Seizing gaseous Fe^{2+} to O_2-accessible densify NC sites for proton exchange membrane fuel cells

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It is well known that the commercial applications of proton exchange membrane fuel cells (PEMFCs) rely heavily on efficient and low-cost catalysts to drive the cathodic oxygen reduction reaction (ORR). Platinum (Pt), the noble metal, has the highest kinetic activity in cathodic ORR. Nevertheless, the extensive use of Pt in fuel cells will add significant cost to PEMFCs, which is an obstacle to its large-scale and sustainable deployment. Much attention has been therefore paid to the development of Pt group metals free (PGM-free) ORR catalysts. The US Department of Energy (DOE) has set a 2025 ORR target for PGM-free PEMFCs cathode as a current density of 0.044 A cm^{-2} under 1.0 bar H_2–O_2 at 0.9 $V_{iR\text{-}free}$, comparable to the ORR activity of PGM-based catalysts.[1] The utilization of Fe is a crucial parameter for evaluating Fe-N-C catalysts in proton exchange membrane fuel cells (PEMFCs), yet it exhibits a decreasing tendency as the density of Fe-N_4 sites increases. Herein, gaseous Fe^{2+} was seized into NC support with surface-rich pyridinic-N to form surfaced Fe–N_{2+2} with higher density and intrinsic activity on carbon substrate. The surfaced Fe–N_{2+2} has improved both the site density and Fe utilization, which provided a large number of O_2-accessible active sites at the three-phase interface (TPB) of the fuel cells. Moreover, dense Fe–N_{2+2} exposed to the outermost layer of the catalyst layer could shorten the transport pathways of protons and O_2, reducing mass transfer resistance. These structural advantages make Fe_g-NC/Phen the best ORR catalysts evidenced by a high current density of 0.046 A cm^{-2}@0.9$V_{iR\text{-}free}$ and a high peak power density (P_{max}) of 1.53 W cm^{-2} in a H_2–O_2 PEMFCs, which outperformed almost all the reported M–N–C catalysts.

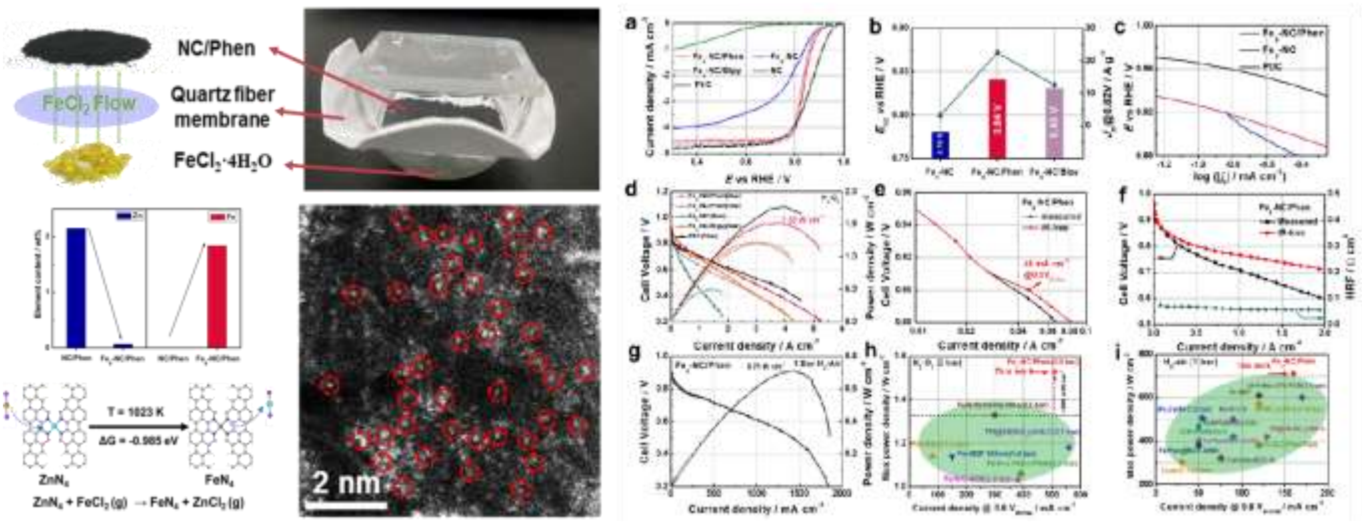

Figure 1. LEFT: Schematic diagram illustrating the bottom-up "confined steaming" strategy, and; AC HAADF-STEM images of Fe_g-NC/Phen; RIGHT: ORR and PEMFC performance measurements. (a) ORR polarization curves; (b) $E_{1/2}$ and J_m at 0.82 V; (c) Tafel plots curves of Fe_g-NC/Phen, Fe_g-NC and Pt/C; (d) H_2-O_2 PEMFC polarization and power density curves. Cathode, 3.5 mg_{cat} cm^{-2} for Fe-N-C; anode, 0.4 mg_{Pt} cm^2; Nafion 211 membrane; 4.41 cm^2 electrode; 80 °C, 100% relative humidity (RH); 400 mL O_2 min^{-1} and 300 mL H_2 min^{-1}. (e) Tafel plots of Fe_g-NC/Phen; (f) Polarization curves of Fe_gNC/Phen with and without iR-free. The atrovirens dotted curve represents the high-frequency resistance (HRF). (g) H_2-air PEMFC polarization and power density curves. The max powder density and the area metric current density at 0.8 $V_{iR\text{-}free}$ between Fe_g-NC/Phen and the literature reported Fe-based catalysts in (h) H_2-O_2 fuel cell and (i) H_2-air fuel cell

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References

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