Highly durable electrocatalyst with low-loading platinum-cobalt nanoparticles dispersed over single-atom Co-N-Graphene nanofiber for efficient fuel cell

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Development of highly-active, durable and cost-effective oxygen reduction electrocatalyst for proton exchange membrane fuel cell is crucial and greatly desired to enable fuel cell powered vehicles that are competitive with internal combustion engine automobiles. The support’s structure is known to strongly influence the performance of Pt particles. Here, we present a new catalyst containing PtCo core-shell nanoparticle supported over hierarchical tailored porous carbon nanofibers with densely populated single-atomic Co-Nx sites embedded in N-doped graphene. In a fuel cell with a total Pt loading (anode + cathode) of 0.091 mg cm⁻², the new catalyst delivered unprecedented mass activity of 2.28 A mg⁻¹Pt at 0.9 Virr-free, Pt utilization of 11.1 kW g⁻¹Pt at 150 kPaabs, and high durability with 80% retention of initial mass activity after 30,000 accelerated-stress-test cycles, significantly higher than that of the state-of-the-art Pt₃Co/C. In-situ X-ray absorption spectroscopy revealed structure reversibility of the catalyst
during oxygen reduction reaction and indicated that the enhanced activity can be attributed to simultaneous PtCo and Co-N$_x$ contributions.

Proton Exchange Membrane Fuel Cells (PEMFCs) are considered a promising high-efficiency, clean energy technology having a theoretical specific energy sufficient for transportation and stationary applications$^{1-3}$. The four-electron transfer oxygen reduction reaction (ORR) at the cathode is paramount for fuel cell operation, and its sluggish kinetics, which is six orders of magnitude lower than the hydrogen oxidation reaction at the anode, limits overall performance of the PEMFC$^{3,4}$. The Pt usage of a commercial fuel cell powered vehicle is 30 g per stack, which is substantially higher than the 2-8 g$_{Pt}$ in incumbent internal combustion engine (ICE) vehicles, and far from the long term sustainability target of < 5 g$_{Pt}$ per vehicle$^5$. To compete with ICE vehicles, the total Platinum-group-metal (PGM) loading, including anode and cathode on the membrane electrode assembly (MEA), should be restricted to less than 0.125 mg$_{Pt}$ cm$^{-2}$, giving 8 g of PGM per vehicle. Designing highly active, durable and cost-effective electrocatalysts, to boost ORR and reduce the Pt consumption without compromising performance in a fuel cell, is challenging and critical for the widespread commercial application of PEMFC$^{3,6}$.

The widely used Pt catalysts are loaded on carbon supports with high surface area and high porosity to enable sufficient increase of Pt mass-specific surface area and to secure enough pores for reactant O$_2$ gas to access Pt, thus ensuring maximum mass activity. It is believed that Pt nanoparticles (NPs) are located in the interior of the micropores$^7$ (pore diameter < 2 nm) of the high surface area carbon, which enhance the Pt mass activity but restrict its direct contact with ionomer and reactant gas at low voltage, therefore hindering its performance at high current density. While, pore diameter of 4-7 nm for Pt deposition facilitates Pt to achieve both excellent
ORR activity and mass transport property. To further improve the Pt ORR activity, one can introduce PGM-free ORR catalyst as support for Pt to replace the conventional carbon forming a synergistic catalyst. For example, in our previous work, we synthesized synergistic catalysts where high surface area Co-N-C PGM-free catalyst was used as support for low loading PtCo alloy (LP@PF). The LP@PF presented an extraordinarily high Pt mass activity up to 1.77 A mgPt⁻¹ in a H₂-O₂ PEMFC.

In addition to activity, the high durability is another criterion for evaluation of an efficient ORR catalyst. For both PGM and PGM-free catalysts, carbon corrosion and demetallation are the two main factors leading to fast degradation of catalyst performance. Increasing the carbon graphitization, strengthening the anchoring effect between Pt NPs and the support, coating Pt NPs with protecting layers are effective approaches for Pt to achieve sustained stability. In a catalyst, micropores host the active site (e.g. Co-N₄), and mesopores govern the mass transfer and ionomer distribution. Therefore, to maximize the Pt performance in term of activity and stability by introducing PGM-free catalyst as support, a rational design of the PGM-free catalyst with high surface area, balanced micro- and meso- (pore size 2 nm - 50 nm) porosity, excellent corrosion resistance, electron conductivity, and strong affinity to Pt NPs, is essential.

Additionally, in an ideal PGM-free catalyst, within each micropore, a dense population of active sites should be freely accessible to the reactant and product. And the meso-/macro-pores should offer minimal transport resistance and be interconnected through a robust, continuous conductive matrix. As a consequence, the accessibility of reactant to the active sites is enhanced, giving rise to the excellent electrocatalytic activity for PGM-free catalyst toward ORR.

In this work, we introduce a new design of a low loading PtCo catalyst (LPCNGF), where a Co-N-graphene nanofiber (Co-N-GF) PGM-free catalyst is used as support for PtCo core-shell
alloy NP. The newly developed Co-N-GF possesses high surface area, hierarchical pore structures, high density of atomically dispersed Co-Nx, and N-doped graphene, which result in the new LPCNGF catalyst achieving the highest Pt mass activity and sustained electrode stability. Cobalt zeolite imidazole framework, a member of the metal organic framework (MOF; Co-MOF) family, was selected for this study as the source for Co-Nx active site formation. Also, it served as the metallic Co source which was the nucleation center for further PtCo alloy synthesis. We chose PtCo alloy because the ordered core@shell structured PtCo alloy with ~3 layers of Pt shell demonstrated remarkable activity and stability among PGM NPs.

