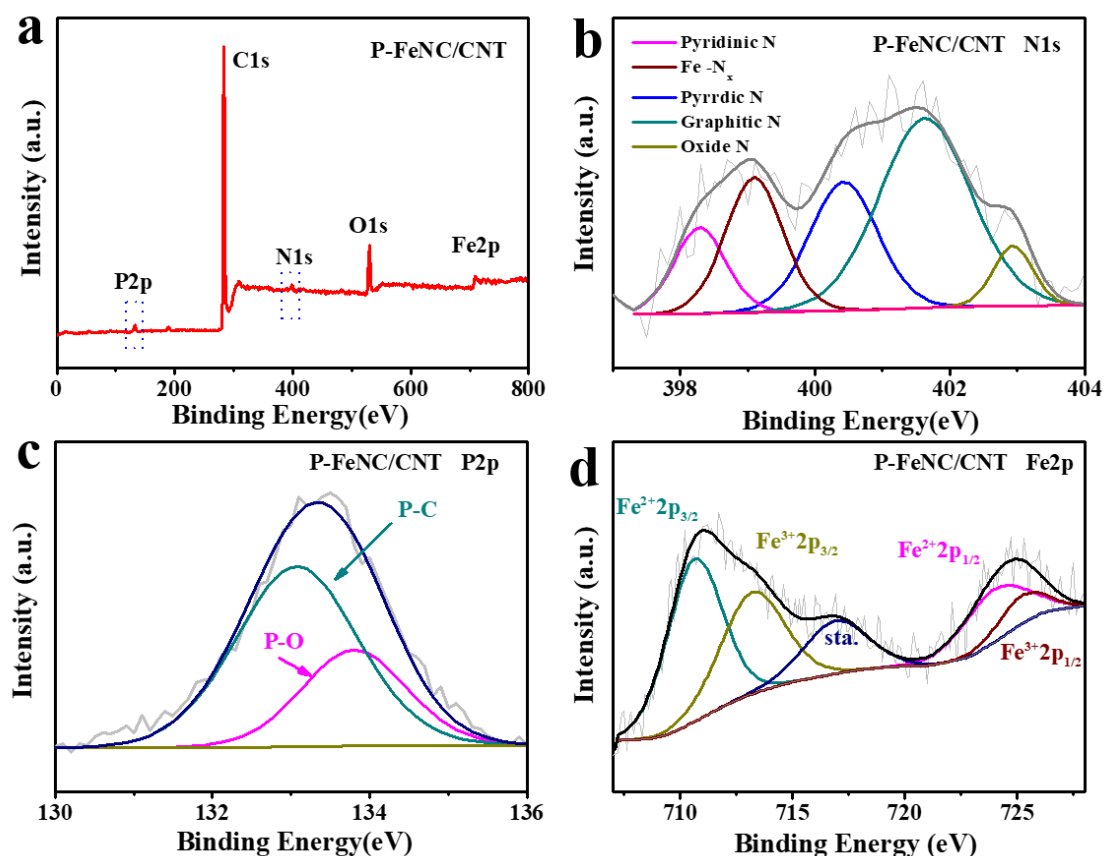


Figure 3. (a) XPS survey spectrum, (b) the high-resolution N1s spectrum, (c) P2p spectrum, and (d) Fe2p spectrum of P-FeNC/CNT.

The N 1s peaks (Figure 3b) can be divided into pyridine N (398.3 eV), Fe-N_x (399.1 eV), pyrrole N (400.4 eV), graphite N (401.6 eV), and oxidized N (402.9 eV) [22,23,27]. Of these, pyridine N, Fe-N_x, and graphite N, which are considered to be favorable for the ORR, account for 74% of the total nitrogen content, indicating that the majority of the doped N atoms are capable of acting as active sites for the ORR and enhancing the electrochemical activity of the catalyst.

