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Selective nitrogen doping on porous hard carbons using polymer dopants for high-performance fuel cells

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Nitrogen (N)-doped carbon materials have gained significant attention as promising electrocatalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs), yet their practical deployment is hindered by high synthesis cost and insufficient electrochemical stability. Herein, we introduce a polymer-assisted strategy leveraging poly(4-vinylpyridine) (P4VP) as both an N precursor and dispersing agent, enabling controlled N incorporation (1–2 at%) and homogeneous catalyst dispersion. The strong affinity of P4VP for graphitic surfaces mitigates aggregation, facilitating homogeneous doping and enhanced electrochemical durability. The catalyst demonstrates exceptional durability, exhibiting only a 4% voltage loss at 0.8 A cm⁻² after 30 000 cycles while retaining over 50% of its initial electrochemically active surface area (ECSA), whereas the N-free counterpart suffers a severe 39% voltage loss, highlighting the crucial role of N doping introduced via P4VP in enhancing electrochemical stability. This work establishes polymer-assisted N doping as a cost-effective strategy for durable, high-performance PEMFC electrocatalysts.

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1 Introduction

Addressing the rising global energy demand and fossil-fuel-induced pollution has accelerated the expansion of renewable energy solutions. Among them, proton exchange membrane fuel cells (PEMFCs) are recognized as a key technology for generating electricity from hydrogen.^{1–5} In PEMFCs, carbon supports are essential components of the membrane electrode assembly (MEA),^{6,7} providing a stable platform for platinum (Pt) catalysts to facilitate the sluggish oxygen reduction reaction (ORR).^{8–13} As the demand for green vehicles accelerates, the development of cost-effective and durable carbon-based catalysts has become increasingly significant.^{10,14} Fuel cell and electric vehicles are expected to last at least ten years,¹⁵ requiring catalysts to endure over 30 000 cycles while retaining ≥80% of their initial activity,¹⁶ as specified by the U.S. Department of Energy (DOE). Despite progress with mesoporous carbons,^{17–21} graphene-derived materials,^{22–24} and carbon

nanocages,^{25–27} most carbon supports still fail to meet these stringent durability and performance targets.

One effective approach to improving the efficiency of carbon-supported catalysts is heteroatom doping,^{21,28–30} especially nitrogen (N) incorporation,^{21,31–33} which has attracted considerable attention for its potential to enhance electrical conductivity and catalyst-support interactions. N-doped carbon materials exhibit superior charge transfer properties compared to unmodified supports,^{33,34} primarily due to the introduction of specific N functionalities such as pyrrolic N^{34–36} and pyridinic N.^{34–37} Furthermore, N doping enhances the metal-support interaction, thereby mitigating catalyst degradation.⁵ Cai *et al.* demonstrated that a 1.52 at% N doping reduced catalyst degradation by 16% after 30 000 cycles.³³ N-doped carbons are particularly attractive as catalyst supports for the ORR due to their tunable electronic structure, high surface area,⁴ and physicochemical stability.^{8,9,36,38,39} A range of N-rich precursors including pyrroles,^{38,40} melamine,⁴⁰ urea,^{29,40–43} adenine,^{29,44} and arginine^{29,45,46} have been utilized to prepare N-doped carbons with notable ORR activity. While it is well documented that these materials show promising electrochemical performance, recent studies suggest that the ORR activity is more strongly influenced by the type and distribution of N functional groups (*e.g.*, pyridinic N, graphitic N) than by the total N content alone.^{34,35,38,39,47,48}

However, conventional N doping methods are limited in their ability to selectively incorporate catalytically active N species.^{31–33} Bottom-up synthesis allows for higher N content

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but often requires customized precursors, reducing scalability.^{39,40,43} Conversely, post-synthetic modification (*e.g.*, top-down synthesis) is more straightforward but generally suffers from low N incorporation efficiency (< 1%) and poor control over functional group distribution.^{40,49} For instance, pyrolysis of N sources such as NH₄Cl or urea tends to yield graphitic N or pyrrolic N depending on the temperature, while selective formation of pyridinic N remains challenging.^{29,42,43} Additionally, these methods are often temperature-sensitive and prone to side effects such as pore collapse or particle agglomeration, which degrade surface properties and hinder mass transport. In particular, conventional NH₃ gas annealing, one of the most widely used N-doping approaches, poses inherent challenges for practical implementation.⁵⁰ The highly corrosive nature of NH₃ can partially etch or degrade the carbon framework, leading to safety concerns, equipment corrosion, and reduced material yield. Moreover, the gas-phase process is difficult to control and unsuitable for large-scale synthesis due to its high-temperature operation and poor selectivity toward catalytically active N species. In contrast, the polymer-assisted strategy proposed in this study enables a solid-phase and solution-processable route for N incorporation, maintaining the structural integrity of the carbon while providing enhanced selectivity and scalability. To overcome these drawbacks, advanced doping techniques are required that can introduce pyridinic N selectively and stably while preserving the graphitic low-defect domains and porous frameworks of the carbon support. Importantly, this strategy enables the facile introduction of selective N functionalities into existing carbon platforms, highlighting its strong potential for commercial implementation without the need for major changes to current manufacturing practices.

In this study, we synthesize N-doped carbon composites using poly(4-vinylpyridine) (P4VP), a pyridine-based polymer known for its strong affinity toward graphitic materials.^{51,52} By leveraging the intrinsic interaction between P4VP and carbonaceous surfaces, a uniform dispersion of the polymer within the carbon matrix is achieved, which is essential for improving electrochemical performance. The resulting composites exhibit N doping levels of approximately 1–2 at%, making them suitable for application in PEMFCs. We systematically examine the impact of polymer synthesis variables and carbonization parameters on the chemical structure, N configuration, and electrochemical robustness of the materials. Importantly, this polymer-assisted doping strategy functions as an add-on to existing template-based carbon synthesis, avoiding disruption of established production routes and highlighting its scalability for large-scale implementation. These results provide valuable insights into the rational design of N-doped carbon-based electrocatalysts and contribute to the development of cost-effective and durable alternatives to precious metal catalysts for hydrogen fuel cell technology.