Polyacrylonitrile (PAN) was selected as the polymer for fabrication of nanofiber containing Co-MOF, as PAN fiber is known as the chemical precursor of a high-quality carbon fiber. PAN can be converted to n-type N-doped graphene possessing excellent electron conductivity and corrosion resistance through high temperature pyrolysis. Moreover, carbon surface modified with N-functional groups facilitate the homogenous distribution of ionomer, resulting in enhanced Pt utilization, thus high current density at low voltage. The use of Co-MOF and PAN here not only promise a high-quality graphene with hierarchical pore structure, but also a high concentration and uniform distribution of Co-Nx sites and nitrogen sites throughout the carbon surface, which can further enhance catalyst performance. The catalyst exhibits a high mass activity of $5.08 \text{ A mg}_\text{Pt}^{-1}$ at 0.9 V measured in a rotating disk electrode experiment, which is 52 and 13 times that of Pt/C and the state-of-the-art Pt$_3$Co/C (umico), respectively. In a H$_2$-O$_2$ PEMFC cell with total Pt loading (anode + cathode) of 0.091 mg cm$^{-2}$, LPCNGF achieved unprecedented mass activity of $2.28 \text{ A mg}_\text{Pt}^{-1}$ at 0.9 V$_{\text{iR-free}}$, and Pt utilization of 11.1 kW g$_\text{Pt}^{-1}$ at 150 kPa$_{\text{abs}}$, which rank the highest among the reported (Supplementary Table 3). The catalyst was highly stable which retained 80% of initial mass activity after 30,000 accelerated stress test.
cycles. The synergistic oxygen reduction reaction was studied by performing operando X-ray absorption spectroscopy experiments.

Results and Discussion

Synthesis and characterization of LPCNGF catalyst. Co-MOF was first fabricated into interconnected nanofiber by electrospinning its mixture with PAN (Supplementary Fig. 1a). The obtained fiber mat was subjected to heat treatment at 1000 °C for 1.5 h under Ar atmosphere. After pre-leaching in 0.5 M H₂SO₄, the obtained Co-N-GF was used as support and nucleation center for the in-situ reduced Pt NPs. A second heat treatment under NH₃ was performed as the final step of the catalyst synthesis. The synthesis process is schematically shown in Fig. 1a. The optimizations of LPCNGF are shown in the Supplementary Fig. 2-5. The NH₃ was used as an additional nitrogen precursor, as NH₃ gasifies the disordered domains of the carbon, I) creating micropores into the support; II) producing N-bearing functionalities to bind cobalt cations forming Co-Nₓ sites; III) generating n-type graphene by donating electrons to graphene¹⁹, facilitating ORR²⁰. The created nitrogen functional groups interact with the ionomer chain, promoting homogeneous distribution of ionomer throughout the catalyst layers¹⁸,²¹. The catalyst achieved a surface area of 824.7 m² g⁻¹ (Supplementary Fig. 4c), as determined by the Brunauer-Emmett-Teller (BET) method. The pore size analysis indicates a high volume of micropores, and appropriate volume of meso-/macro-pores in Co-N-GF (Fig. 1b, Supplementary Table 1-2). Raman spectrum (Fig. 1c) confirms the graphene nature of the carbon fiber as evidenced by the peaks at 2653 cm⁻¹ and 2915 cm⁻¹ corresponding to 2D-band and D+G-band of graphene²².

