Designing fuel cell catalyst support for superior catalytic activity and low mass-transport resistance

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The development of low-Platinum content polymer electrolyte fuel cells (PEFCs) has been hindered by inexplicable reduction of oxygen reduction reaction (ORR) activity and unexpected O2 mass transport resistance when catalysts have been interfaced with ionomer in a cathode catalyst layer. In this study, we introduce a bottom-up designed spherical carbon support with intrinsic Nitrogen-doping that permits uniform dispersion of Pt catalyst, which reproducibly exhibits high ORR mass activity of 638 ± 68 mA mgPt\textsuperscript{-1} at 0.9 V and 100% relative humidity (RH) in a membrane electrode assembly. The uniformly distributed Nitrogen-functional surface groups on the carbon support surface promote high ionomer coverage directly evidenced by high-resolution electron microscopy and nearly humidity-independent double layer capacitance. The hydrophilic nature of the carbon surface appears to ensure high activity and performance for operation over a broad range of RH. The paradigm challenging large carbon support (~135 nm) combined with favourable ionomer film structure, hypothesized recently to arise from the interactions of an ionic moiety of the ionomer and Nitrogen-functional group of the catalyst support, results in an unprecedented low local oxygen transport resistance (5.0 s cm\textsuperscript{-1}) for ultra-low Pt loading (34 ± 2 μgPt cm\textsuperscript{-2}) catalyst layer.

Hydrogen fuel cells are experiencing a resurgence as zero-emission power source for vehicles, especially mid-size and heavy-duty vehicles and light railway transits. For large-scale commercialization, a key developmental target for these polymer electrolyte fuel cells (PEFCs) is to reduce the expensive Platinum (Pt) catalyst loading in a 100 kW stack from 30 g to <10 g. To attain this target, we need: (a) a catalyst with high mass activity for oxygen reduction reaction (ORR)\textsuperscript{1-3} to reduce kinetic losses, (b) a catalyst layer (CL) microstructure designed for facile oxygen transport to mitigate the unexpectedly high local transport losses observed in low-Pt loading CLs\textsuperscript{4,5} and (c) a high coverage of ionomer to ensure proton accessibility of the catalyst sites to maximize Pt utilization. Independent studies by General Motors, Toyota, and Nissan researchers showed that reduction of total Pt loading in the cathode (<0.1 mgPt cm\textsuperscript{-2}) to attain lower Pt content in a stack resulted in a surprisingly much lower cell performance and an increased O2 transport resistance beyond what would be expected due lower amount of catalyst\textsuperscript{4-9}. This drove the development of several new catalysts, including alloys and shape-controlled nanoparticles with impressive oxygen reduction reaction (ORR) activity (20× activity of pure Pt catalyst) in liquid electrolyte\textsuperscript{10-12}. Inexplicably, these catalysts have failed to exhibit the same high ORR activity in the membrane electrode assembly (MEA) of a fuel cell\textsuperscript{11}. Concerns regarding the retention of the physical structure (nanoframe catalysts) or the chemical features (alloy composition, core-shell architecture) upon their
integration in a CL have also been raised. A promising alternative that can alleviate these concerns is the use of high activity, pure Pt catalyst tailored for its particle size within the 1.8-3 nm range to maximize surface sites with generalized coordination number (GCN) between 7.5 and 8.3. Separately, recent studies by Strasser and Gasteiger groups postulate that Nitrogen-functionalized carbon (N-C) support for Pt improves both ionomer coverage and local oxygen transport resistance, and another very recent study by the Toyota group reports that upon coating Pt/C catalysts with ~1 nm dopamine layer, the mass activity was enhanced but the local oxygen transport resistance increased. Yet, the use of 20–30 nm carbon black as catalyst support has remained unchanged. Such small catalyst support particles limit the CL pores to dimensions comparable to the mean free path length of oxygen ($\lambda_{O_2}$), thereby constraining the gas-phase oxygen transport in a CL to occur by the restrictive Knudsen diffusion. Lack of surface functional groups or non-uniform distribution of surface functional groups result in non-uniform ionomer coverage of the Pt/C catalyst, which further limit the proton accessibility of Pt catalyst under low RH (dry) conditions. Bottom Panel: To mitigate these issues, a NH$_2$-containing small molecule is polymerized to create large spherical particles with well-distributed N-functional group on the particle surface. The particle is carbonized prior to Pt deposition. The uniformly distributed N-functional groups on carbonized particles enable deposition of uniformly distributed Pt and size-controlled nanoparticles with large Pt-Pt interparticle distance ($l_{Pt-Pt}$) which addresses territory effect. Large carbon support results in large pores improving gaseous oxygen transport while the uniformly distributed N-functional groups hypothesized to have favorable interaction with the ionomer induces high ionomer coverage, which improves catalyst utilization.

**Catalyst support development**

Uniformly sized polymerized dopamine (PDA) particles spherical in shape and 215 ± 11 (SD) nm in diameter (Fig. 2a) are synthesized by a facile, one-step aerobic polymerization method optimized for size and poly-dispersity control (details in method section). TEM image (Fig. 2b) confirmed that the shape and structure of the PDA nanoparticles were retained upon carbonization. However, the carbonized PDA (cPDA) nanoparticles were smaller compared to the PDA nanoparticles, i.e., a 37% reduction from 215 nm to 135 nm. A previous study utilizing high-resolution TEM and Raman spectroscopy had revealed that cPDA nanoparticles possess graphite-like nanostructure consisting of several tens of stacking carbon layers. Upon carbonization, the Brunauer–Emmett–Teller (BET) surface area of PDA particles increased from 17 m$^2$ g$^{-1}$ to 365 m$^2$ g$^{-1}$, as indicated by N$_2$-adsorption data (Supplementary Table S1). The micro/meso-pores contributed to -82% of the total BET surface area of cPDA (Supplementary Table S1).