The high-resolution P 2p spectrum of P-FeNC/CNT contains two characteristic peaks (Figure 3c), P-C (133.1 eV) and P-O (133.8 eV), respectively [28]. Most of the doped P is

present as P-C. As P has an electronegativity of 2.19, weaker than C's 2.55, the P atom attached to C is positively charged and can act as an oxygen reduction active site in alkaline media [29]. At the same time, P atoms existing in the P-O phase can enhance the electronegativity of the oxygen atom, thus increasing the electron-leaving domain of the carbon atom around the oxygen atom, which, in turn, facilitates its adsorption to oxygen molecules. In addition, P doping into the carbon lattice can cause the carbon skeleton to distort and deform [28], forming a large number of folded structures and allowing for the active site to be fully exposed to the three-phase interface, which will significantly improve the activity of the catalyst.

Figure 3d shows the high-resolution Fe 2p spectrum in P-FeNC/CNT, in which two peaks at 725.2 eV and 723.9 eV correspond to Fe(III) and Fe(II) in the Fe 2p_{1/2} peak and the peaks at 713.2 and 710.6 eV correspond to Fe(III) and Fe(II) in the Fe 2p_{3/2} peak, while the peaks at 716.9 eV are satellite peaks [30]. The iron content of the catalyst was calculated to be 1.31 wt% based on the XPS measurements, which is close to the 1.21 wt% analyzed using ICP-MS. It was demonstrated that the presence of Fe facilitates the adsorption of oxygen and oxygen-containing intermediate species, thus promoting the oxygen reduction activity of the catalyst. The elemental mapping of P-FeNC/CNT (Figure 4a–f) displays that the N, P, and Fe elements are uniformly distributed in the carbon nanotube skeleton. Thanks to the excellent porous CNT structure of the P-FeNC/CNT catalyst, these heteroatoms are fully exposed to the three-phase interface as active sites for the ORR.

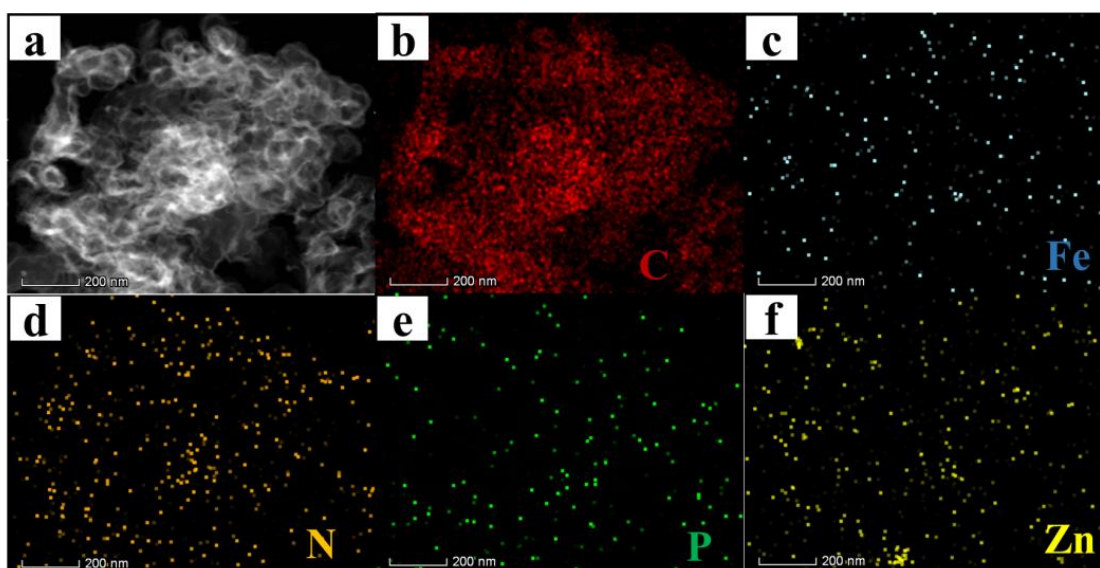


Figure 4. The HAADF-STEM image of P-FeNC/CNT and the corresponding elemental mappings of P-FeNC/CNT catalyst (a–f).