2 Experimental section

2.1 Materials

4-Vinylpyridine (4VP, 97%, Sigma-Aldrich), 2,2'-azobis(2-methylpropionitrile) (98%, Daejung), and 4-cyano-4-

[[dodecylsulfanylthiocarbonyl]sulfanyl]pentanoic acid (97%, Sigma-Aldrich) were purchased from commercial suppliers. These reagents were used as the monomer, initiator, and chain-transfer agent (CTA) for reversible addition–fragmentation chain transfer (RAFT) polymerization. All other reagents, including chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), ethylene glycol (EG), sodium hydroxide, sodium acetate, and perchloric acid (HClO₄), were used without further purification. All solvents, including methanol, tetrahydrofuran, dimethyl sulfoxide, toluene, isopropyl alcohol, and *N,N*-dimethylformamide, were purchased from Daejung. Commercial Pt/C catalyst (TEC10E50E, 50 wt% Pt on carbon black) was obtained from Tanaka Kikinzoku Kogyo (Japan), and porous crystalline carbon (PCC) was provided by The Carbon Studio, Inc. (South Korea). Unless otherwise stated, all reagents and materials were used as received.

2.2 Synthesis of P4VP

4VP was distilled under reduced pressure (0.1 mbar) at 68 °C prior to use. P4VP was synthesized *via* RAFT polymerization. In a typical procedure, 4VP (9.40 mmol, 494 mg) was dissolved in tetrahydrofuran together with recrystallized 2,2-azobis(2-methylpropionitrile) (0.0049 mmol, 0.4 mg) and 4-cyano-4-[[dodecylsulfanylthiocarbonyl]sulfanyl]pentanoic acid (0.0988 mmol, 19.94 mg). The solution was purged with N₂ gas for 30 min to remove dissolved oxygen and then sealed. The reaction mixture was conducted at 72 °C in an oil bath under constant stirring for 14 h. Upon completion, the polymer was precipitated in cold toluene and dried under vacuum overnight. To further purify, the product was dissolved in dimethyl sulfoxide and reprecipitated in cold toluene. This purification cycle was repeated until a constant yield was obtained.

2.3 Synthesis of N-doped PCCs

PCC was dispersed in *N,N*-dimethylformamide containing the synthesized P4VP, followed by ultrasonication in an ice-cooled bath for 1 h to achieve uniform adsorption of P4VP onto the PCC surface. After sonication, the resulting suspension was equilibrated to room temperature and centrifuged at 10 000 rpm for 30 min to collect the PCC/P4VP complex. The detailed composition and weight ratios of each sample are summarized in Table S1. The resulting precipitate was dried in a convection oven at a controlled temperature for 3 days to remove residual solvents. N doping was then conducted by thermal treatment at 700 °C for 5 h under an inert atmosphere, enabling the incorporation of N functional groups into the carbon framework.

2.4 Synthesis of Pt/N-doped PCC catalysts

The Pt catalyst was supported on N-doped PCC *via* a polyol reduction method. First, H₂PtCl₆·6H₂O (0.24 mmol, 123.3 mg) was dissolved in 5 mL of EG, and ultrasonication with a probe ultrasonication was used to ensure complete dissolution of the Pt precursor. Simultaneously, N-doped PCC (100 mg) was dispersed in 5 mL of EG and subjected to ultrasonication for 3 h to achieve uniform dispersion. Separately, sodium hydroxide (3.40 mmol, 136 mg) and sodium acetate (0.46 mmol, 38 mg) were dissolved in

50 mL of EG to prepare a pH-adjusting alkaline solution. The solution was heated to 70 °C and stirred until fully dissolved. The $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution was slowly added dropwise into the alkaline solution with continuous stirring. The resulting mixture was reduced at 150 °C for 3 h under an inert atmosphere, resulting in the formation of Pt nanoparticles *via* thermal reduction. After the reduction, the mixture was cooled naturally to approximately 30 °C. The previously dispersed N-doped PCC was introduced into the Pt-containing solution, followed by mechanical stirring for 24 h to facilitate the deposition of Pt nanoparticles onto the carbon support. The resulting Pt/N-doped PCC catalyst was collected by filtration using a membrane filter (diameter 47 mm, pore size 2.2 μm). To remove any residual EG, the product was thoroughly washed several times with deionized water during the filtration process. Finally, the catalyst was dried in a vacuum oven at 60 °C for 24 h. The obtained catalyst was referred to as Pt/N-doped PCC catalysts.

2.5 Electrochemical measurements

Electrochemical assessments were performed using a standard three-electrode setup with an Ag/AgCl reference electrode. The catalyst ink was prepared by dispersing 5 mg of the catalyst in a solution comprising 20 μL of Nafion ionomer, 1.25 mL of deionized water, and 3.75 mL of isopropyl alcohol. The mixture was ultrasonicated for 1 h to obtain uniform dispersion. For all the catalysts, 10 μL of catalyst ink was drop-cast onto the rotating ring-disk electrode (RRDE). Cyclic voltammetry (CV) was performed in an N_2 -saturated 0.1 M HClO_4 solution at a scan rate of 50 mV s^{-1} . ORR activity was evaluated using linear sweep voltammetry (LSV) at 10 mV s^{-1} with an electrode rotation speed of 1600 rpm in an O_2 -saturated 0.1 M HClO_4 solution.