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**Fig 1** | Schematic diagram depicting the bottlenecks of conventional CL and new catalyst design strategy. Top Panel: In conventional Pt/C catalysts, Pt nanoparticles are distributed non-uniformly due to the non-uniform surface functional group, which results in low platinum interparticle distance ($l_{Pt-Pt}$) inducing territory effect that leads to reduced mass specific activity and poor catalyst utilization at high current densities. The usage of small carbon particles (20–40 nm) results in catalyst layers with small pore diameter ($d_{pore}$), which leads to restrictive gas-phase oxygen transport dominated by Knudsen diffusion. Lack of surface functional groups or non-uniform distribution of surface functional groups result in non-uniform ionomer coverage of the Pt/C catalyst, which further limit the
The bottom-up approach of creating catalyst support particles using N-containing precursor ensures uniformly distributed Nitrogen groups on the cPDA surface. The TEM/EDS images (Fig. 2c–e) confirm the uniform distribution of Nitrogen on the cPDA spheres. This homogenous distribution of N-species plays an instrumental role in the uniform spatial distribution of Pt particles during the catalyst deposit process, leading to high inter-particle distance (l_{Pt-Pt}). Identification of N-functional groups by X-ray photoelectron spectra (XPS) also revealed the chemical changes upon carbonization of PDA and subsequent interaction of Pt with cPDA. XPS survey spectra (Supplementary Fig. S2a) reveals the presence of N 1s (~400 eV), C 1s (~284 eV), and O 1s (~532 eV) peaks for all the samples, and Pt 4f (~72 eV) as well as Pt 4d (~314 eV) peaks for Pt/cPDA sample. High-resolution XPS spectra permitted deconvolution of Cls, O1s and Pt 4f peaks (Supplementary Fig. S2b–d) as well as of N 1s peak, which led to the identification of Nitrogen functional groups (Fig. 2f) — pyridinic (~398 eV), amino (~399 eV), pyrrolic (~400.5 eV) and graphitic (~401.5 eV)24,25. Quantitative analyses of the peaks (Fig. 2g) reveal that PDA carbonization resulted in a dramatic decrease in amino groups, a slight increase in the pyrrolic group and an evolution of the graphitic-N group, whereas the pyridinic remained relatively unchanged. Subsequent Pt deposition caused a slight positive shift in pyridinic peak and a significant shift in graphitic-N peak, which arises from Pt-N interactions resulting in a decrease in electron density of the neighboring atom manifesting as an increase in binding energy and peak shift.

Pt/cPDA catalyst characterization

The synthesized Pt/cPDA catalyst were characterized for key physical properties to ascertain that first of the four design targets, i.e., high Pt dispersion and size control in 2–3 nm range, was achieved. In addition, the location of Pt catalyst (surface versus embedding within micropores of cPDA) and the Pt content on cPDA were determined.

The uniform distribution of Nitrogen-rich moieties (3.5 at% – from XPS data) and pyridinic type Nitrogen on the cPDA surface are expected to induce uniform nucleation of Pt, resulting in high spatial dispersion of Pt nanoparticles26,27 and controlled Pt size. TEM micrograph (Fig. 3a) of Pt nanoparticles deposited cPDA nanospheres provides direct evidence of very well-dispersed Pt nanoparticles. The average inter-particle distance (AID) calculated via equation S1 (see Supplementary information) developed by Meier et al.28 yields a value of ~26 nm for Pt/cPDA, which is larger than the ~16 nm AID for commercial Pt/C (TJK 10 wt% Pt on Vulcan carbon) catalyst. For poorly dispersed catalysts with short Pt-to-Pt nearest neighbor distance (l_{Pt-Pt}) or AID < 20, the effective ORR activity is adversely affected by the so-called territory effect, first proposed by Watanabe and colleagues29. The physical location of Pt particles determines if they interface with ionomer or not, depending on whether they are on the carbon support surface or embedded within micropores. Pt particles, if present in micropores are not prone to poisoning by the sulfonic group of the ionomer, thereby are thought to exhibit higher activity, but such Pt catalyst particles may have proton accessibility problems29,30. The 3D TEM of Pt/cPDA catalysts confirmed that the Pt particles were located on the surface of the cPDA support and not within the micropores (see video as supplementary information). STEM images of a ~100 nm thin microtomed CL slice (Fig. 3d and Fig. 5I) show cross-sections of the cPDA particles with Pt placed only on the surface of the particles and their absence inside the cPDA support.
Another design target for our Pt/cPDA catalyst is to control the Pt particle size to a range of 2–3 nm, which was determined from a theoretical study to possess the highest ORR activity. The TEM image analyses of the Pt/cPDA catalyst (Fig. 3b) revealed that a majority of the particles are in the 1.8–2.5 nm range, which is expected to exhibit the high mass activity of 0.9–1.2 A mgPt−1 as per the GCN correlation. The Pt surface area computed from this size distribution was determined to be 117 m2 gPt−1, which was close to the value of 107 ± 4 m2 gPt−1 (via H2 ads) obtained from ECSA measurement of the ionomer-free catalyst in 0.1 M HClO4 electrolyte. The Pt content of Pt/cPDA catalyst (wt% Pt in Pt+cPDA), required for ECSA calculation, was determined from thermogravimetric analyses (Fig. 3c, Table S2). The Pt content of two commercial Pt/C TKK with supplier stated Pt loadings of 10.2 and 19.8% catalysts for the determination of Pt content (details in supplementary information), and STEM images of micromted Pt/cPDA CL in (i) and (ii) dark field and (iii) bright field mode. The marked regions are the cross-section of Pt/cPDA catalysts highlighting that the Pt particles are located at the exterior of the cPDA support.

**Characterization of Pt/cPDA CLs**

Successful implementation of our catalyst design strategy should manifest in a Pt/cPDA catalyst layer that exhibits: (i) high ionomer coverage arising from favorable interaction between ionomer and N-containing group, (ii) high ORR activity in MEA (and not merely in the liquid electrolyte) and (iii) improved local oxygen transport resistance.