The catalyst has an interconnected network structure, with “beads” lining up on the “string” (Fig. 2a, Supplementary Fig. 1b-1c). The “beads” were converted from Co-MOF, maintaining
MOF-like morphology with hollowed structure. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, combined with energy-dispersive X-ray spectroscopy (EDS) element mapping, revealed the formation of PtCo alloy and homogenous distribution of N in the carbon matrix (Fig. 2b-2c, 2e). The average particle size was ~ 3 nm (Supplementary Fig. 1d, 1e). The formation of PtCo alloy was further confirmed by X-ray Diffraction (XRD) (Supplementary Fig. 6). The atomic ratio of Co:N:Pt:C was 1.6:4.0:0.4:94 determined by EDS (Supplementary Fig. 7). Atomic-resolution HAADF-STEM revealed the dense atomically-dispersed Co embedded in the carbon matrix, and the bright dots are assigned to Co based on electron energy-loss spectroscopy (EELS) results (Fig. 2d, Supplementary Fig. 8). EELS also revealed the co-existence of N with Co, suggesting Co-N\textsubscript{x} populations, which are the active sites in PGM-free catalysts\textsuperscript{23}. High-resolution TEM (HRTEM) indicated that the carbon mainly consisted of graphene sheets, with ~ 0.35 nm d-spacing of the (002) basal plane in both “beads” and “string” (Fig. 2f, Supplementary Fig. 1f). This value is larger than the d-spacing of well-ordered graphite (0.34 nm), suggesting the incorporation of N into the graphitic structure. The carbon contains plenty of mesopores (Fig. 2f, Supplementary Fig. 1f). Co-N-GF possesses high BET surface area, hierarchical tailored porosity, homogenous distributed Co-N\textsubscript{x}, and plenty of N-doped graphene, a high ORR activity and durability with optimized mass transport property can be expected. HRTEM image also revealed that the PtCo alloy had a core-shell structure: 2 ~ 3 atomic layers of Pt shell and the ordered PtCo alloy core (Fig. 2g). The Pt shell was strained and partially covered with CoN\textsubscript{x}/C terraces (Fig. 2g, Supplementary Fig. 9), which could protect Co/Pt against leaching under the high voltage harsh operating conditions in the fuel cell\textsuperscript{4}. 
**Electrocatalytic performance evaluation.** Rotating ring-disk electrode (RRDE) testing in oxygen saturated 0.1 M HClO$_4$ revealed a half-wave potential of 0.93 V (vs. RHE) for LPCNGF (Fig. 3a). The average number of transferred electrons per O$_2$ molecule ($n_e$) was 3.94~3.99, corresponding to a low H$_2$O$_2$ yield of < 3% (Fig. 3b). The Pt/C and the state-of-the-art Pt$_3$Co/C catalyst from Umicore (Pt$_3$Co/C(Um)) were tested under the same condition as benchmarks. Even with higher Pt loading in Pt/C and Pt$_3$Co/C(Um) than that in LPCNGF, the half-wave potential of Pt/C and Pt$_3$Co/C(Um) were 0.86V and 0.91 V, 70 mV and 20 mV lower than that of LPCNGF (Fig. 3a), respectively. Tafel plots of mass activities obtained from Fig. 3a normalized by the total mass of the loaded Pt, exhibited a slope of 63 mV dec$^{-1}$ for LPCNGF (Fig. 3c), smaller than that of Pt/C (89 mV dec$^{-1}$) and Pt$_3$Co/C(Um) (71 mV dec$^{-1}$), suggesting the better ORR kinetics for the former. Furthermore, the LPCNGF displayed a mass activity (MA) of 5.08 A mg$_{Pt}^{-1}$ at 0.9 V, 52 and 13 times higher than that of Pt/C (0.098 A mg$_{Pt}^{-1}$) and Pt$_3$Co/C(Um) (0.39 A mg$_{Pt}^{-1}$), respectively. The high mass activity of LPCNGF in the kinetic range (voltage > 0.8 V) ranks it among the best ORR catalysts (Supplementary Table 3). The MA and specific activity (SA) retain ~ 90% of the initial values, with only 6 mV loss in half-wave potential after 10,000 potential cycles, demonstrating the high durability of LPCNGF in acid (Fig. 3d, Supplementary Fig. 10c).

The high ORR activity measured through RRDE does not directly reflect the performance in a practical fuel cell due to the fundamentally different operating conditions, e.g. temperature, electrolyte, electrode structure, etc. To measure its fuel cell performance, we integrated LPCNGF into a MEA, evaluated its performance in an operating PEMFC including H$_2$-Air and H$_2$-O$_2$ cells (Supplementary Fig. 11-12), and benchmarked to Pt$_3$Co/C(Um). For comparison, the Pt loading at cathode and anode for all the MEAs were $\leq$ 0.056 mg$_{Pt}$ cm$^{-2}$ and $\leq$ 0.035 mg$_{Pt}$ cm$^{-2}$,
respectively. For each test, MEA was manufactured and tested for reproducibility purpose for at least 3 times. Fig. 4a shows H₂-Air cell performance at 200 KPa_{abs}. The current-voltage polarization profile of LPCNGF is dramatically higher than that of Pt₃Co/C(Um) throughout the entire polarization curve. In addition, the current density at 0.8 V is 438 mA cm⁻² for LPCNGF, 4 times larger than that of Pt₃Co/C(Um) (106 mA cm⁻² at 0.8 V). In the mass transport region at 1.75 A cm⁻² current density, a significant reduction in voltage loss of up to 136 mV was achieved in LPCNGF relative to Pt₃Co/C(Um).

Durability represents another critical challenge for the development of ORR catalyst for fuel cell. We performed accelerated stress test (AST) to investigate the stability of LPCNGF in H₂-Air cell followed by testing in H₂-O₂ cell on the same MEA, using DOE’s durability evaluation protocol⁵. At 150 KPa_{abs} pressure in the H₂-Air cell (Fig. 4b), the performance of LPCNGF was superior to that of Pt₃Co/C(Um) in terms of higher current density and peak power density (0.63 W cm⁻² vs. 0.45 W cm⁻²) throughout the entire voltage range. After 30,000-AST cycles, the voltage loss at 0.8 A cm⁻² was negligible for LPCNGF, surpassing the target set by DOE (< 30 mV loss at 0.8 A cm⁻² after 30,000 AST cycles)⁵. The high peak power density was also maintained, indicating that the catalyst is extremely durable. The in-situ formed graphene and the well-protected PtCo alloy contribute significantly to the enhanced stability. By contrast, the voltage loss at 0.8 A cm⁻² for Pt₃Co/C(Um) was 156 mV, and the peak power density showed 31% decay after 30,000 AST cycles. Power per gram of PGM (kW g_{PGM}⁻¹) is a valuable metric for the evaluation of PGM catalyst being used in vehicles. Compared with DOE’s 2025 target of 8 kW g_{PGM}⁻¹, the Pt power metric of LPCNGF at both beginning of life (BOL, 11.1 kW g_{Pt}⁻¹ at 150 kPa_{abs}, 12.2 kW g_{Pt}⁻¹ at 200 kPa_{abs}) and end of life (EOL, 10.9 kW g_{Pt}⁻¹ at 150 kPa_{abs}) after
30,000 cycles test in H₂-Air cell are noteworthy (Fig. 4d, right). In contrast, Pt₃Co/C(Um) failed to meet DOE’s target both at BOL and EOL at 150 kPa_{abs}.