For the single-cell measurements, a proton exchange membrane (PEM) station was used, with MEAs featuring a geometric active area of 25 cm^2 , fabricated *via* the catalyst-coated membrane (CCM) method. The catalyst ink for the single-cell configuration was prepared by dispersing the catalyst in a solvent mixture of deionized water and isopropyl alcohol at a fixed ratio of 0.5, with Nafion ionomer solution added to achieve an ionomer-to-carbon weight ratio of 0.8. The mixture was homogenized *via* ball milling at 250 rpm for 3 h. The cathode layer was then deposited onto an FPI film using a decal transfer method and dried at 60 °C, while the anode was prepared using TEC10EA20E catalyst. The CCM was fabricated by vacuum-pressing the catalyst-coated film onto a Nafion NRE 211 membrane at 145 °C under 20 bar pressure. During operation, the cell temperature was maintained at 80 °C with fully humidified conditions (100% RH). The initial performance (beginning of life, BOL) and catalyst durability were assessed following the DOE protocol. Durability testing was conducted over 30 000 CV cycles between 0.6 V (3 s) and 1.0 V (3 s), with N_2 (75 sccm) supplied to the cathode and humidified H_2 (200 sccm) fed to the anode.

2.6 Characterizations

A range of analytical techniques were employed to characterize the polymer and PCC/P4VP complexes. Proton nuclear magnetic

resonance (^1H NMR, Jeol, JNM-ECZ500R/S1) was utilized to verify the successful synthesis of P4VP, and fourier transform infrared (FTIR, Bruker, Vertex 70) spectroscopy was conducted to identify the functional groups present in the complexes. Thermogravimetric analysis (TGA, TA Instruments, SDT Q600) was conducted to examine the thermal decomposition behavior, while particle size analysis (Microtrac, S3500) was performed to evaluate changes in dispersibility. The morphology of the N-doped PCCs and Pt/N-doped PCCs catalysts was examined by scanning electron microscopy (SEM, Hitachi, SU8600) and transition electron microscopy (TEM, Tecnai, FEI). The Brunauer–Emmett–Teller (BET) surface area and pore size were measured using a surface area and pore size analyzer (ASAP 2460, Micromeritics). High-resolution TEM (HR-TEM), scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF), and energy-dispersive X-ray spectroscopy (EDS) mapping were conducted with a double spherical aberration corrected TEM (Spectra Ultra, Thermo-Fisher). The composition of the N-doped PCCs and Pt/N-doped PCCs was analyzed by high-resolution X-ray diffraction (XRD, SmartLab, Rigaku) and X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific). Inductively coupled plasma optical emission spectroscopy (ICP-OES, AVIO 550, PerkinElmer) was used to determine the Pt ratio and loading amount in the Pt/N-doped PCCs. For single-cell measurements, a PEM station (SF600-PE, SCITECH) was utilized.

3 Results and discussions

3.1 Synthesis of N-doped PCCs

The experimental procedure for fabricating PCC/P4VP complexes is schematically illustrated in Fig. 1a. This approach prioritizes simplicity and scalability, providing a viable route for scalable N-doping. P4VP was synthesized *via* RAFT polymerization, allowing precise control over molecular weight and polymer architecture (Fig. S1). The molecular weight (M_n) was determined from ^1H NMR spectra in DMF-d_7 , yielding a value of 12 257 g mol^{-1} . The M_n of P4VP increased linearly with the $[\text{Monomer}]/[\text{CTA}]$ ratio, following the relation $M_n = 0.823 \times [\text{M}]/[\text{CTA}]$ (kg mol^{-1} , $R^2 = 0.98$), confirming the high precision of molecular weight control (Fig. S2). To achieve uniform N incorporation, a static dispersion method was employed, facilitating the interaction between the N functional groups of P4VP and oxygen-containing species on the PCC surface.

The FTIR spectra were performed to elucidate the interactions between PCC and P4VP (Fig. S3). The spectrum of P4VP showed characteristic peaks at 3674 cm^{-1} (O–H stretching),^{53–57} 2985 and 2908 cm^{-1} (asymmetric and symmetric CH_2 stretching),^{55,56,58,59} 1604 cm^{-1} (C=N stretching of pyridine rings),^{54,60} and 1071 cm^{-1} (C–N stretching).^{60,61} In contrast, PCC showed a relatively featureless spectrum in these regions, indicating the absence of N-containing functional groups. After blending with PCC, the FTIR spectra of the PCC/P4VP complexes retained most of the characteristic peaks of P4VP. Notably, the intensity of the C=N stretching peak at 1604 cm^{-1} was significantly reduced, suggesting strong interactions between the pyridine N

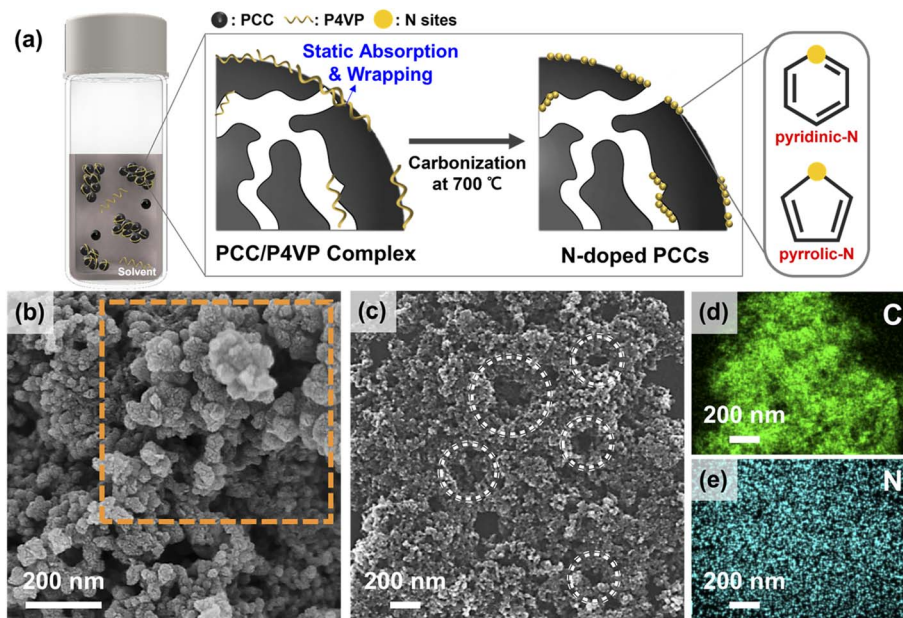


Fig. 1 (a) Schematic illustration of the synthesis of N-doped PCC particles. SEM images of (b) PCC/P4VP complex (20:1) and (c) N-doped PCC (20:1). EDS mapping of N-doped PCC (20:1), showing (d) C (green), and (e) N (cyan) distributions.

and the PCC surface. The persistence of the C=N and C-N stretching bands at 1604 and 1071 cm^{-1} , respectively, further supports the formation of hydrogen bonding and potential coordination interactions. The excess P4VP was removed through a rigorous washing step, ensuring the selective retention of adsorbed polymer on the PCC surface. Subsequently, the complex was carbonized at $700\text{ }^{\circ}\text{C}$ for 5 h, yielding N-doped PCCs.