STEM/EDX mapping reveals a Fluorine signal over the Pt/cPDA particles indicating high ionomer coverage (Fig. 4a). The double layer capacitance (Cdl) determined from the cyclic voltammograms in MEA over 30–100% RH range (Fig. 4b) indicates that Cdl remain almost unchanged (-1 F m−2 cPDA) further indicating well hydrated Pt/cPDA-ionomer interfacial structure. This value is also within 10% of the Cdl determined by CV in HClO4, where support accessibility by electrolyte is maximum. The weak dependency of ECSA on RH also supports the high ionomer coverage. The ECSA in MEA was 113 m2 gPt−1 via CO stripping (101 ± 5 m2 gPt−1 via H2 ads) and 70 m2 gPt−1 (via CO stripping) for Pt/cPDA and commercial Pt/C catalyst (TKK 10 wt% Pt/C), respectively. The ECSA of Pt/cPDA calculated from TEM-based average particle size is around 117 m2 gPt−1, almost similar compared to the ECSAMEA and ECSAh2O/Liquid electrolyte. The dry proton accessibility (ECSA(decay)) was calculated to be ~80% (using CO stripping; Fig. S13) for Pt/cPDA CL compared to ~70% for TKK Pt/C CL. A dry proton accessibility value of 0.8 compared to that of 0.7 for TKK Pt/C CL might indicate higher ionomer coverage or more homogeneous ionomer distribution in the Pt/cPDA CL. Similar dry proton accessibility (80%) has also been reported by Padgett et al. for 10 wt% Pt/V sample. However, the CL composition was different—Padgett et al. employed a higher ionomer to carbon ratio (0.95 vs 0.8 in this study), and the ionomer had a shorter side chain ionomer (EW-950 vs 1100). The hydrophilic nature of cPDA, likely due to N-functional groups, as noted by spreading of water on a layer of particle, may help to keep the ionomer/Pt and ionomer/cPDA interfaces well hydrated. Thus, the slightly high ionomer coverage coupled with the hydrophilic nature of support is expected to result in a well-hydrated Pt/ionomer interface even in dry conditions facilitating the proton accessibility to most of the Pt particles.

A critical design target for the developed Pt/cPDA catalyst is the attainment of high ORR activity in MEA under fuel cell conditions. ORR activity for ionomer-free Pt/cPDA (in 0.1 M HClO4) determined from rotating disk electrode measurements yielded specific and mass activity of 0.95 ± 0.07 mA cmPt−2 and 944 ± 10 mA mgPt−1 (Supplementary Fig. S7, Table S4), respectively at 0.9 V in O2 saturated electrolyte. Upon incorporation in MEA, Pt/cPDA exhibited area-specific and mass activity of 0.632 ± 0.06 mA cmPt−2 and 638 ± 68 mA mgPt−1 (Fig. 4c, Table S6) at 0.9 V in a fuel cell operated
at 70 °C, 100% RH and 140 kPa\textsubscript{abs} pressure in O\textsubscript{2}, which exceeds the DOE target (0.44 A mgPt\textsuperscript{−1}). A comparison with other Pt-based catalysts reported further confirms the impressive attribute of Pt/cPDA catalysts (Fig. 4d). Pt/cPDA illustrated almost 1.7 times higher activity compared to the next best-reported activity of 372 mA mgPt\textsuperscript{−1} at 0.9 V in a liquid electrolyte (0.1 M HClO\textsubscript{4}), as evident from the comparison of activity between ionomer-free and ionomer-containing catalysts reported in literature\textsuperscript{16,17,31,36}. The exact role of cPDA support in minimizing the activity suppression is not fully understood and may be due either to the ionomer/cPDA interactions\textsuperscript{16} or to the larger pores of CL and better O\textsubscript{2} transport in the ionomer coating the catalyst/support. The Pt/cPDA catalyst in MEA condition\textsuperscript{17} was assumed to be 150 kPa\textsubscript{abs} operating pressure was not mentioned; \textsuperscript{18} measured at 300 kPa\textsubscript{abs}, recalculated at 150 kPa\textsubscript{abs} following the method explained in ref. 49. The error bar in red deviation from the average of data from three individual testing, except for the mass transport resistance (e), which was repeated twice.

The last design target for Pt/cPDA catalyst is the realization of low local oxygen transport resistance (R\textsubscript{O2}) hypothesized to result from the combined effect of enhanced gas phase mass transport in the larger pores of CL and better O\textsubscript{2} transport in the ionomer film with better permeability hypothesized to arise from the open structure of ionomer film due to N-functional group/ionomer interactions\textsuperscript{16}. Limiting current measurements\textsuperscript{40} for a range of O\textsubscript{2} concentration (2−6 mol%) and several total pressure (140−290 kPa) was undertaken at 80% RH to quantify O\textsubscript{2} transport characteristics—total (R\textsubscript{O2, total}), pressure-dependent (R\textsubscript{O2, dep}), and -independent (R\textsubscript{O2, ind}) oxygen transport resistances (Fig. S21). The breakdown of R\textsubscript{O2, total} and calculation of R\textsubscript{O2, dep} and (R\textsubscript{O2, ind}) is shown in Equations S4, S5 and S6 in Supplementary Information. Many different factors, including porous transport layer (carbon paper), flow-field configuration and catalyst layer microstructure, influence the cell oxygen transport resistance (and overall cell performance), as briefly discussed in Supplementary Information. Thus, a comparison of total R\textsubscript{O2} is not meaningful unless similar component materials and cell design were accounted for. It has been emphasized in the literature that the main concern with low-Pt content cathodes (especially when the roughness factor falls below 50) is the unusually high pressure-independent transport resistance (R\textsubscript{dep} which is the cumulative effect of gas-phase Knudsen diffusion in the CL and the microporous layer as well as of O\textsubscript{2} transfer/transport in ionomer film coating the catalyst/support. The R\textsubscript{O2, dep} for Pt/cPDA CL is the lowest compared with other low Pt-loaded electrodes reported in the literature\textsuperscript{3,9,18,17,36}. The Pt/cPDA CL also exhibited significantly lower pressure-dependent R\textsubscript{O2, dep} transport resistance (0.25 ± 0.04 s cm\textsuperscript{−1}).
compared to the in-house CL made with commercial Pt/C TKK 10 wt% catalyst (−0.55 s cm⁻²) (Fig. 4e). The pressure-independent O₂ transport resistance of Pt/cPDA CL is even lower than those reported for Pt supported on N-functionalized KB CLs (Fig. 4d) reported in recent works despite having lower Pt loading (0.034 mgPt cm⁻² compared to that 0.1 mgPt cm⁻²). Remarkably, the Ω²⁰₂ for Pt/cPDA CL at different roughness factor (Fig. S21d) is significantly lower than those pure-Pt based CL with similar low RF or low-Pt loading. In fact, it appears that the Fig. S21d) is significantly lower than those pure-Pt based CL with similar low RF or low-Pt loading. In fact, it appears that the approach in Ott et al. is the contribution of Knudsen diffusion and transport/transfer through ionomer to Ω²⁰₂ was estimated (Fig. S21e). As hypothesized, the large cPDA particles result in dramatic decrease in the Knudsen resistance, which is estimated to be around 0.04 s cm⁻¹ compared to the values of 0.14 s cm⁻¹ and 0.08 s cm⁻¹ reported for Pt/KB and Pt/KB-N CLs. Despite having a higher estimated effective average ionomer thickness (~6 nm) for Pt/cPDA CL is even lower than those reported for Pt/cPDA CL. Although the Pt loading for the reference CL was higher, the roughness factor of both CLs was similar (~40 cm² g⁻¹) upon decreasing Pt particle density at a particular Pt loading. For Pt/cPDA CLs, the lower oxygen transport resistance can be attributed at least to the dual effects of our design strategy: first, a facile gas-phase transport in large CL pores and second via the mitigation of the territory effect.