2.4. Electrocatalytic Activity Analysis

The oxygen reduction activity of the catalysts was investigated using rotating disc electrode tests in alkaline medium. The CV curves (Figure S2) show that P-FeNC/CNT has the largest bilayer capacitance in comparison to P-NC and P-FeNC, which is consistent with the specific surface area analysis. P-FeNC/CNT presents the highest oxygen reduction activity (Figure 5a) with a half-wave potential of 0.89 V (vs. RHE), which is significantly higher than that of P-FeNC at 0.87 V (vs. RHE), indicating that the porous CNT catalysts fabricated by the semi-closed molten salt-assisted one-step strategy are superior to the bulk catalysts prepared in the conventional open system. The absence of a limiting current plateau in the linear sweep voltammetry (LSV) curve of P-NC suggests that its catalytic reaction may be a two-electron process with an incomplete ORR, suggesting that iron doping plays an important role in enhancing the catalyst activity. Encouragingly, under the same conditions, P-FeNC/CNT outperforms the commercial Pt/C catalysts in terms of both half-wave potential and ultimate current plateau, classifying it as one of the most

active NPMC catalysts (Table S2). To further study the electron transfer process of the P-FeNC/CNT catalyst, we recorded the LSV lines (Figure 5b inset) at different rotation speeds in an O₂-saturated 0.1 M KOH solution. The almost coincident K-L curves (Figure 5b) indicate that the catalytic process of the P-FeNC/CNT catalyst is a primary reaction kinetic with a high selectivity for complete four-electron oxygen reduction reactions (Figure S3). As shown in Figure S4, The fast ORR kinetics for P-FeNC/CNT are further confirmed by its Tafel slope (95 mV dec⁻¹), which is only a little larger than that of the Pt/C catalyst (71.8 mV dec⁻¹).

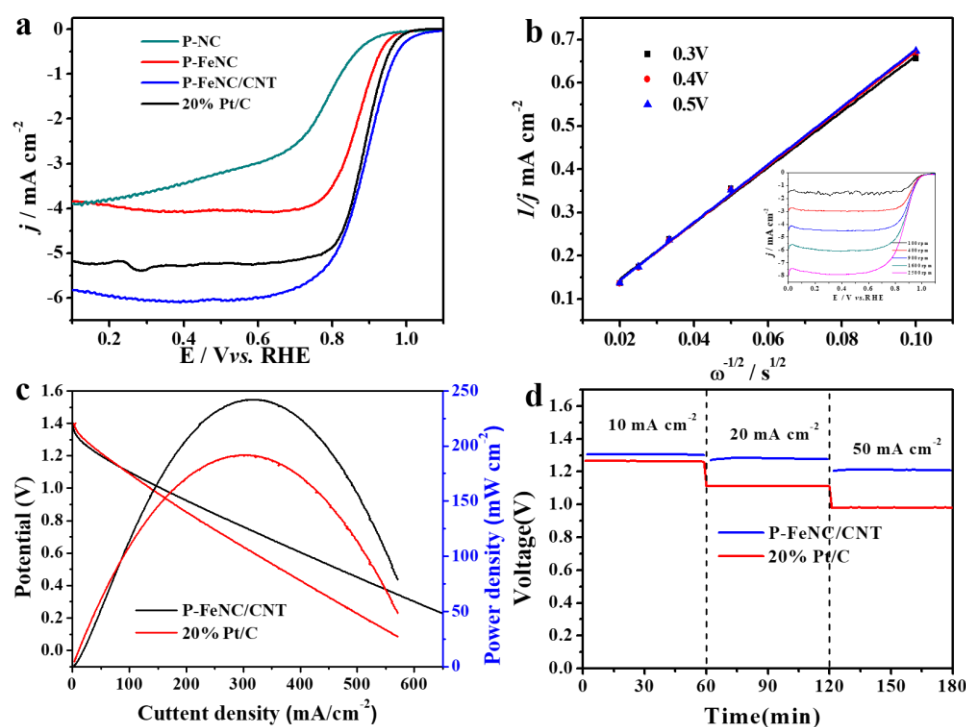


Figure 5. (a) LSV of prepared catalysts and 20% Pt/C in O₂-saturated 0.1 M KOH at a speed of 1600 rpm and a sweep rate of 10 mVs⁻¹. (b) K-L curves and LSV at different rotating speeds (inset) of P-FeNC/CNT. (c) Polarization and power density curves of the Zn–O₂ batteries. (d) Discharge curves of the Zn–O₂ battery.