To ensure sufficient PCC surface coverage, excess polymer conditions in the range of 10:1 to 20:1 were employed. For reference, linear P4VP without strong surface interactions is completely decomposed under high-temperature pyrolysis (Fig. S4). In contrast, as discussed above, the strong interaction between PCC and P4VP shifts the onset of thermal degradation ($\sim 150\text{ }^{\circ}\text{C}$) to much higher temperatures in the complex. Ultimately, the carbonization yields reached 92% (10:1) and 93% (20:1), indicating that the polymer was not fully decomposed but rather remained adsorbed on the PCC surface. This result demonstrates that N-doping was successfully achieved using only the polymer adsorbed on the PCC surface. SEM images reveal that the PCC/P4VP complexes are fully wrapped without forming separate P4VP domains, as highlighted by the dashed rectangle (Fig. 1b and S5a). After carbonization, the distribution of pores within the structure becomes apparent, indicated by dashed circles (Fig. 1c and S5d). EDS mapping of the resulting carbon reveals a uniform distribution of both C and N (Fig. 1d, e and S5b, c, e, f).

Furthermore, to elucidate the particle-scale transformations occurring during P4VP wrapping and subsequent carbonization, particle size distribution (PSD) analysis was conducted (Fig. S6). The pristine PCC exhibited relatively broad PSD centered around $2\text{--}3\text{ }\mu\text{m}$ (average: $2.6 \pm 1.6\text{ }\mu\text{m}$), indicating partial aggregation and structural irregularity of the porous carbon materials. Upon

the formation of the PCC/P4VP complex (10:1), the particle size decreased markedly to $0.8 \pm 1.3\text{ }\mu\text{m}$, suggesting that P4VP wrapping improved dispersion and provided steric stabilization through polymer-assisted surface modification. After carbonization, N-doped PCC (10:1) showed $14.1 \pm 20.6\text{ }\mu\text{m}$, which is attributed to partial re-aggregation and mild fragmentation during the pyrolytic conversion of P4VP into N-doped carbon.^{62,63} These results collectively confirm that P4VP wrapping promotes uniform dispersion and steric stabilization, while subsequent carbonization induces controlled structural densification and pore opening with minimal collapse.

The crystalline structure and graphitization degree of the carbonized composites were analyzed by XRD (Fig. 2a). PCC and N-doped PCC (10:1) and (20:1), exhibited a sharp (002) peak characteristic of graphitic carbon near 25.4° . Notably, the domain spacing remained nearly constant ($\sim 0.35\text{ nm}$) regardless of the N-doping ratio introduced *via* P4VP. XPS analysis of the resulting carbon materials revealed that PCC contained no detectable N species, whereas N-doped PCC (10:1) and (20:1) exhibited prominent N functionalities (Fig. 2d–f). Moreover, elemental analysis confirmed that N-doped PCC (10:1) had a higher N content (1.68 at%) than N-doped PCC (20:1) (0.91 at%), reflecting the reduced availability of N precursor at the higher PCC/P4VP ratio (Table S2). To further investigate the adsorption behavior, P4VP samples with varying M_n were employed under identical conditions. The resulting N-doped PCCs exhibited a dependence of N content on M_n , with the highest incorporation observed for P4VP (Table S3). This trend implies that balanced chain mobility and surface affinity are crucial for effective adsorption of P4VP onto PCC, ultimately leading to optimized N doping during carbonization. Specifically, pyridinic N (40% and 36%) and graphitic N (32% and 37%) were the dominant N configurations in N-doped PCCs, with these proportions calculated relative to