**Performance and durability characterization**

The performance and durability characteristics of Pt/cPDA CL is reported for the sake of completeness of catalyst layer characterization. As with Ω²⁰₂, a direct comparison of the performance of fuel cells is fraught with challenges of delineating the differences arising from different fuel cell components, including membrane (type and thickness) and porous transport layer, as well as cell hardware (most notably flow-field plate design). Accordingly, for comparison, results from two cells varying only in the in-house made cathode CLs—Pt/cPDA and commercial Pt/C (TKK 10 wt% Pt on Vulcan carbon)—are reported. Polarization measurements were conducted under fuel cell conditions at varying RH (30–100%) (70 °C, 140 kPa abs, in both Air and pure O₂). The cells with Pt/cPDA CLs exhibited higher ohmic resistance (high-frequency resistance or HFR) compared to cells with Pt/C CLs. Although the origin of high HFR for Pt/cPDA is not known, it is speculated to arise from contact resistance between CL and MPL. The HFR-free performance data are included in SI (Fig. S16). Overall, the Pt/cPDA catalyst layer illustrated better-uncorrected performance (560 mA cm⁻²) compared to that of 330 mA cm⁻² (TKK Pt/C CL) as well as better HFR-free performance (700 mA cm⁻²) compared to that of 420 mA cm⁻² (TKK Pt/C CL) on an electrode geometric area basis at 0.6 V in H₂/Air (Fig. S5a, Supplementary Fig. S16). TKK Pt/C CL showed a sharp drop in performance in the transport-dominated region (~1000 mA cm⁻²) due to higher transport resistance as opposed to the Pt/cPDA CL. Although the Pt loading for the reference CL was higher, the roughness factor of both CLs was similar (~40 cm² g⁻¹).

**Fig. 5 | Fuel cell performance and catalyst durability comparison for MEAs made with Pt/cPDA and commercial Pt/C catalysts.**

(a) Uncorrected cell performance and (b) Uncorrected Pt mass loading normalized performance comparison between Pt/cPDA and commercial Pt/C (TKK 10 wt% Pt catalyst in H₂/Air), c ECSA loss during square wave AST degradation cycles (AST protocol: DOE square wave, 0.6–0.95 V, potential changed at −700 mV s⁻¹), at 70 °C, 100% RH and atmospheric pressure in H₂/N₂ (0.2/0.2 NLPM), d Uncorrected cell performance at BOL and EOL (after 30,000 AST cycles) at 70 °C, 100% RH and 140 kPa pressure in H₂/Air. ECSA was measured using CO stripping method. The error bar presented is the average of three individual testing results. *MEA condition: 70 °C, 100% RH; 140 kPa abs, H₂/Air (0.3/0.5 NLPM) for performance.

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**Table 1**

| Condition | Performance | Durability |
|-----------|-------------|------------|
| Pt/cPDA   | 560 mA cm⁻² | 330 mA cm⁻² |
| Pt/C      | 420 mA cm⁻² | 700 mA cm⁻² |

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**Supplementary Information**

See supplementary information for further details and supporting data.
benefits of large carbon support particles and favorable interaction of ionomer with N-containing functional groups of the dopamine coating. Further investigation would be needed to determine optimal support size and to delineate the effect of the N-functional group in controlling ionomer-support interaction.

**Methods**

**Synthesis of PDA nanospheres**

The monomer (Dopamine hydrochloride, 1 g) was dispersed in DI water in a 20 mL glass vial. A dispersion medium was prepared separately by mixing water-ethanol with 2.1 vol% of (aq) NH₄OH (aq, 28–30 vol%) in a 500 mL glass beaker. Subsequently, the dopamine dispersion was added slowly to the dispersion medium; here, dopamine concentration was kept constant at 3.3 mg mL⁻¹ while maintaining the final water:ethanol ratio at 67:33 vol%. Then, the mixture was stirred for 4 h at 1600 rpm in the presence of Air at room temperature (23 °C). Once polymerized, the sample was centrifuged at 27216 × g (15,000 rpm) (Beckman coulter Avanti J-26X SP, USA) and washed with an ample amount of DI water and ethanol to remove unreacted monomer and other residues. The sample was re-dispersed in DI water and ethanol by sonication and then centrifuged again. The procedure was repeated three times till the dispersion media became pH neutral.