The methanol cross-effect was evaluated using the potentiostatic method in oxygen-saturated 0.1 M KOH (Figure S5). After the addition of methanol, the current quickly returned to the initial state after a transient perturbation, indicating that the P-FeNC/CNT catalyst has a strong resistance to methanol poisoning. The stability of the catalyst was further investigated using an accelerated durability test (ADT). After 10,000 CV cycles, the negative half-wave potential shift of P-FeNC/CNT was less than 10 mV (Figure S6a), while the performance of the commercial Pt/C catalyst decreased significantly, with a negative half-wave potential shift of up to 50 mV (Figure S6b). These results indicate that P-FeNC/CNT has a high stability in alkaline media and shows potential for replacing high-cost Pt-based ORR catalysts.

The ORR activity of P-FeNC/CNT was further evaluated under real operating conditions using a homemade Zn–O₂ cell. As shown in Figure 5c, the maximum power density of the Zn–O₂ cell with P-FeNC/CNT as a catalyst was 240 mWcm⁻², which is much higher than that of Pt/C at 190 mWcm⁻². The constant current discharge curves (Figure 5d) reveal that the voltage gap between the P-FeNC/CNT and Pt/C catalysts broadened with an increase in the current, indicating that the porous CNT structure of the P-FeNC/CNT catalyst has a higher mass transfer rate and can achieve the rapid transport of reaction-related substances at high current densities. This comparison substantiates that the Zn–O₂ cell

using P-FeNC/CNT as a catalyst has a better discharge performance, confirming its high oxygen reduction activity and revealing its application value in practical battery systems.

3. Materials and Methods

Typically, 1.8 g of a 50% phytic acid (PA) solution and 5 g of ZnCl_2 were successively added to 3 mL of deionized water. Then, 300 mg of 1,10-phenanthroline (Phen) was dissolved in 2 mL of ethanol and added to the above mixed solution. In total, 500 mg of $\text{Fe}(\text{NO}_3)_3$ was dissolved in 2 mL of water, added to the above mixture, and stirred continuously at room temperature for 2 h. Then, the above mixture was put into a Petri dish, which was put into a muffle furnace at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ to $200\text{ }^\circ\text{C}$ for 5 h. The cooled sample was transferred to a 25 mL porcelain crucible and carbonized in a tube furnace at $900\text{ }^\circ\text{C}$ for 2 h under a nitrogen atmosphere, with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. After this carbonization, the sample was acid-treated with $0.5\text{ M H}_2\text{SO}_4$ at $80\text{ }^\circ\text{C}$ for 8 h. The product was filtered, washed, dried, ground, and then carbonized again for one hour at $900\text{ }^\circ\text{C}$ in a nitrogen atmosphere.

In comparison, P-NC is prepared without the addition of iron nitrate precursors and P-FeNC is prepared the same way as P-FeNC/CNT, except that ZnCl_2 is not included.

4. Conclusions

In summary, a semi-closed molten salt-assisted one-step method has been applied to prepare N-P-Fe tridoped porous CNT catalysts. Due to the catalytic effect of Fe and the pore-building effect of ZnCl_2 , the prepared catalysts exhibited a tightly packed porous carbon nanotube structure and a very large specific surface area, providing a fast channel for electron conduction and mass transport. Electrochemical tests demonstrated that the P-FeNC/CNT catalysts outperformed commercial Pt/C catalysts in terms of their oxygen reduction activity and electrochemical stability. They also demonstrated a higher maximum power density than commercial Pt/C in zinc–oxygen cell tests, revealing excellent promise for application. In addition, this semi-closed molten salt-assisted one-step strategy provides a simple, convenient, and practical way to prepare other types of heteroatom-doped carbon nanotube catalysts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13050824/s1>, Figure S1: XRD patterns of P-NC, P-FeNC and P-FeNC/CNT; Figure S2: CV curves of the as prepared catalysts in O_2 -saturated 0.1 M KOH at a sweep rate of 50 mVs^{-1} ; Figure S3: The electron transfer numbers (n) of P-FeNC/CNT; Figure S4: Tafel slopes of P-FeNC/CNT and Pt/C; Figure S5: Current-time curve of P-FeNC/CNT catalysts in O_2 -saturated 0.1 M KOH , before and after the addition of $0.5\text{ M CH}_3\text{OH}$; Figure S6: Polarization curves of the P-FeNC/CNT and commercial Pt/C catalysts in O_2 -saturated 0.1 M KOH at 1600 rpm with a sweep rate of 10 mV s^{-1} before and after the accelerated durability test; Table S1: The element content of P-FeNC/CNT catalyst obtained from XPS and the Fe content obtained from ICP-MS; Table S2: Comparison of the ORR activity of P-FeNC/CNT catalyst with other reported electrocatalysts in alkaline electrolytes with a rotation rate of 1600 rpm ; Table S3: Comparison of the power density of Zn- O_2 batteries in this work with other reported electrocatalysts [22,23,26,28,31–45].