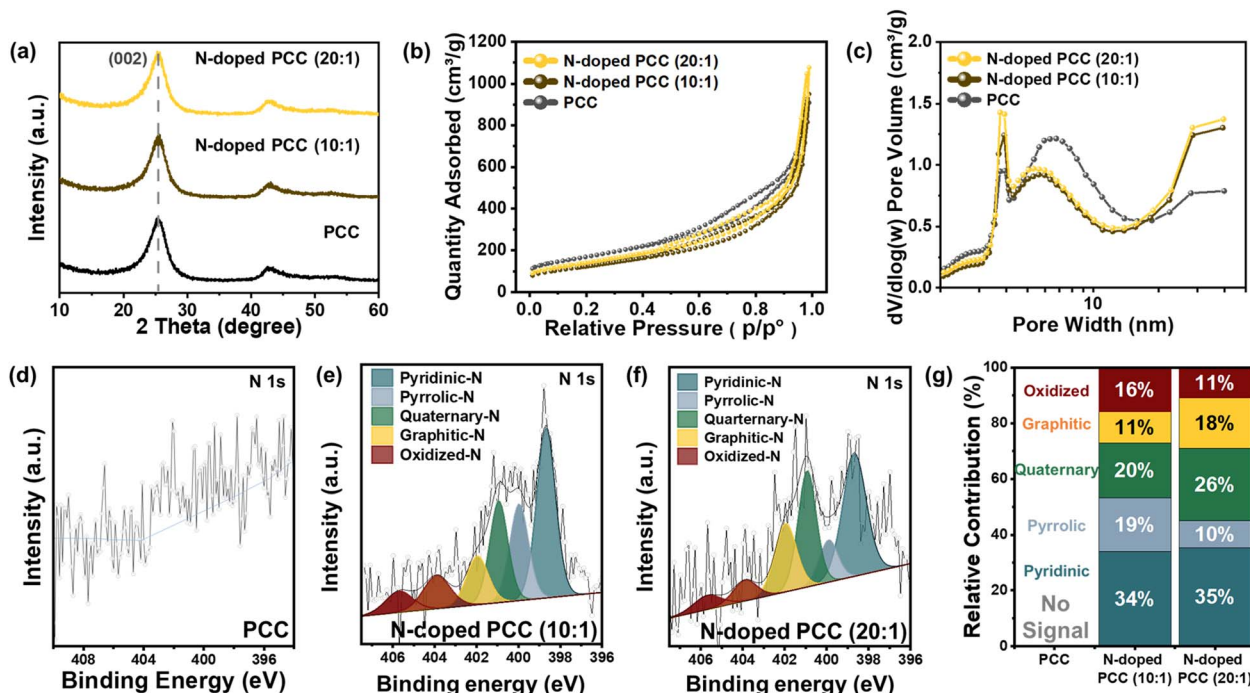


Fig. 2 Characterization of PCC and N-doped PCC prior to Pt catalyst loading. (a) XRD patterns, (b) N_2 -sorption isotherms, and (c) pore size distribution curves obtained from BJH desorption analysis. High-resolution N 1s XPS spectra of (d) PCC, (e) N-doped PCC (10:1), and (f) N-doped PCC (20:1). (g) Relative contribution of N species (%) derived from N 1s deconvolution.

the total N content (Fig. 2g). This suggests that although the overall crystallinity of PCC was preserved, N incorporation occurred primarily at the surface.

To confirm that the selective N doping originates from the use of the P4VP polymer, XPS analyses were conducted on samples carbonized at various temperatures (Fig. S7). The results revealed that the evolution of pyridinic and graphitic N species is predominantly governed by the presence of P4VP rather than by the pyrolysis temperature itself. In addition, a control experiment using monomeric pyrrole under identical conditions showed negligible N incorporation (Fig. S8), highlighting the essential role of the polymeric P4VP layer in facilitating N retention. The thermal stability and intimate interfacial contact of P4VP with the carbon surface enable progressive N fixation during carbonization, thereby selectively yielding pyridinic and graphitic N functionalities.

Their textural properties were characterized by N_2 -sorption isotherms (Fig. 2b). The BET surface area of PCC was $600.1 \text{ m}^2 \text{ g}^{-1}$, which decreased to $446.5 \text{ m}^2 \text{ g}^{-1}$ for N-doped PCC (10:1) and further to $399.5 \text{ m}^2 \text{ g}^{-1}$ for N-doped PCC (20:1) (Table S4). This reduction in surface area is primarily attributed to partial pore blockage and framework densification occurring during polymer adsorption and subsequent carbonization, where the P4VP precursor occupies micropores and induces minor structural contraction within the carbon matrix.^{61,64} The t -plot analysis further revealed that the surface area loss mainly originated from micropores ($< 2 \text{ nm}$), while the average pore width increased from 8.1 nm to approximately $9.3\text{--}9.7 \text{ nm}$. This indicates that N doping suppresses microporosity and induces

a slight structural rearrangement toward a more mesopore-dominant architecture. The pore size distribution analyzed using the Barrett-Joyner-Halenda (BJH) method in Fig. 2c, indicated that PCC contained both $3\text{--}4 \text{ nm}$ mesopores and a secondary distribution near 8 nm . Upon N doping, the proportion of $3\text{--}4 \text{ nm}$ mesopores increased, while larger mesopores around 8 nm diminished, likely due to polymer adsorption and structural rearrangement during thermal treatment, which altered the pore architecture.^{33,65,66} Such evolution in pore structure is advantageous for mass transport, as excessive microporosity often traps water and electrolytes, increasing diffusion resistance under high-current operation.^{67,68} In contrast, the preserved mesoporous channels facilitate reactant/product diffusion and ionomer penetration within the catalyst layer, ensuring efficient triple-phase boundary formation.

Furthermore, to verify the broader applicability of the P4VP-assisted N-doping strategy, the same process was applied to other porous carbons with distinct pore structures and surface areas (A4 and FB, The Carbon Studio Inc.). As detailed in Tables S5, S6 and Fig. S9, both carbons successfully incorporated N species despite their structural differences, confirming that this approach is not limited to PCC but can be universally extended to other crystalline or porous carbon frameworks.

3.2 Characterization of Pt/N-doped PCCs

Pt deposition onto N-doped PCC was carried out *via* the polyol method,⁶⁹ yielding Pt/N-doped PCC. The Pt loading, determined by ICP-OES, was $46.7 \text{ wt\%}$ and $45.5 \text{ wt\%}$ for the 10:1 and 20:1