A continued durability evaluation in H₂-O₂ cell further corroborates the excellent durability and the high activity of LPCNGF. Because Pt₃Co/C(Um) was deactivated after durability measurement in the H₂-Air cell, we prepared a new MEA with Pt₃Co/C(Um) at cathode as a benchmark for the H₂-O₂ cell. Even having undergone 30,000 AST cycles in a H₂-Air cell, the H₂-O₂ cell performance with LPCNGF at cathode still outperformed Pt₃Co/C(Um), displaying larger current density and higher peak power density throughout the entire voltage range (Fig. 4c, iR-corrected polarization shown in Supplementary Fig. 13). The peak power density of LPCNGF reached 1.11 W cm⁻² at BOL (150 kPa_{abs}), corresponding to an effective Pt utilization of 0.044 g_{Pt} kW⁻¹ at cathode, which is 1.7 times that of the recently reported Pt/nitrogen modified C (0.075 g_{Pt} kW⁻¹, 230 kPa_{abs})¹⁸, and rank among the highest reported in the literatures (Fig. 4f). The LPCNGF delivered a MA of 2.28 A g_{Pt}⁻¹ at 0.9 V_{iR-free} at BOL (Fig. 4d, left), 2.5 times that of Pt₃Co (Um) (0.92 A g_{Pt}⁻¹ at 0.9 V_{iR-free}), and 5 times of US DOE’s 2025 target of 0.44 A g_{Pt}⁻¹ at 0.9 V_{iR-free}. After the 30,000 AST cycles, the MA of LPCNGF maintained 80% retention (1.83 A g_{Pt}⁻¹ at 0.9 V_{iR-free} at EOL) (Fig. 4d, left), exceeding DOE’S target which requires less than 40% loss of initial MA after the 30,000-cycle AST test (0.26 A g_{Pt}⁻¹ at EOL). To the best of our knowledge, this is the highest MA and durability achieved ever in a PEM H₂-O₂ cell (Fig. 4e, Supplementary Table 3). In comparison, Pt₃Co/C(Um) displayed significant degradation, with MA loss of 45% (0.51 A g_{Pt}⁻¹ at 0.9 V_{iR-free} at EOL). Our results suggest that LPCNGF is a promising candidate for widespread fuel cell use in automotive applications.
**Structure evolution and possible mechanism during ORR.** The morphology of interconnected carbon nanofiber with MOF-structured beads in LPCNGF was maintained after the AST in fuel cell and EDS attested to the negligible change in atomic ratios of Co:Pt:N:C (Supplementary Fig. 14). The average particle size and the core-shell structure of PtCo alloy were also preserved (Supplementary Fig. S15). All these results suggest a durable LPCNGF structure under the harsh operating conditions of a fuel cell. To better understand the origin of this extraordinary ORR performance, we performed X-Ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS) to elucidate the surface composition, oxidation states, and local atomic structure of LPCNGF. The Pt XPS spectrum shows a 0.2 eV positive shift in binding energy after NH$_3$ annealing, relative to that of the material before NH$_3$ treatment (LPCNGF-BN, Fig. 5a), indicating an electron transfer between Pt and Co as a consequence of PtCo alloy formation. The Co XPS result shows a re-distribution from Co$^0$ dominated surface to more Co-N$_x$ terminations after NH$_3$ treatment (Fig. 5b). Analysis of the N 1s XPS spectrum from LPCNGF-BN reveals 3 groups of N functionalization (Fig. 5c), pyridinic- (398.6 eV), pyrrolic- (400.2 eV) and oxidic-N (402-405 eV)$^{24}$. NH$_3$ treatment leads to additional N incorporated into the carbon matrix, and decomposition of pyrrolic-N to form additional pyridinic groups$^{9,23}$. As a consequence, the surface is dominated with pyridinic-N. NH$_3$ treatment, inducing surface modification by creating additional Co-N$_x$ and pyridinic-N, would positively influence the activity and electronic conductivity of the catalyst$^4,24$. Moreover, the abundant nitrogen functional groups could facilitate the homogenous distribution of ionomer throughout the catalyst layer, further enhancing the activity.

X-ray absorption near edge structure (XANES) at the Co K-edge in LPCNGF-BN includes contributions from metallic Co and Co-N$_x$ with four different features, labeled as A, B, C, and D.
(Fig. 5d). After NH₃ treatment, features A and B were shifted to lower energy, suggesting the formation of Co-Pt bonds. Feature D was blue shifted, suggesting that cobalt is positively charged. Feature C increased substantially, reflecting hybridization of Co 4s and 4p orbital by Pt in the alloy and N in Co-Nₓ. The extended X-ray absorption fine structure (EXAFS) result at Co K-edge (Supplementary Fig. 16a) further confirms the formation of Co-Nₓ centers, evidenced from the enhanced peak intensity at 1.44 Å corresponding to Co-N bond, consistent with XPS result. XANES spectrum at Pt L-III edge in LPCNGF suggests the formation of PtCo alloy as evidenced by the appearance of peak at 11576 eV (Fig. 5e, red arrow). The white line (WL) intensity at Pt L-III edge in LPCNGF decreased relative to that in LPCNGF-BN, indicating electron transfer from Co to Pt, which tuned the Pt d-band energy leading to weakened OH_ads binding on the Pt surface, thus improving ORR catalytic properties. The formation of ordered PtCo alloy is further confirmed by EXAFS (Supplementary Fig. 16b). It is worth noting that R_Pt-Co (2.19 Å) is similar to the R_Co-Co (2.18 Å) (Supplementary Fig. 16a), suggesting that the majority of the hetero-atomic interactions in LPCNGF are located in the Co-rich core, consistent with the Pt_thin-shell/single-PtCo_core structure. The surface structure of LPCNGF catalyst is schematically outlined in Fig. 5f.