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References

1. Qi, Y.; Bian, T.; Choi, S.; Jiang, Y.; Jin, C.; Fu, M.; Zhang, H.; Yang, D. Kinetically controlled synthesis of Pt-Cu alloy concave nanocubes with high-index facets for methanol electro-oxidation. *Chem. Commun.* **2014**, *50*, 560–562. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Zhang, J.; Sasaki, K.; Sutter, E.; Adzic, R.R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. *Science* **2007**, *315*, 220–222. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Stephens, I.E.L.; Bondarenko, A.S.; Grenbjerg, U.; Rossmeisl, J.; Chorkendorff, I. Understanding the electrocatalysis of oxygen reduction on platinum and its alloys. *Energy Environ. Sci.* **2012**, *5*, 6744–6762. [\[CrossRef\]](#)
4. Wang, C.; Markovic, N.M.; Stamenkovic, V.R. Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction. *ACS Catalysis* **2012**, *2*, 891–898. [\[CrossRef\]](#)
5. Li, M.; Zhao, Z.; Cheng, T.; Fortunelli, A.; Chen, C.; Yu, R.; Zhang, Q.; Gu, L.; Merinov, B.V.; Lin, Z.; et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. *Science* **2016**, *354*, 1414–1419. [\[CrossRef\]](#)
6. Attard, G.A.; Brew, A.; Ye, J.-Y.; Morgan, D.; Sun, S.-G. Oxygen Reduction Reaction Activity on Pt{111} Surface Alloys. *ChemPhysChem* **2014**, *15*, 2044–2051. [\[CrossRef\]](#)
7. Attard, G.A.; Ye, J.-Y.; Brew, A.; Morgan, D.; Bergstrom-Mann, P.; Sun, S.-G. Characterisation and electrocatalytic activity of PtNi alloys on Pt{111} electrodes formed using different thermal treatments. *J. Electroanal. Chem.* **2014**, *716*, 106–111. [\[CrossRef\]](#)
8. Markovic, N.M.; Adzic, R.R.; Cahan, B.D.; Yeager, E.B. Structural effects in electrocatalysis: Oxygen reduction on platinum low index single-crystal surfaces in perchloric acid solutions. *J. Electroanal. Chem.* **1994**, *377*, 249–259. [\[CrossRef\]](#)
9. Zheng, X.; Li, L.; Li, J.; Wei, Z. Intrinsic effects of strain on low-index surfaces of platinum: Roles of the five 5d orbitals. *Phys. Chem. Chem. Phys.* **2019**, *21*, 3242–3249. [\[CrossRef\]](#)
10. Huang, X.; Zhu, E.; Chen, Y.; Li, Y.; Chiu, C.Y.; Xu, Y.; Lin, Z.; Duan, X.; Huang, Y. A facile strategy to Pt₃Ni nanocrystals with highly porous features as an enhanced oxygen reduction reaction catalyst. *Adv. Mater.* **2013**, *25*, 2974–2979. [\[CrossRef\]](#)
11. Zhou, W.; Wu, J.; Yang, H. Highly Uniform Platinum Icosahedra Made by Hot Injection-Assisted GRAILS Method. *Nano Lett.* **2013**, *13*, 2870. [\[CrossRef\]](#)
12. Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y.M.; et al. High-performance transition metal-doped Pt₃Ni octahedra for oxygen reduction reaction. *Science* **2015**, *348*, 1230–1234. [\[CrossRef\]](#)
13. Chen, S.; Wei, Z.; Qi, X.; Dong, L.; Guo, Y.G.; Wan, L.; Shao, Z.; Li, L. Nanostructured polyaniline-decorated Pt/C@PANI core-shell catalyst with enhanced durability and activity. *J. Am. Chem. Soc.* **2012**, *134*, 13252. [\[CrossRef\]](#)
14. Nie, Y.; Chen, S.; Ding, W.; Xie, X.; Zhang, Y.; Wei, Z. Pt/C trapped in activated graphitic carbon layers as a highly durable electrocatalyst for the oxygen reduction reaction. *Chem. Commun.* **2014**, *50*, 15431–15434. [\[CrossRef\]](#)