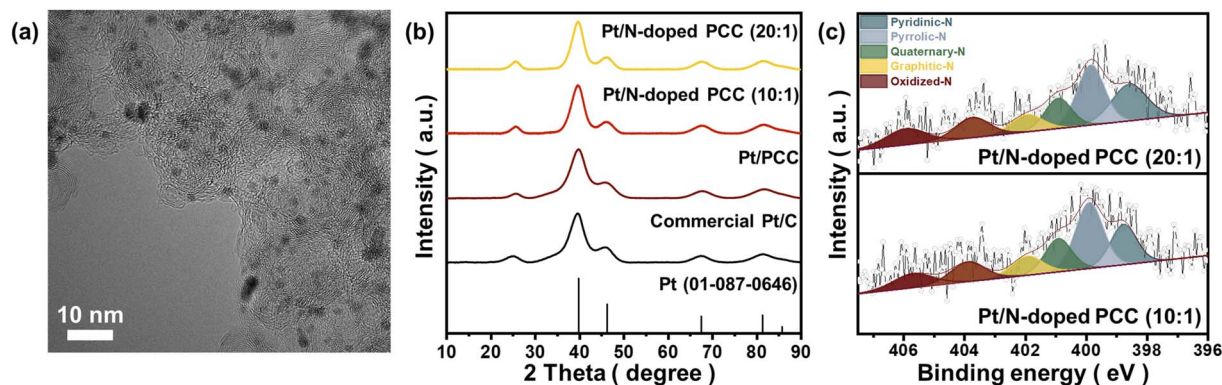


Fig. 3 Structural and chemical characterization of Pt/N-doped PCC. (a) TEM image of Pt/N-doped PCC (20:1). (b) XRD patterns of commercial Pt/C, Pt/PCC, and Pt/N-doped PCC (10:1, 20:1), with Pt reference peaks (JCPDS No. 01-087-0646). (c) N 1s XPS spectra of Pt/N-doped PCC (10:1, 20:1).

samples, respectively. TEM images of Pt/N-doped PCC (20:1) and Pt/N-doped PCC (10:1) reveal that Pt nanoparticles are uniformly distributed on the N-doped PCC support, with an average particle size of 2.06 ± 0.43 , 4.88 ± 1.15 nm, respectively (Fig. 3a and S10). As discussed from the BET results, the smaller Pt particle size in the 20:1 sample originates from its thinner polymer coating and lower degree of pore blockage. These structural features expose more surface N functionalities, particularly pyridinic N, which promote uniform Pt nucleation.^{70,71} In contrast, excess P4VP in the 10:1 sample fills micropores and embeds part of the N species within the carbon framework, reducing the number of accessible coordination sites. Consequently, larger Pt nanoparticles are formed in the 10:1 sample despite its higher overall N content. EDS mapping confirms the homogeneous distribution of Pt (red), C (green), and N (blue) within the catalyst, highlighting the effective interaction between Pt and the N-doped carbon matrix (Fig. S11 and Table S7). To further investigate the effect of N doping, XRD patterns were conducted on the Pt phase (Fig. 3b). Diffraction peaks corresponding to Pt (111) and Pt (200) appeared in all samples, with the Pt (111) peak shifting to a higher diffraction angle in Pt/N-doped PCC (20:1) (39.8°) compared to Pt/N-doped PCC (10:1) and commercial Pt/C (39.7°). This shift suggests a lattice contraction effect, likely induced by electron density redistribution from N doping, which enhances metal-support interactions and potentially improves catalytic stability. The strengthened metal-support interactions in N-doped PCCs may contribute to improved Pt dispersion and stability,⁷² further enhancing the catalytic durability of Pt/N-doped PCC (20:1).

In addition, XPS analysis was conducted to elucidate the electronic effects of N doping on Pt nanoparticles (Fig. 3c and S12). The C 1s and O 1s spectra confirmed consistent chemical environments across all samples (Fig. S12a and b). In contrast, the Pt 4f spectra exhibited characteristic symmetric doublets corresponding to metallic Pt⁰ (Fig. S12c and Table S8). The Pt⁰ content in Pt/N-doped PCC (10:1), Pt/N-doped PCC (20:1), and Pt/N-doped PCC catalysts was approximately 32.9% and 25.6% higher, respectively, than that of the commercial Pt/C catalyst. This result indicates that the N-doped carbon support effectively donates electron density to the Pt nanoparticles, thereby

stabilizing Pt in a more metallic state.^{61,66,73–75} Such electronic interactions are considered to contribute to the enhanced electrochemical activity of the catalyst. The N 1s spectra of the Pt/N-doped PCCs (Fig. 3c) revealed that pyridinic N (18.7% and 23.0%) and pyrrolic N (32.1% and 29.0%) were the dominant N species in Pt/N-doped PCC (10:1) and (20:1), respectively. Notably, the binding energy shifts for each N species after Pt loading were minimal (<0.1 eV), indicating that the electronic environment of the N sites remained largely unchanged and suggesting a uniform distribution of Pt nanoparticles among the different N species.⁶⁶ Accordingly, pyridinic N sites are expected to promote strong orbital hybridization with Pt nanoparticles, enhancing their dispersion and anchoring stability against agglomeration. In addition, pyrrolic N is believed to facilitate interfacial charge transfer, contributing to the electronic stabilization of Pt.^{73,76–79}

3.3 Electrochemical performance and durability of Pt/N-doped PCCs

The ORR kinetic performance of the Pt/N-doped PCC catalysts was evaluated using a conventional three-electrode RRDE system. CV and LSV measurements were conducted in a 0.1 M HClO₄ solution. At 0.9 V_{RHE} with *i*R correction, the catalysts exhibited initial mass activities of 0.10, 0.16, and 0.19 A mg_{Pt}^{−1} for Pt/PCC, Pt/N-doped PCC (10:1) and Pt/N-doped PCC (20:1), respectively, which are comparable to the commercial Pt/C (0.18 A mg_{Pt}^{−1}) (Fig. 4). Moreover, the half-wave potentials of all three catalysts were similar to that of commercial Pt/C, indicating that PCC-based catalysts effectively preserve the intrinsic electrochemical activity of Pt. Overall, the ORR activity of all PCC-based catalysts, independent of N doping, is comparable to that of commercial Pt/C, indicating that N doping exerts minimal influence on the intrinsic catalytic performance of Pt in acidic media. This trend aligns with previous studies by Ma *et al.*⁶⁶ and Hornberger *et al.*,⁷⁰ which similarly reported negligible differences in half-cell ORR activity among Pt catalysts supported on N-doped and undoped carbon materials.