To examine evolution of the local atomic structure or metal oxidation states in LPCNGF during ORR, we collected in-situ XANES and EXAFS spectra at the Co K-edge and Pt L-edge in O₂ saturated 0.1 M HClO₄ at various applied potentials (Fig. 6). When 0.8 V potential was applied, XANES spectrum at Co K-edge showed that the absorption energy was slightly blue-shifted compared to the dry sample (Supplementary Fig. 17a), suggesting the absorption of oxygenated species (O* or OH*) on the surface Co. As the applied potential increased to 1.3 V, the absorption edge at 7728 eV shifted to 7729 eV with slightly enhanced WL intensity (Fig. 6a,
inset), indicating charge transfer from Co to the oxygenate intermediate. EXAFS spectrum at the Co K-edge at 0.8 V (Fig. 6c, Supplementary Fig. 17b) displayed appearance of Co-Co bonds at 2.78 Å, indicating Co atoms interconnected by di-µ-xox (µ3-O)(µ2-OH) bridges which suggests the formation of edge-sharing Co octahedron27. The new peak at 4.86 Å further confirms the edge-sharing CoO6 octahedron in the in-situ sample. At 1.3 V, the Co-Co bond distance decreased by 0.09 Å relative to that at 0.8 V (Fig. 6c, inset), implying oxidation of Co. Moreover, the peak at 1.44 Å assigned to Co-N bond shifted to 1.49 Å corresponding to Co-O bond, indicating ORR takes place on Co-N site by absorbing oxygenated intermediates on to the Co center.

WL intensity at Pt LIII-edge increased at elevated potential (red arrow, Fig. 6b), accompanied with intensity decrease in the post-edge region (red circle). This result indicates the absorption of oxygenated intermediate on the Pt surface, which increases the unoccupied d-orbitals of Pt via the charge transfer from Pt to O28. It is worth noting that the WL intensity at 1.3 V is still lower than that of Pt foil, emphasizing the metallic state of Pt. EXAFS spectra at Pt LIII-edge shows decreased Pt-Co peak intensity with increasing potential (Fig. 6d, inset), suggesting that the surface becomes disordered during ORR. As the potential reached 1.3 V, a new weak peak at 1.72 Å appeared. This peak is assigned to a Pt-OH bond, which is 0.12 Å larger than the Pt-O bond (1.6 Å)28, 29. When the potential decreased to 0.6 V, both XANES and EXAFS spectra at Co K-edge and Pt LIII-edge reverted to their initial state, which indicates that the chemical absorption of oxygenate intermediates on the surface of Co in Co-N-GF and Pt in PtCo alloy, is a reversible process during ORR. The in-situ experiments reveal that both PtCo NP and Co-N-GF simultaneously contribute to the ORR activity.
Conclusions

We have presented a highly active, durable and robust LPCNGF catalyst composed of core-shell structured PtCo NP dispersed over self-ORR active Co-N-GF. The Co-N-GF was synthesized through electrospinning a polymer solution containing PAN and Co-MOF, followed by pyrolysis at high temperature. The Co-N-GF possesses I) densely populated atomic Co-N_x catalytic active sites, II) tailored high porosity, III) interconnected micro-/meso-/macro-pores, V) N-doped graphene. Such a unique hierarchical porous structure, on one hand, enhances Pt mass activity by improving Pt accessibility to the reactant; on the other hand, facilitates an excellent water management capability. The abundant nitrogen functionalities enable the uniform distribution of ionomer throughout the electrode layer, which further enhances the Pt activity. Moreover, Co-N-GF is self-ORR highly active. Therefore, with a total Pt loading (anode + cathode) of 0.091 mg cm^-2, MEA assembled with LPCNGF as cathode catalyst delivered the highest mass activity of 2.28 A g_Pt^-1 at 0.9 V_{IR-free} in PEM H_2-O_2 cell, 438 mA cm^-2 current density at 0.8 V in PEM H_2-Air cell, and exhibited excellent durability with 80% MA retention after a 30,000-cycle AST in H_2-Air cell and a continued 30,000-cycle AST in H_2-O_2 cell, surpassing US DOE’s 2025 target for ORR catalyst under PEMFC conditions. The MEA displayed an effective Pt utilization of 0.044 g_Pt kW^-1 in H_2-O_2 cell, and 11.1 kW g_PGM^-1 at 150 kPa_{abs} in H_2-Air cell. These performance metrics enable a fuel cell powered vehicle to be competitive with ICE autos. The in-situ formed N-doped graphene, benefiting from the combination of Co-MOF and PAN fiber, contributes to the significantly improved durability, and electron conductivity of LPCNGF. Furthermore, insights obtained from in-situ XANES and EXAFS experiments reveal that a) oxygenated species are formed in-situ over the surface of Co-N-GF during ORR; b) Co-N-GF catalyst and PtCo contribute to the ORR simultaneously; c) the
structure evolution of both Co-N-GF and PtCo alloy are reversible during ORR. We believe that the unprecedented activity and durability of LPCNGF will boost widespread commercialization of fuel cells in automobile applications, which will help to reduce reliance on fossil fuels.