15. Byambasuren, U.; Jeon, Y.; Altansukh, D.; Shul, Y.-G. Doping effect of boron and phosphorus on nitrogen-based mesoporous carbons as electrocatalysts for oxygen reduction reaction in acid media. *J. Solid State Electrochem.* **2016**, *20*, 645–655. [\[CrossRef\]](#)
16. Wang, S.; Iyyamperumal, E.; Roy, A.; Xue, Y.; Yu, D.; Dai, L. Vertically Aligned BCN Nanotubes as Efficient Metal-Free Electrocatalysts for the Oxygen Reduction Reaction: A Synergetic Effect by Co-Doping with Boron and Nitrogen. *Angew. Chem.* **2011**, *50*, 11756–11760. [\[CrossRef\]](#)
17. Wu, Y.; Li, Y.; Mao, J.; Wu, H.; Wu, T.; Li, Y.; Zeng, B.; Xu, Y.; Yuan, C.; Dai, L. Metallosupramolecular Polymer Precursor Design for Multi-Element Co-Doped Carbon Shells with Improved Oxygen Reduction Reaction Catalytic Activity. *Catalysts* **2019**, *9*, 102. [\[CrossRef\]](#)
18. Akula, S.; Balasubramaniam, B.; Varathan, P.; Sahu, A.K. Nitrogen-Fluorine Dual Doped Porous Carbon Derived from Silk Cotton as Efficient Oxygen Reduction Catalyst for Polymer Electrolyte Fuel Cells. *ACS Appl. Energy Mater.* **2019**, *2*, 3253–3263. [\[CrossRef\]](#)
19. Sibul, R.; Kibena-Pöldsepp, E.; Mäeorg, U.; Merisalu, M.; Kikas, A.; Kisand, V.; Treshchalov, A.; Sammelselg, V.; Tammeveski, K. Sulphur and nitrogen co-doped graphene-based electrocatalysts for oxygen reduction reaction in alkaline medium. *Electrochem. Commun.* **2019**, *109*, 106603. [\[CrossRef\]](#)
20. Shen, H.; Gracia-Espino, E.; Ma, J.; Zang, K.; Luo, J. Synergistic Effects between Atomically Dispersed FeNC and CSC for the Oxygen Reduction Reaction in Acidic Media. *Angew. Chem. Int. Ed.* **2017**, *56*, 13800–13804. [\[CrossRef\]](#)
21. Deng, J.; Chen, S.; Zhou, Q.; Nie, Y.; Li, J.; Wu, R.; Wang, Q.; Wei, Z. Phytic acid-assisted self-templating synthesis of n-p-fe-tridoped hierarchical porous carbon for efficient oxygen reduction reaction. *J. Power Sources* **2020**, *451*, 227808. [\[CrossRef\]](#)
22. Li, J.; Chen, S.; Li, W.; Wu, R.; Ibraheem, S.; Li, J.; Ding, W.; Li, L.; Wei, Z. A eutectic salt-assisted semi-closed pyrolysis route to fabricate high-density active-site hierarchically porous Fe/N/C catalysts for the oxygen reduction reaction. *J. Mater. Chem. A* **2018**, *6*, 15504–15509. [\[CrossRef\]](#)
23. Guo, S.; Yuan, P.; Zhang, J.; Jin, P.; Sun, H.; Lei, K.; Pang, X.; Xu, Q.; Cheng, F. Atomic-scaled cobalt encapsulated in P,N-doped carbon sheaths over carbon nanotubes for enhanced oxygen reduction electrocatalysis under acidic and alkaline media. *Chem. Commun.* **2017**, *53*, 9862–9865. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Cui, J.; Liu, H. Mesoporous SiO₂ produced by mineralization of yeast cells as an efficient electrocatalyst for oxygen reduction reaction. *Russ. Chem. Bull.* **2017**, *66*, 969–974. [\[CrossRef\]](#)
25. Han, Y.; Wang, Y.; Xu, R.; Chen, W.; Li, Y. Electronic structure engineering to boost oxygen reduction activity by controlling the coordination of the central metal. *Energy Environ. Sci. EES* **2018**, *11*, 2348–2352. [\[CrossRef\]](#)
26. Ahn, S.H.; Yu, X.; Manthiram, A. “Wiring” Fe-Nx-Embedded Porous Carbon Framework onto 1D Nanotubes for Efficient Oxygen Reduction Reaction in Alkaline and Acidic Media. *Adv. Mater.* **2017**, *29*, 1606534. [\[CrossRef\]](#)