PEMFC performance was evaluated using single cells incorporating Pt/N-doped PCC catalysts, with commercial Pt/C and Pt/PCC serving as a reference. The Pt loading on the cathode

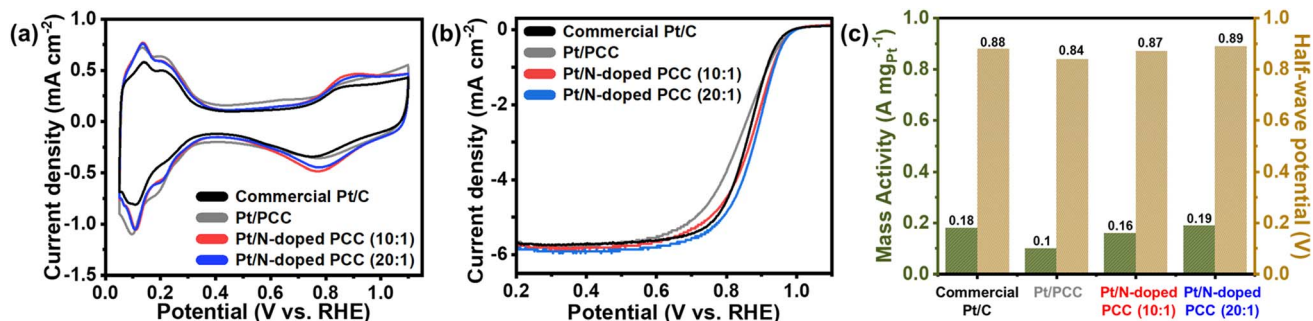


Fig. 4 (a) CV and (b) LSV curves of commercial Pt/PCC and Pt/N-doped PCCs in 0.1 M HClO₄. (c) Comparison of mass activity at 0.9 V (green) and half-wave potential (orange).

was fixed at 0.2 mg_{Pt} cm⁻² for all MEAs. Fig. 5b and c show the *I*-*V* polarization and power density curves measured under H₂/O₂ at 40% RH, simulating practical automotive conditions. The

maximum power densities were 834, 446, 696, and 789 mW cm⁻² for the commercial Pt/C, Pt/PCC, Pt/N-doped PCC (10:1), and Pt/N-doped PCC (20:1), respectively. Notably, the Pt/N-

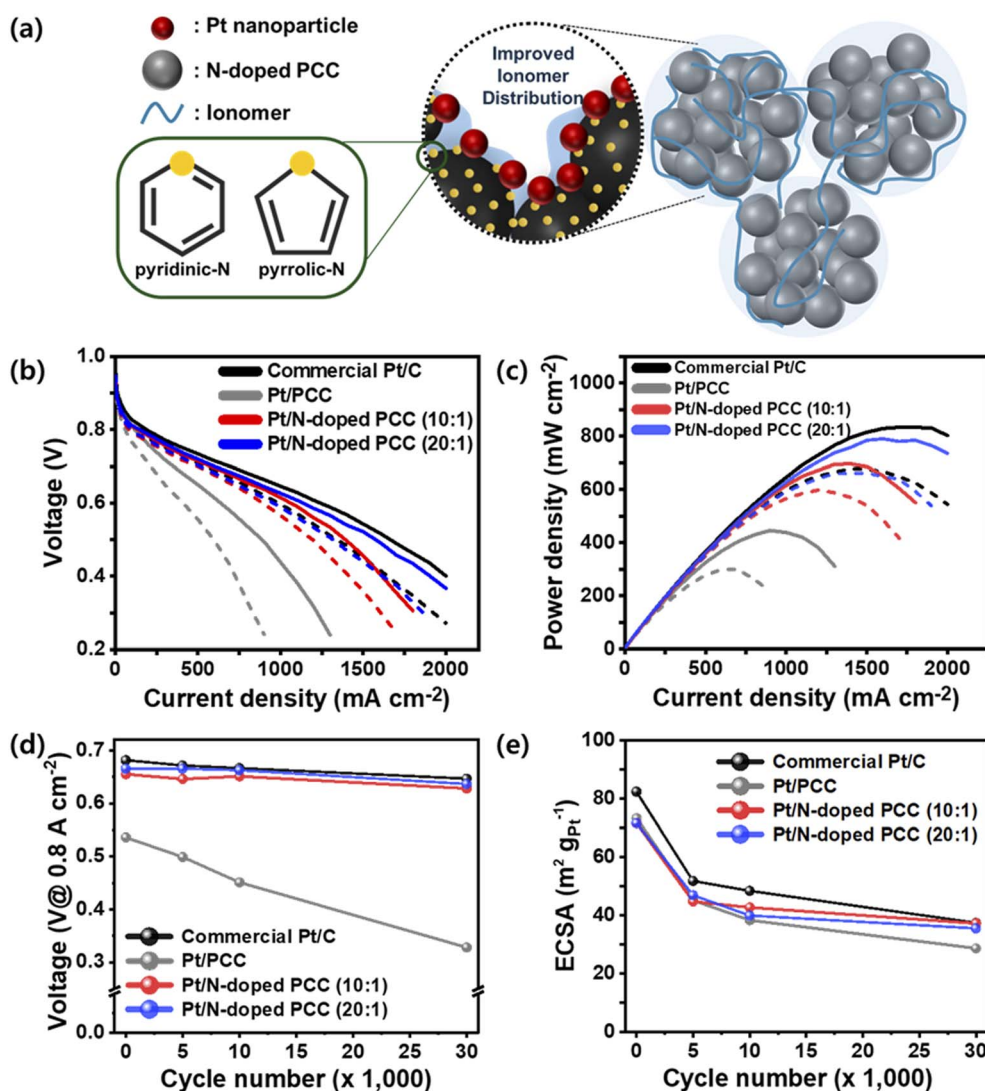


Fig. 5 (a) Schematic illustration of the Pt/PCC and Pt/N-doped PCC catalyst structures. Single-cell performance at 40% RH: (b) polarization (*I*-*V*) and (c) power density curves at BOL (solid lines) and EOL (dashed lines). Durability evaluation: (d) voltage retention at 0.8 A cm⁻² and (e) ECSA degradation over cycles.