The sample was then vacuum dried at 60 °C. The overall yield (starting from monomer to final recovered dry PDA spheres) was calculated to be around 65% (gravimetrically). Carbonization of the PDA nanoparticles was carried out at 700 °C under an N₂ atmosphere which yielded smaller-sized but spherical carbonized PDA (cPDA) nanoparticles. The carbonization protocol featured three stages: (i) heating from room temperature to 700 °C with a heating rate of 5 °C/min; (ii) a dwell time of 1 h at 700 °C for complete carbonization; and (iii) slow, uncontrolled cooling to room temperature.

**Platinum deposition on cPDA nanospheres**

500 mg of cPDA were added to 140 mL of Ethylene Glycol (EG) in a 400 mL round bottom flask and sonicated for around 30 min, followed by magnetic stirring at 1600 rpm to obtain a well-dispersed slurry. In order to achieve a 10 wt% Pt loading on cPDA, 105 mg of H₂PtCl₆ was dissolved in 35 mL of water. The cPDA dispersion was preheated at 140 °C in an oil bath, and H₂PtCl₆ (aq) solution was added dropwise to the dispersion. Subsequently, the pH of the mixture was adjusted to around 10–11 by adding a pre-made 5 M NaOH (aq) solution. The reaction mixture was stirred at 1600 rpm for ~4 h under reflux. The pH was monitored using a pH meter (Model EL20, Mettler Toledo, USA) during this period and maintained at the desired level (between 10 and 11) by adding the NaOH (aq) solution if required. The level of the dispersion in the round bottom flask was maintained by the addition of a 20% (v/v) water/EG mixture. After the completion of the reaction, the sample was filtered and washed with DI water, ethanol, and acetone, followed by vacuum drying at 60 °C. Next, the dried sample was reduced under a 10% H₂ in N₂ atmosphere inside a furnace to ensure complete reduction of deposited Pt. Prior to H₂ treatment, the furnace was purged with N₂. Thereafter, the gas was changed to 10% H₂ in N₂ and the temperature was raised to 300 °C at 5 °C min⁻¹, held for 3 h, and afterwards cooled to room temperature under an N₂ atmosphere.

**PDA, cPDA, and Pt/cPDA characterization**

The size and the morphology of PDA and cPDA nanospheres were examined by using Hitachi H-600 (Japan) Scanning Electron Microscopy (SEM), Tecnai F20 200 kV (USA) Transmission Electron Microscope (TEM) and Talos F200X Scanning transmission electron microscope (USA) equipped with a Super-X four silicon drift detectors of energy dispersive spectrometry (Super-X SSD EDS, EDAX). The TEM thin sections (~100 nm) were cut by Leica UCT ultramicrotome setup (Germany) equipped with an Ultra 45°DIATOME knife (USA) from a block prepared by embedding a small piece of the catalyst-coated
membrane (CCM) in a 1:1 mixture of trimethylolpropane triglycidyl ether resin (Sigma-Aldrich, USA) and 4,4’-Methylenebis (2-methylcy- clohexylamine, Sigma-Aldrich, USA) hardener, polymerized overnight at 60 °C. The sections were situated onto multiple 200 mesh Cu/Pd grids. Laboratory-based X-ray photoelectron spectroscopy (XPS) measurements were carried out at room temperature in an ultrahigh vacuum (UHV, 3 × 10⁻⁹ Torr) setup using a monochromatized Al Kα (1486.6 eV) excitation and a hemispherical analyzer (Kratos Axis Ultra DLD, UK).

**Electrochemical characterization in liquid electrolyte**

Electrochemical characterization of the Pt/cPDA catalyst and commercial TKK 10% Pt/C catalyst was performed via a rotating disk electrode (RDE) test. Extensive care was taken to clean the glassware and work with high purity electrolyte as described in the following subsection.

**Rotating disk electrode test**

**Glassware and component cleaning.** The electrochemical cell glassware (Pine Instrument, USA) and the components were soaked in concentrated sulfuric acid (Millipore Sigma, USA) overnight, followed by a 5–6 times repeat sequence of boiling with DI water followed by DI water replacement after each boil. This procedure is followed after each experiment to eliminate the trace amount of impurities. Before the electrochemical testing, the electrochemical cell and the components are rinsed 2–3 times with freshly prepared 0.1 M HClO₄ (diluted from 70% Veritas Doubly Distilled GFS Chemicals, USA). The glassy carbon (5 mm diameter, Pine Instrument) tips are polished before each experiment using 0.05 µm alumina slurry (Pine Instrument, USA), followed by rinsing and subsequent sonication for 3–5 min using DI water. The glassy carbon (GC) tip was dried using nitrogen gas before the catalyst coating.

**Ink formulation and coating.** Two different fabrication techniques were applied for the two different catalyst films—(i) ionomer-free and (ii) ionomer-based catalysts. For ionomer-free catalyst film preparation, the stationary air-dry technique was followed, whereas the rotational air-dry approach was adopted for the ionomer-based catalyst film.

The ionomer-free ink was prepared by adding 9.6 mg of catalysts in a 20 vol% IPA in a water mixture. The resulting ink was sonicated in an ice water bath sonicator for ~20 min to obtain a good dispersion slurry (10 µL aliquot, ~10 µgPt cm⁻²). For ionomer-based catalyst, 9.6 mg of catalyst was dispersed in the required amount of 20 vol% IPA in a water mixture to which 0.05 µm alumina slurry (Pine Instrument, USA), followed by rinsing and subsequent sonication for 3–5 min using DI water. The resulting ink was sonicated in an ice water bath sonoating for ~20 min to obtain a good dispersion slurry (10 µL aliquot, ~10 µg Pt cm⁻²). For ionomer-based catalyst, 9.6 mg of catalyst was dispersed in the required amount of 20 vol% IPA in a water mixture to which 0.05 µm alumina slurry (Pine Instrument, USA), followed by rinsing and subsequent sonication for 3–5 min using DI water. The glassy carbon (GC) tip was dried using nitrogen gas before the catalyst coating.