27. Wan, W.; Wang, Q.; Zhang, L.; Liang, H.-W.; Chen, P.; Yu, S.-H. N-, P- and Fe-tridoped nanoporous carbon derived from plant biomass: An excellent oxygen reduction electrocatalyst for zinc-air batteries. *J. Mater. Chem. A* **2016**, *4*, 8602–8609. [[CrossRef](#)]
28. Zhang, J.; Zhao, Z.; Xia, Z.; Dai, L. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions. *Nat. Nanotechnol.* **2015**, *10*, 444–452. [[CrossRef](#)]
29. Choi, C.H.; Park, S.H.; Woo, S.I. Binary and Ternary Doping of Nitrogen, Boron, and Phosphorus into Carbon for Enhancing Electrochemical Oxygen Reduction Activity. *Acs Nano*. **2012**, *6*, 7084–7091. [[CrossRef](#)]
30. Liu, Z.; Wang, F.; Li, M.; Ni, Z.-H. N, S and P-ternary doped carbon nano-pore/tube composites derived from natural chemicals in waste sweet osmanthus fruit with superior activity for oxygen reduction in acidic and alkaline media. *RSC Adv.* **2016**, *6*, 37500. [[CrossRef](#)]
31. Ye, Y.; Duan, W.; Yi, X.; Lei, Z.; Li, G.; Feng, C. Biogenic precursor to size-controlled synthesis of Fe₂P nanoparticles in heteroatom-doped graphene-like carbons and their electrocatalytic reduction of oxygen. *J. Power Sources* **2019**, *435*, 226770. [[CrossRef](#)]
32. Li, Y.; Li, Z.; Wu, Y.; Wu, H.; Zhang, H.; Wu, T.; Yuan, C.; Xu, Y.; Zeng, B.; Dai, L. Carbon particles co-doped with N, B and Fe from metal-organic supramolecular polymers for boosted oxygen reduction performance. *J. Power Sources* **2019**, *412*, 623–630. [[CrossRef](#)]
33. Wang, W.; Chen, W.; Miao, P.; Luo, J.; Wei, Z.; Chen, S. NaCl Crystallites as Dual-Functional and Water-Removable Templates To Synthesize a Three-Dimensional Graphene-like Macroporous Fe-N-C Catalyst. *ACS Catal.* **2017**, *7*, 6144–6149. [[CrossRef](#)]
34. Meng, F.-L.; Wang, Z.-L.; Zhong, H.-X.; Wang, J.; Yan, J.-M.; Zhang, X.-B. Reactive Multifunctional Template-Induced Preparation of Fe-N-Doped Mesoporous Carbon Microspheres Towards Highly Efficient Electrocatalysts for Oxygen Reduction. *Adv. Mater.* **2016**, *28*, 7948–7955. [[CrossRef](#)]
35. Lu, Z.; Wang, J.; Huang, S.; Hou, Y.; Li, Y.; Zhao, Y.; Mu, S.; Zhang, J.; Zhao, Y. N,B-codoped defect-rich graphitic carbon nanocages as high performance multifunctional electrocatalysts. *Nano Energy* **2017**, *42*, 334–340. [[CrossRef](#)]
36. Li, Y.; Chen, B.; Duan, X.; Chen, S.; Liu, D.; Zang, K.; Si, R.; Lou, F.; Wang, X.; Rønning, M.; et al. Atomically dispersed Fe-N-P-C complex electrocatalysts for superior oxygen reduction. *Appl. Catal. B Environ.* **2019**, *249*, 306–315. [[CrossRef](#)]