doped PCC (20:1) demonstrated a 43.5% higher power density than Pt/PCC, achieving a performance level comparable to that of commercial Pt/C. A clear improvement in performance at high-current-density performance was observed with increasing N content in the carbon support, from Pt/PCC to Pt/N-doped PCC (10:1) and Pt/N-doped PCC (20:1). This trend indicates that N functionalities on the carbon surface enhance oxygen mass transport, likely by promoting a more uniform ionomer distribution within the catalyst layer,^{80,81} as illustrated in Fig. 5a. Specifically, coulombic interactions between N dopants (such as pyridinic N and graphitic N) and the ionomer are known to reduce local oxygen transport resistance, particularly under low-humidity conditions.^{76,80,81}

For long-term durability evaluation, an accelerated stress test (AST) was conducted following the DOE protocol, cycling the cell potential between 0.6 and 1.0 V at 40% RH for 30 000 cycles (Fig. S13). After cycling, the maximum power densities decreased to 678, 299, 598, and 660 mW cm⁻² for commercial Pt/C, Pt/PCC, Pt/N-doped PCC (10:1), and (20:1), respectively. Pt/PCC exhibited the most severe degradation (32.9% loss), whereas Pt/N-doped PCC (20:1) retained 83.6% of its initial performance. This durability trend was further supported by the electrochemical active surface area (ECSA) values after cycling, as shown in Fig. 5e. The ECSA was evaluated from hydrogen adsorption/desorption regions obtained *via* CV performed on the MEA under N₂-saturated conditions (Fig. S14). After the AST, the ECSAs were reduced to 37.7, 28.4, 37.2, and 35.4 m² g_{Pt}⁻¹, respectively, corresponding to losses of 56.1%, 61.3%, 48.0%, and 50.5% from their initial values. The greatest ECSA loss occurred for Pt/PCC, indicating significant Pt nanoparticle agglomeration during AST. In contrast, the Pt/N-doped PCC catalysts exhibited relatively lower ECSA degradation, maintaining values comparable to commercial Pt/C. This improved ECSA retention is attributed to the presence of N functional groups, which modulate the local electronic structure of the carbon support and strengthen the interaction between Pt nanoparticles and the support. These effects suppress Pt dissolution and aggregation, thereby enhancing the structural stability of the catalyst under PEMFC operating conditions. The enhanced long-term durability can be ascribed to the coordination between Pt nanoparticles and pyridinic N sites in the carbon support.^{70,76} Pyridinic N provides lone-pair electrons to Pt atoms, forming interfacial Pt–N bonds that strengthen metal–support interactions and suppress nanoparticle migration, agglomeration, and dissolution during potential cycling. This anchoring effect accounts for the superior ECSA retention and minimal voltage loss observed after 30 000 cycles. These results are further supported by theoretical studies reporting that N dopants stabilize Pt nanoparticles through strengthened Pt–N–C bonding and interfacial electronic modulation.^{30,66,82} Notably, the Pt/N-doped PCC (20:1) catalyst maintained a high fraction of its initial ECSA and exhibited strong voltage and power stability even after 30 000 cycles, confirming the beneficial impact of N doping on both catalyst activity and durability.

Electrochemical impedance spectroscopy (EIS) was performed to evaluate the interfacial and transport properties of the MEAs (Fig. S15). The N-doped catalyst showed a significantly lower

charge-transfer resistance ($R_{ct} = 3.39$ m Ω) compared with the undoped Pt/PCC ($R_{ct} \geq 5.02$ m Ω), indicating that N incorporation effectively reduces interfacial resistance and facilitates faster electrochemical kinetics.⁸³ Moreover, the EIS spectra revealed a more ideal Warburg-type diffusion behavior for Pt/N-doped PCC (20:1), suggesting enhanced oxygen transport and mitigated mass-transfer losses. These results collectively demonstrate that N doping improves both ionic and gaseous transport across the catalyst layer, thereby leading to superior single-cell performance.^{84,85}

4 Conclusions

We developed N-doped PCC support derived from physically adsorbed P4VP for use as a highly durable PEMFC cathode catalyst. Through a simple and scalable blending strategy followed by thermal treatment, N functionalities were selectively introduced onto the PCC surface without compromising its structural properties. The resulting N-doped PCC enabled the uniform deposition of Pt nanoparticles, yielding catalysts with enhanced oxygen mass transport and metal–support interactions. Importantly, increasing N content from PCC to N-doped PCC (10:1) and (20:1) resulted in progressively improved single-cell performance, particularly at high current densities under dry (40% RH) conditions. These enhancements were attributed to favorable interactions between N species and the ionomer, which facilitated homogeneous ionomer distribution and reduced local oxygen transport resistance. The Pt/N-doped PCC (20:1) catalysts exhibited superior power density and long-term durability, retaining up to 95.9% of their initial voltage after 30 000 cycles under DOE stress testing protocols. These results underscore the effectiveness of polymer-assisted N doping as a viable strategy for engineering advanced carbon supports, and provide valuable insights into the design of high-performance fuel cell electrocatalysts.

Author contributions

Yoon-A Jang: writing—original draft, methodology, investigation, data curation, conceptualization. Daehyeon Seo: investigation, formal analysis, data curation. Taewook Kim: methodology, investigation, formal analysis, data curation. Jae Hyun Park: formal analysis, data curation. Youngkyu Bae: data curation. Gilhwan Lee: data curation. Young Jun Lee: writing—review & editing, supervision, project administration, funding acquisition, conceptualization. Chan Ho Park: writing—review & editing, visualization, project administration, funding acquisition, conceptualization.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this article have been included as part of the of the supplementary information (SI). Supplementary information: detailed experimental procedures, additional

characterization data (NMR, FTIR, TGA, SEM, TEM, STEM-HAADF, XPS, BET analyses), supplementary electrochemical measurements (polarization curves, CV, and EIS), and supporting figures and tables that further substantiate the findings presented in the main manuscript. See DOI: <https://doi.org/10.1039/d5ta08085a>.

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