**Fabrication of membrane electrode assembly (MEA)**

In this study, the decal transfer method was used in order to prepare an MEA. First, the desired amount of IPA to achieve a solid to liquid ratio (S/L) of 0.18 (20% water/IPA) and 20 wt% Nafion ionomer dispersion (EW 1100, Ion Power Inc.) was added to achieve an overall I/C mass ratio of 0.8 with catalyst (Pt/cPDA) in a 20 mL glass vial and dispersed ultrasonically using an ultrasonic bath for 20 minutes; both procedures were performed under the ice to avoid Pt degradation. For the commercial TKK 10% Pt/C catalyst, a similar ink preparation recipe was used. Here, an ionomer to carbon ratio (I/C) of 0.8, a solid to liquid ratio (S/L) of 0.18 and a solvent mixture of 20% water/IPA were used to prepare the catalyst ink for the commercial TKK 10% Pt/C catalyst. Then, to further homogenize, the inks (both Pt/cPDA and TKK Pt/C) were magnetically stirred in a 20 mL glass vial containing 5 g of 5 mm diameter ZrO₂ beads for 24 h at room temperature (23 °C) prior to its use. The catalyst layers were then coated onto a 75 µm thick PTFE substrate (McMaster-Carr, 8569K75) using an automatic film coater (MSK AFA-II, MTI Corporation, USA) at a speed of 10 mm s⁻¹. During the coating, a wet film thickness of 100 µm was set. Subsequently, the catalyst-coated decal was Air dried for 1 h followed by drying under vacuum for 12 h at 80 °C to evaporate residual solvents. CCMs with an active area of 1 cm² (sub-framed and controlled by Kapton window) were prepared by hot-pressing catalyst coated decal against 25 µm thick Nafion 212 (NRE-211, Fuel cell store, USA) membrane at 150 °C and 2 MPa pressure for 3 minutes with an applied force of 0.12 kN cm⁻². Pt loading in the prepared CCMs was calculated gravimetrically by weighting the decals before and after the catalyst layer transfer. The thickness of Pt/cPDA and TKK Pt/C Cls was determined by a
micrometer (Marathon digital micrometer, Fisher scientific, USA) 9 ± 1 µm and 10 ± 1 µm, respectively.

After hot-pressing, a cell was assembled by sandwiching hot-pressed CCM between two gas diffusion layers with a microporous layer (~230–240 µm, Toray, TGP-H-060; Fuel Cell Store, USA) guided by 175 µm thick PTFE gaskets to ensure around 25% compression of GDL. GDL dimensions were 1.5 cm × 1.5 cm on both cathode and anode sides. The area of the GDL was designed to be larger than the active area of the CCM to ensure independent control of compression of the catalyst layer and the GDL and also to avoid edge degradation. A torque of 30 in-lb was applied during the cell assembly in three steps (10-20-30 in-lb). Fuel cell hardware consisting of 50 cm² flow field with a serpentine channel (16 cm² channel area) was used (purchased from fuel cell technologies, USA).

Fuel cell testing
Fuel cell testing with in situ high-frequency resistance (HFR, for IR correction) measurement at each voltage were performed using a Biologic SP-200 potentiostat and a commercial 100 W, G20 Greenlight Innovation test station (Greenlight Innovation corp., Canada) in a high differential cell. The following sequence of events were followed and are described in Fig S10.

Diagnostics. First, a series of primary diagnostic tests (HUPD, CV, LSV and EIS) was performed to determine the electrochemical surface area (ECSA), H₂ crossover and series resistance or high-frequency resistance (HFR) of the assembled cell at 70 °C, 100% RH, 140 kPaₐ, in H₂/N₂ (0.1/0.2 NLPM). The reactants, i.e. compressed Air (99.999%), carbon monoxide (99.5%), hydrogen, oxygen (99.999%), and nitrogen (99.999%), were obtained from Air Liquide, Canada. The anode (hydrogen electrode) served as the reference (RHE) and counter electrode (CE), while the cathode was the working electrode (WE). The impedance spectra were obtained at 0.4 V by sweeping frequencies in the range of 1 MHz to 1 Hz with an amplitude of 10 mV. The anode and working electrode (cathode) were fed with different humidiﬁed hydrogen and nitrogen at the rate of 0.1 NLPM and 0.2 NLPM, respectively.

Activation Protocol. All cells were conditioned prior to testing to activate the MEA, hydrate the ionic network and remove possible contamination. The entire conditioning protocol is summarized in Table S5.

H₂ pumping. First, an H₂ pumping procedure was performed while the cell (both anode and cathode), anode humidifier and cathode humidifier temperature was set at 30 °C, 45 °C and 45 °C, respectively. H₂ pumping was performed for 30 min by applying a current of 50–200 mA cm⁻² while the resulting voltage was mildly negative. Then, the cell was purged with high flow N₂.

Flooding. The cell was supplied with over-humidiﬁed gas H₂/N₂ (0.1/0.2 NLPM) for around 8–12 h by setting the cell and humidifier temperature (both anode and cathode) at 70 °C and 80 °C, respectively to hydrate the membrane and ionomer network. This step resulted in a 10–20 mℓ-cm⁻² reduction in the series resistance. Subsequently, the cell was purged again with a high flow of N₂ for 20 min to remove excess water, and the humidifier temperature was decreased to 70 °C.

0.6 V hold. Once the temperature is equilibrated, humidiﬁed H₂ and Air were introduced to the anode and cathode, respectively, and the back pressure was set at 200 kPaₐ for both sides. When an open circuit voltage (OCV) of ~1.0 V or steady state was reached, a constant voltage hold of 0.6 V was applied to the cell and current was drawn from the cell for ~12 h until the current stabilizes (±5 mA cm⁻²). A typical current proﬁle is provided in Fig. S11.

Potential cycling. The cell was purged again with a high ﬂow of N₂ gas to remove the excess water. Finally, the cathode potential was cycled between OCV to 0.6 V by holding for 5 min at each potential at 70 °C, 100% RH and 50 kPaₐ pressure in H₂/Air (0.3/0.5 NLPM); this was repeated 5 times. Finally, the cell was purged with a high ﬂow rate of N₂ for 20 min after the conditioning to remove any excess moisture trapped in the cell.