Methods

Synthesis of Co-MOF: Preparation of Co-MOF was based on the existing literature\textsuperscript{15}. Specifically, 1 g Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O was dissolved in 80 ml of methanol, sonicated for 10 min and labeled as solution A. 2.25 g mI\textsubscript{m} was dissolved in 100 ml of methanol, sonicated for 10 min and labeled as solution B. Solution A mixed with B dropwise, followed by stirring for 10 min at room temperature to produce a heterogeneous violet mixture, which was then sealed and kept at R.T for 12 h. The violet crystal was collected by centrifugation with a rotation rate of 6000 rpm, and then dried at 60 °C under vacuum overnight.

Fabrication of Co-MOF/PAN fiber: PAN was dissolved in DMF at concentration of 150 mg ml\textsuperscript{-1}. The mixture was stirred at 40 °C overnight. Co-MOF was dissolved into DMF at concentration of 100 mg ml\textsuperscript{-1}, and ball milled at 400 rpm for 3 h in a planetary ball mill. Taking 36% Co-MOF in Co-MOF/PAN fiber as a representative composition, PAN solution and Co-MOF solution were mixed with volume ratio of 2:3 followed by ball milling at 400 rpm for 1 h to prepare the final slurry. This slurry was transferred to 2 ml syringe and then fabricated into Co-MOF/PAN nanofiber using the electrospinning conditions – 10 kV, feed rate of 0.003 ml min\textsuperscript{-1} and a spinneret-to-collector distance of 10 cm.

Co-N-GF catalyst synthesis: The Co-MOF/PAN nanofiber was converted to Co-N-GF nanofiber by pyrolysis first at 750 °C for 6 h, and then at 1000 °C for 1.5 h under flowing Ar, with a heating ramp rate of 3 °C min\textsuperscript{-1}. After pyrolysis, the carbon nanofiber was soaked in 0.5 M H\textsubscript{2}SO\textsubscript{4} at R.T for 2 h to leach out the inactive Co metal, followed by stirring in DI water overnight and drying at 80 °C under vacuum. The obtained nanofiber was denoted as Co-N-GF. The cobalt content in Co-N-GF was ~ 8 wt.\%.
LPCNGF catalyst synthesis: 5.1 mg trimethyl(methylcyclopentadienyl)platinum(IV) was dissolved in oleylamine, and sonicated for 1 min to form a transparent solution, followed by rapid addition of 60 mg Co-N-GF. The mixture was sonicated for 9 min to form a homogenous slurry, which was then sealed under air and heated at 196 °C in an oil bath for 1 h. The resulting sample was collected by centrifuging, and followed by drying at 60 °C under vacuum. The obtained porous powder was finally heat-treated under flowing ammonia at 750 °C for 30 min. The catalyst thus obtained was named as LPCNGF. The overall Pt loading in the sample was quantified by EDS.

Electrochemical measurement: The electrochemical performance was first evaluated in O₂ saturated 0.1 M HClO₄ electrolyte at room temperature using CHI electrochemical station (Model 760C) in a conventional three-electrode electrochemical cell with mercury/mercury sulfate as reference electrode and gold wire as counter electrode. The ink was prepared by mixing 1 mg of catalyst powder with 600 µl of mixture solution of 5 % Nafion and methanol. After 2 h of sonication, 10 µl of ink was applied onto a glass carbon electrode (0.2472 cm²) representing the working electrode. The Pt loading of the electrode was ~ 4.0 µgPt·cm⁻² for LPCNGF. An initial conditioning step of ~ 20 cyclic voltammogram (CV) cycles between 0 V and 1.2 V vs. RHE was applied. Afterward, ORR activity was recorded using linear sweep voltammetry (LSV) in a range from 0 V to 1.2 V versus reversible hydrogen electrode (RHE) at a scan rate of 10 mV s⁻¹ and rotation rate of 1600 rpm in oxygen saturated 0.1 M HClO₄ electrolyte. Catalyst stability was studied by CV between 0.4 V and 1.0 V with 10,000 cycles at a scan rate of 50 mV s⁻¹. Electrochemical surface area was determined by integrating hydrogen adsorption charge on CV curve after double-layer correction and assuming a value of 210 µC cm⁻² for the absorption of a hydrogen monolayer. For comparison, commercial 30 wt.% Pt₃Co obtained from Umicore company was studied as benchmark catalyst using the same ink deposition technique and testing protocol. The Pt loading of the electrode was ~ 80 µgPt·cm⁻² and ~ 14 µgPt·cm⁻² for Pt/C and Pt₃Co/C(Um), respectively. The number of transferred electrons n, the percentage of yield H₂O₂, and Pt mass activity were derived from the following equations:

\[
n = \frac{4I_d}{I_d + I_r N} \quad (1)
\]
Where $I_k$ is the kinetic current, $m_{Pt}$ is the Pt mass in the catalyst deposited on the disk, $I_d$ is the disk current, $I_r$ is the ring current and $N$ is the ring collection efficiency (37%).