37. Li, S.; Cheng, C.; Zhao, X.; Schmidt, J.; Thomas, A. Active Salt/Silica-Templated 2D Mesoporous FeCo-Nx-Carbon as Bifunctional Oxygen Electrodes for Zinc–Air Batteries. *Angew. Chem. Int. Ed.* **2018**, *57*, 1856–1862. [[CrossRef](#)]
38. Li, X.G.; Guan, B.Y.; Gao, S.Y.; Lou, X. A general dual-templating approach to biomass-derived hierarchically porous heteroatom-doped carbon materials for enhanced electrocatalytic oxygen reduction. *Energy Environ. Sci.* **2019**, *12*, 648–655. [[CrossRef](#)]
39. Ibraheem, S.; Chen, S.; Li, J.; Li, W.; Gao, X.; Wang, Q.; Wei, Z. Three-Dimensional Fe,N-Decorated Carbon-Supported NiFeP Nanoparticles as an Efficient Bifunctional Catalyst for Rechargeable Zinc–O₂ Batteries. *ACS Appl. Mater. Interfaces* **2018**, *11*, 699–705. [[CrossRef](#)]
40. Wang, M.; Qian, T.; Zhou, J.; Yan, C. An efficient bifunctional electrocatalyst for a zinc–air battery derived from Fe/N/C and bimetallic metal–organic framework composites. *ACS Appl. Mater. Interfaces* **2017**, *9*, 5213–5221. [[CrossRef](#)]
41. Liu, X.; Park, M.; Kim, M.G.; Gupta, S.; Wu, G.; Cho, J. Integrating NiCo Alloys with Their Oxides as Efficient Bifunctional Cathode Catalysts for Rechargeable Zinc–Air Batteries. *Angew. Chem. Int. Ed.* **2015**, *54*, 9654–9658. [[CrossRef](#)] [[PubMed](#)]
42. Lei, Y.; Chen, F.; Jin, Y.; Liu, Z. Ag-Cu nanoalloyed film as a high-performance cathode electrocatalytic material for zinc-air battery. *Nanoscale Res. Lett.* **2015**, *10*, 197. [[CrossRef](#)] [[PubMed](#)]
43. Sharifi, T.; Espino, E.G.; Jia, X.; Sandström, R.; Wågberg, T. Comprehensive study of an earth-abundant bifunctional 3D electrode for efficient water electrolysis in alkaline medium. *ACS Appl. Mater. Interfaces* **2015**, *7*, 28148–28155. [[CrossRef](#)] [[PubMed](#)]
44. Lee, D.U.; Choi, J.Y.; Feng, K.; Park, H.W.; Chen, Z. Advanced extremely durable 3D bifunctional air electrodes for rechargeable zinc-air batteries. *Adv. Energy Materials* **2014**, *4*, 1301389. [[CrossRef](#)]
45. Li, B.; Ge, X.; Goh, F.W.T.; Hor, T.S.A.; Geng, D.; Du, G.; Liu, Z.; Zhang, J.; Liu, X.; Zong, Y. Co₃O₄ nanoparticles decorated carbon nanofiber mat as binder-free air-cathode for high performance rechargeable zinc-air batteries. *Nanoscale* **2015**, *7*, 1830–1838. [[CrossRef](#)]

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