Polarization curve
All polarization curves were determined in potentiostatic mode. The tests were recorded at desired operating conditions with H₂ and Air or O₂ (0.3/0.5 NLPM) at 140 kPaₐ pressure. Both cathode and anode reactant gases were maintained at the same pressure during testing. Polarization plots were obtained from open circuit voltage (OCV) to around 0.1 V (until limiting current) potentiostatically by holding the voltage constant at each voltage for 3 min (steps of ~0.1 V after 0.9 V), and the resulting equilibrated current values were averaged over the final 30 s. In the case of pure O₂, polarization plots were obtained potentiostatically by recoding the 1 V plot for kinetic parameter determination (as explained in SI, from OCV to around 0.8 V), followed by recording current from 0.8 V to around 0.1 V.

Accelerated Stress Test (AST) protocol
The square-wave catalyst AST protocol was used in this work to study the durability of Pt catalyst, with the only exception that the temperature was 70 °C instead of 80 °C. It consisted of potential cycling between 0.6 V and 0.95 V by holding the voltage at each potential for 3 s for 30,000 cycles. It was conducted in H₂(anode)/N₂(cathode) at 0.2/0.2 NLPM at 70 °C, 100% RH and atmospheric pressure.

The detailed experimental method of N₂ sorption isotherm, Platinum and Ionomer content determination by TGA, Platinum content determination by TEM image analysis, equation used to estimate the average inter-particle platinum distance, ECSA determination by both HUPD and CO-stripping, determination of kinetic parameter and limiting current study to determine the O₂ transport resistance are explained in SI.

Data availability
Relevant data supporting the key findings of this study are available within the article and the Supplementary Information file. All raw data generated during the current study are available from the corresponding authors upon request.

References
1. Banham, D. & Ye, S. Current status and future development of catalyst materials and catalyst layers for proton exchange membrane fuel cells: an industrial perspective. ACS Energy Lett. 2, 629–638 (2017).
2. Gittleman, C. S., Kongkanand, A., Masten, D. & Gu, W. Materials research and development focus areas for low cost automotive proton-exchange membrane fuel cells. Curr. Opin. Electrochem. 18, 81–89 (2019).
3. Wang, X. X., Swihart, M. T. & Wu, G. Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation. Nat. Catal. 2, 578–589 (2019).
4. Kongkanand, A. & Mathias, M. F. The priority and challenge of high-power performance of low-platinum proton-exchange membrane fuel cells. J. Phys. Chem. Lett. 7, 1127–1137 (2016).
5. Weber, A. Z. & Kusoglu, A. Unexplained transport resistances for low-loaded fuel-cell catalyst layers. J. Mater. Chem. A 2, 17207–17211 (2014).
6. Greszler, T. A., Caulk, D. & Sinha, P. The impact of platinum loading on oxygen transport resistance. J. Electrochem. Soc. 159, F831–F840 (2012).
7. Nonoyama, N., Okazaki, S., Weber, A. Z., Ikogi, Y. & Yoshida, T. Analysis of oxygen-transport diffusion resistance in proton-exchange-membrane fuel cells. J. Electrochem. Soc. 158, B416–B423 (2011).

8. Owejan, J.-P., Owejan, J.-E. & Gu, W. Impact of platinum loading and catalyst layer structure on PEMFC performance. J. Electrochem. Soc. 160, F238–F245 (2013).

9. Ono, Y. et al. The analysis of performance loss with low platinum loaded cathode catalyst layers. ECS Trans. 28, 69–78 (2010).

10. Li, B. et al. High performance octahedral PtNi/C catalysts investigated from rotating disk electrode to membrane electrode assembly. Nano Res. 12, 281–287 (2019).

11. Mauger, S. A. et al. Fuel cell performance implications of membrane electrode assembly fabrication with platinum-nickel nanowire catalysts. J. Electrochem. Soc. 165, F238–F245 (2018).

12. Stamenkovic, V. R., Strmcnik, D., Lopes, P. P. & Markovic, N. M. Energy and fuels from electrochemical interfaces. Nat. Mater. 16, 57 (2017).

13. Stephens, I. E. L., Rossmeisl, I. & Chorkendorff, I. Toward sustainable fuel cells. Science 354, 1378–1379 (2016).

14. Ercolano, G., Cavaliere, S., Roziere, J. & Jones, D. J. Recent developments in electrocatalyst design thrifting noble metals in fuel cells. Curr. Opin. Electrochem. 9, 271–277 (2018).

15. Ruck, M., Bandarenka, A., Calle-Vallejo, F. & Gagliardi, A. Oxygen reduction reaction: rapid prediction of mass activity of nanostructured platinum electrocatalysts. J. Phys. Chem. Lett. 9, 4463–4468 (2018).

16. Ott, S. et al. Ionomer distribution control in porous carbon-supported catalyst layers for high-power and low Pt-loaded proton exchange membrane fuel cells. Nat. Mater. 19, 77–85 (2020).

17. Orfanidi, A. et al. The key to high performance low Pt loaded electrodes. J. Electrochem. Soc. 164, F418–F426 (2017).

18. Yamada, H., Kodama, K. & Kato, H. Cell performance and durability of Pt/C cathode catalyst covered by dopamine derived carbon thin layer for polymer electrolyte fuel cells. J. Electrochem. Soc. 167, 084508 (2020).

19. Karan, K. PEFC catalyst layer: Recent advances in materials, microstructural characterization, and modeling. Curr. Opin. Electrochem. 5, 27–35 (2017).

20. Sabharwal, M., Pant, L. M., Patel, N. & Secanell, M. Computational analysis of gas transport in fuel cell catalyst layer under dry and partially saturated conditions. J. Electrochem. Soc. 166, F3065–F3080 (2019).

21. Watanabe, M., Sei, H. & Stonehart, P. The influence of platinum crystal size on the electroactivity of oxygen. J. Electroanal. Chem. Interfacial Electrochem. 261, 375–387 (1989).