**MEA preparation and fuel cell test:** The catalyst ink was prepared by ultra-sonicating the mixture of catalyst powder and Nafion ionomer solution diluted by isopropanol/DI water for 2 h. The weight ratios of ionomer to carbon were ~ 0.76 – 0.86 for cathode and 0.6 for anode. The “ink” was applied directly to Nafion 211 membrane (DuPont) with active area of 5 cm$^2$ through air brush painting, which was then sandwiched between two gas diffusion layers (Sigracet 25BC) to assemble the final MEA. The performance testing was conducted in a fuel cell test station (Scribner 850e). Polarization curves were recorded at various temperatures (60, 70, 80, 90 °C), relative humidity (RH) levels (50, 75, 100%) and absolute pressures (100, 150, 230 kPa$_{abs}$). For H$_2$-O$_2$ cell, the flow-rate was fixed at 200 ml min$^{-1}$ for both H$_2$ and O$_2$. For H$_2$-Air cell test, the flowrate for H$_2$ was maintained at 200 ml min$^{-1}$, while different flow-rates (200, 520, 580, 780, 1000 ml min$^{-1}$) were applied for air. The accelerated stress test (AST) was conducted by square wave voltage cycling at 0.6 V for 3 s and 0.95 V for 3 s with 200 ml min$^{-1}$ H$_2$ feeding into the anode and 75 ml min$^{-1}$ N$_2$ feeding into the cathode based on DOE’s AST protocol required for MEA durability evaluation; the cell was set at 80 °C and 100 % RH and the back pressures of both cathode and anode were set at ambient (101 KPa). After completion of the voltage cycles, a voltage recovery (VR) process was performed: the cell was held at 0.1 V under H$_2$-Air for 1 h at 40 °C, 150 % RH, and 150 kPa$_{abs}$, followed by application of various voltages between 0.1 V and 0.85 V for different time periods. Current-voltage polarization was then recorded to measure changes in catalyst activity and durability. The H$_2$-Air cell and H$_2$-O$_2$ cell durability tests were performed on the same MEA for our LPCNGF catalyst. For Pt mass activity evaluation, the H$_2$-O$_2$ cell was held at 0.9 V for 15 min, and the Pt mass activity was recorded by averaging the last minute value after applying hydrogen cross-over.
correction and a short VR process for cathode at 0.9 V with flowing N₂ for 5 min. Each durability evaluation of LPCNGF was conducted 3 times to ensure reproducibility. EIS was recorded at various voltages of 0.9 V, 0.8 V, 0.7 V, 0.6 V, 0.5 V, 0.4 V for both H₂-O₂ cell and H₂-Air cell at 1000 Hz. Prior to the experiments, a “break-in ” step was applied: first, the cells was heated to 80 °C and held at open circuit voltage (OCV) in H₂-Air. After this step, a series of voltage cycles between 0.6 and 0.9 V with different RH were conducted.

**Characterization:** The catalyst structure was probed using a Bruker diffractometer D8 Advance with Cu Kα radiation (characteristic wavelength λ = 1.54051 Å). XPS data was acquired using a PHI 5000 VersaProbe II system (Physical Electronics) that is attached to an argon-atmosphere glovebox to avoid any contamination of moisture and air. The X-ray source was monochromatic Al Kα radiation (hυ = 1486.6 eV) which was set at Ar+ -ion and electron beam sample neutralization, fixed analyzer transmission mode. The spot size for X-ray beam was set to 100 μm. The spectra of all samples were collected at pass energy of 23.50 eV and electron escape angle of 45° to the sample plane. The catalyst morphologies and elemental compositions were characterized by high-resolution transmission electron microscopy (HR-TEM) and Electron energy-loss spectroscopy (EELS) using Argonne’s Chromatic Aberration-Corrected TEM (ACAT) operated at 80 KV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray spectroscopy (EDS) were taken on a FEI Talos operating at 200 KV. Scanning electron microscopy (SEM) images were acquired with a Quanta 400F ESEM microscope. The specific surface area and the micro/meso/macro-porosity of the catalyst were evaluated by the Brunauer-Emmett-Teller (BET) method at liquid nitrogen temperature in a Micromeritics ASAP2020 surface area analyzer. The degree of graphitization of the Co-N-G nanofiber was determined with an Invia Renishaw 2000 microscope spectrometer with an Ar Ne laser at 633 nm wavelength.

**XAS measurement:** XAS measurements, including XANES and EXAFS, were conducted under ambient temperature at Beamline 12 BM of the Advanced Photon Source at Argonne National Laboratory. The XAS measurements were performed in fluorescence-transmission mode, where the data collected from LPCNGF were in fluorescence mode and data collected from references placed behind the sample were in transmission mode. XAS spectra were collected at Pt L₃ edge and Co K-edge, respectively. For ex-situ measurements, samples were packed as fine powder with optical thickness equivalent of e⁻¹ total X-ray absorption. For in-situ measurements, samples
were analyzed in a home-made in-situ cell, where O₂ saturated 0.1 M HClO₄ was used as electrolyte, and Hg/Hg(SO₄)₂ and gold wire were used as reference and counter electrode, respectively. A graphene sheet with 0.1 mg cm⁻² of catalyst loading was used as the working electrode. After activation from 0.05 V to 1 V to achieve a stable state, XAS measurements were performed at elevated voltage of 0.8 V, 1.1 V, 1.3 V, and then decreased to 1.2 V and 0.6 V (re-reduction). At each potential, the catalyst was allowed to stabilize for 10 min before XAS measurement. The applied potential was held for 1 h for data collection at each point. XAS data processing was performed using ATHENA and ARTEMIS. EXAFS data were fit to a K window of 3 ~ 12 Å⁻¹ with single scattering pathways. All spectra were calibrated, aligned, normalized and back-ground-subtracted per ATHENA data analysis protocols.

Data availability

The data that support the findings of this study are available within the paper and its Supplementary Information or from the corresponding author upon reasonable request.

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Author contributions

L.C designed research; L.C, Z.Y, performed research; J.G, Y.L conducted TEM; L.C, Z.Y, D.A analyzed data; and L.C, I.B and D.A wrote the paper. All the authors discussed and commented on the manuscript.

Competing Interests

The authors declare no conflict of interest.

Additional information

Supplementary information is available

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Fig. 1 Overview of synthesis approach and structure characterization. a Schematic illustration for the synthesis of LPCNGF with ammonolysis in pure NH$_3$ to form additional PGM-free active sites including Co-Nx, Pyridinic-N, and micropore, PtCo alloys, as well as CoN/C protecting layer for PtCo alloys. b BET micropore-mesopore size distribution for different Co-N-GF samples as function of Co-MOF content in the CoMOF/PAN fiber precursors. c Raman spectrum of LPCNGF, evidencing the graphene-nature of the formed carbon by introducing PAN fiber.
Fig. 2 Morphology characterization of LPCNGF. a HAADF-STEM image of two single fibers. b HAADF-STEM image of Pt-Co alloy NPs in LPCNGF. c, e the corresponding EDS elemental mapping. d Atomic-resolution HAADF-STEM image of isolated single Co atoms distributed across the carbon surface. f HRTEM image of carbon from “beads”, showing curved thin graphene layer. g HRTEM image of a representative Pt-Co alloy NP with ordered PtCo core and Pt shell partially covered by CoN/C terraces.
Fig. 3 Electrochemical performance evaluation of LPCNGF by the RRDE method. a Steady-state ORR polarization plot of LPCNGF catalyst recorded at a scan rate of 10 mV s\(^{-1}\) and 1600 r.p.m in O\(_2\) saturated 0.1 M HClO\(_4\) electrolyte, and compared with that of 20 wt.% Pt/C and 30 wt.% Pt\(_2\)Co/C(Um). Pt loading is \(\sim 4 \mu g_p \text{ cm}^{-2}\) for LPCNGF, \(\sim 80 \mu g_p \text{ cm}^{-2}\) for Pt/C and \(\sim 14 \mu g_p \text{ cm}^{-2}\) for Pt\(_2\)Co/C(Um). b The corresponding \(H_2O_2\) yield and electron transfer number. c The corresponding MA Tafel plots. d MA and SA as function of cycle number by RRDE.
Fig. 4 PEMFC performance and durability evaluation of LPCNGF. a H₂-Air fuel cell polarization and power density plots of LPCNGF under $P_a=P_c=200$ kPa$_{abs}$. MEA with 30 wt.% Pt₃Co(Um) as cathodic catalyst was tested under the same condition as benchmark. b H₂-Air fuel cell i-v polarization and power density before and after 30 000 cycles AST test under $P_a=P_c=150$ kPa$_{abs}$. c i-v polarization and power density for the same MEA with LPCNGF catalyst in a continued 30 000 AST test in a H₂-O₂ fuel cell after test in (b). d fuel cell MA at 0.9 V$_{irr-free}$ and power per gram of Pt before and after 30 000 AST. e MAs of different catalysts at 0.9 V$_{irr-free}$ before and after 30 000 AST in PEMFC. Catalysts include those from this work and previous reported ones: LP@PF-1/2, L10-CoPt/Pt$^{31}$, P2-
SA, NSTF Pt3Ni, Pt2Ni/CNC-NA, PtCo/HSC-e, Pt-alloy/C and Pt, PtCo/CCS. f power per gram
PGM of catalysts from this work and the previous reported. For all the fuel cell tests, membrane = Nafion 211,
temperature = 80 °C, cathode loading ≤ 0.056 mgPt cm⁻², anode loading ≤ 0.035 mgPt cm⁻², RH_a = RH_c = 100 %.
For H₂-Air cell, P_{H₂} = P_{Air} = 150 kPa_abs or 200 kPa_abs; H₂ flow rate = 200 ml min⁻¹, and air flow rate = 780 ml min⁻¹; for
H₂-O₂ cell, P_{H₂} = P_{O₂} = 150 kPa_abs, H₂ flow rate = O₂ flow rate = 200 ml min⁻¹.
Fig. 5 Structural characterization of the LPCNGF catalyst. XPS spectra of a Pt 4f, b Co 2p$_{3/2}$ and c N 1s binding energy before (-BN) and after NH$_3$ treatment. XANES spectra at d Co K-edge and e Pt L$_{III}$-edge before and after NH$_3$ treatment with the metal foil as reference. f, Schematic illustration of LPCNGF structure.
Fig. 6 In-situ X-ray absorption spectra of LPCNGF. a Co K-edge and b Pt L$_{III}$-edge XANES spectra measured at different potentials ascending from 0.8 V, 1.1 V to 1.3 V and then descending to 1.2 V and 0.6 V in O$_2$ saturated 0.1 M HClO$_4$ electrolyte. Insets magnify the WL region, clearly showing structure evolution during the ORR process.

FT EXAFS spectra at c Co K-edge and d Pt L$_{III}$-edge collected at potentials ascending from 0.8 V, 1.1 V to 1.3 V and then descending to 1.2 V and 0.6 V in O$_2$ saturated 0.1 M HClO$_4$ electrolyte. Insets are enlargements of c Co-Co and d Pt-Co peaks.