22. Ai, K., Liu, Y., Ruan, C., Lu, L. & Lu, G. Sp2 C-dominated N-doped carbon sub-micrometer spheres with a tunable size: a versatile platform for highly efficient oxygen-reduction catalysts. Adv. Mater. 25, 998–1003 (2013).

23. Yu, X., Fan, H., Liu, Y., Shi, Z. & Jin, Z. Characterization of carbonized polydopamine nanoparticles suggests ordered supramolecular structure of polydopamine. Langmuir 30, 5497–5505 (2014).

24. She, Y. et al. Oxygen reduction reaction mechanism of nitrogen-doped graphene derived from ionic liquid. Energy Procedia 142, 1319–1326 (2017).

25. Zhan, Y. et al. Non noble metal catalyst for oxygen reduction reaction and its characterization by simulated fuel cell test. J. Electrochem. Soc. 165, J3008–J3015 (2018).

26. Ma, J. et al. Spectroelectrochemical probing of the strong interaction between platinum nanoparticles and graphitic domains of carbon. ACS Catal. 3, 1940–1950 (2013).

27. Ma, J. et al. Electronic interaction between platinum nanoparticles and nitrogen-doped reduced graphene oxide: effect on the oxygen reduction reaction. J. Mater. Chem. A 3, 11891–11904 (2015).

28. Meier, J. C. et al. Design criteria for stable Pt/C fuel cell catalysts. Beilstein J. Nanotechnol. 5, 44–67 (2014).

29. Corradini, P. G., Pires, F. I., Paganin, V. A., Perez, J. & Antolini, E. Effect of the relationship between particle size, inter-particle distance, and metal loading of carbon supported fuel cell catalysts on their catalytic activity. J. Nanopart. Res. 14, 1080 (2012).

30. Ramaswamy, N., Gu, W., Zieglerbauer, J. M. & Kumaraguru, S. Carbon support microstructure impact on high current density transport resistances in PEMFC cathode. J. Electrochem. Soc. 167, 064515 (2020).

31. Yarlagadda, V. et al. Boosting fuel cell performance with accessible carbon mesopores. ACS Energy Lett. 3, 618–621 (2018).

32. Calle-Vallejo, F. et al. Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors. Science 350, 185–189 (2015).

33. Garlyyev, B. et al. Optimizing the size of platinum nanoparticles for enhanced mass activity in the electrochemical oxygen reduction reaction. Angew. Chem. Int. Ed. Engl. 58, 9596–9600 (2019).

34. Padgett, E. et al. Connecting fuel cell catalyst nanostructure and accessibility using quantitative cryo-STEM tomography. J. Electrochem. Soc. 165, F173 (2018).

35. Yang, F. K. & Zhao, B. Adhesion properties of self-polymerized dopamine thin film. Open Surf. Sci. J. 3, 115–122 (2011).

36. Harzer, G. S., Orfanidi, A., El-Sayed, H., Madkikar, P. & Gasteiger, H. A. Tailoring catalyst morphology towards high performance for low Pt loaded PEMFC cathodes. J. Electrochem. Soc. 165, F770–F779 (2018).

37. Chen, C. et al. Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces. Science 343, 1339–1343 (2014).

38. Guo, D. et al. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. Science 351, 361–365 (2016).

39. Higgins, D. C. & Chen, Z. Recent progress in non-precious metal catalysts for PEM fuel cell applications. Can. J. Chem. Eng. 91, 1881–1895 (2013).

40. Baker, D. R., Caulk, D. A., Neyerlin, K. C. & Murphy, M. W. Measurement of oxygen transport resistance in PEM fuel cells by limiting current methods. J. Electrochem. Soc. 156, B991–B1003 (2009).

41. Stariha, S. et al. Recent advances in catalyst accelerated stress tests for polymer electrolyte membrane fuel cells. J. Electrochem. Soc. 165, F492 (2018).

42. Shi, W. et al. Enhanced stability of immobilized platinum nanoparticles through nitrogen heteroatoms on doped carbon supports. Chem. Mater. 29, 8670–8678 (2017).

43. Schmies, H. et al. Impact of carbon support functionalization on the electrochemical stability of Pt fuel cell catalysts. Chem. Mater. 30, 7287–7295 (2018).

44. Zhou, Y. et al. Enhancement of Pt and Pt-alloy fuel cell catalysts. Beilstein J. Nanotechnol. 5, 44–67 (2014).

45. Takeshita, T., Komata, K., Shinozaki, K., Kodama, K. & Morimoto, Y. Evaluation of ionomer coverage on Pt catalysts in polymer electrolyte membrane fuel cells by CO stripping voltammetry and its effect on oxygen reduction reaction activity. J. Electroanal. Chem. 871, 114250 (2020).

46. Wang, S., Zhu, E., Huang, Y. & Heinz, H. Direct correlation of oxygen adsorption on platinum-electrolyte interfaces with the activity in the oxygen reduction reaction. Sci. Adv. 7, eabb1435 (2021).

47. Kodama, K. et al. Increase in adsorption of sulfonate anions on Pt (111) surface with drying of ionomer. Electrochem. Commun. 36, 26–28 (2013).
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Author contributions
K.K., M.N.I., and V.O.K. conceptualized the catalyst support design. V.O.K. and M.N.I. synthesized and characterized the PDA and cPDA nanoparticles. M.N.I. carried out platinum deposition, MEA fabrication, and fuel cell testing studies. M.N.I. and V.O.K. conducted TEM of Pt/cPDA nanoparticles, and M.N.I. and K.K. analyzed the results. M.N.I. and K.K. analyzed TGA results. A.B.M.B. synthesized an additional batch of Pt/cPDA nanoparticles, performed all the RDE tests, and carried out some MEA testing. M.N.I. and K.K. analyzed the fuel cell data; A.B.M.B. and K.K. analyzed the RDE data. A.P.S. and J.J. performed high-resolution STEM-EDS of catalyst layer and analyzed the STEM-EDS results. All authors contributed to the writing of the manuscript.

Competing interests
The authors declare no competing interests.

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