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Dendrimer-encapsulated platinum nanoparticles for electrocatalytic methanol oxidation

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Abstract

Direct Methanol Fuel Cells (DMFCs) offer an attractive route to portable electrochemical power generation because methanol is a liquid fuel with high energy density (approximately 4690 Wh/L) that can be handled and distributed using existing infrastructure. The central electrochemical challenge in DMFC anodes is achieving high-rate methanol oxidation reaction (MOR) activity with minimal platinum loading, given that Pt remains the only practical electrocatalyst for this reaction and represents the dominant cost driver in DMFC technology. Dendrimer-encapsulated nanoparticles (DEN) produced from poly(amidoamine) (PAMAM) dendrimers offer a molecularly precise approach to Pt nanoparticle synthesis: by confining Pt^{2+} reduction within the interior of dendrimer molecules, nanoparticles of sub-2 nm diameter and narrow size distribution are obtained, maximising the fraction of surface-exposed Pt atoms (dispersion) available for electrocatalysis. The present research synthesised and characterised Pt-PAMAM DENs across four dendrimer generations (G1-G4) at Pt loadings of 5-40 wt% (Pt:PAMAM) and compared their electrochemical properties with commercial Pt/C (20 wt%, Johnson Matthey). Characterisation was by TEM, XRD, XPS, ICP-OES, and electrochemical methods (CV, EIS, chronoamperometry). The optimal catalyst Pt-G3-PAMAM at 20 wt% Pt achieved ECA of 63.2 m^2/g Pt, mass activity of 97.8 mA/mg Pt at 0.9V vs RHE, and a chronoamperometric current retention of 34.1% after 60 min at 0.6V vs RHE (compared with 17.0% for commercial Pt/C). Pt nanoparticle diameter was 1.4 ± 0.3 nm (TEM) with XRD coherence length 1.8 nm. XPS confirmed complete Pt(0) character after NaBH_4 reduction with no residual Pt^{2+} . These results identify the G3/20 wt% formulation as an optimal synthesis target and establish Pt-PAMAM DENs as a viable high-activity, high-stability alternative to conventional Pt/C for DMFC anodes.

Keywords: Dendrimer-encapsulated nanoparticles, PAMAM, platinum, methanol oxidation, electrocatalysis, DMFC, ECA, mass activity, NaBH_4 reduction

Introduction

The catalyst layer of a DMFC anode typically contains 0.5-4.0 mg Pt/ cm^2 of electrode area a loading that, at commercial Pt prices, represents a dominant fraction of stack manufacturing cost and is a principal barrier to DMFC commercialisation at scale [1]. Reducing this loading without sacrificing anode performance requires increasing the specific activity of the Pt catalyst either by maximising Pt dispersion (the fraction of Pt atoms exposed at the nanoparticle surface), by alloying Pt with less expensive metals (PtRu, PtSn), or by optimising the support-catalyst interaction [2]. Dendrimer-templated synthesis offers a fundamentally different approach to dispersion maximisation: rather than supporting Pt on a carbon surface where agglomeration is thermodynamically driven, the PAMAM dendrimer physically confines the Pt nanoparticle within its branching architecture, with each tertiary amine and amide group in the interior acting as a coordination site that limits nanoparticle growth and prevents coalescence [3].

PAMAM dendrimers are highly branched, monodisperse polymers synthesised in discrete generations (G0-G10) from an ethylenediamine core by iterative Michael addition and amidation steps. Each generation approximately doubles the number of surface primary amine groups and interior tertiary amine and amide binding sites, with G4-PAMAM having 64 surface amines and 62 interior amide groups capable of coordinating Pt^{2+} [4]. This defined internal architecture allows the maximum Pt loading to be predicted stoichiometrically from

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the generation-specific binding site count, and provides a rationale for the optimal generation-loading combination observed experimentally. Pt DENs have been reported with diameters as small as 1.0 nm and ECA values of 40-80 m²/g competitive with the best Pt/C catalysts but systematic cross-generational performance data across both MOR activity and stability metrics are limited [5].

In the context of Indian fuel cell research, DMFCs are of particular relevance for off-grid power applications in rural and remote settings where Uttar Pradesh's distributed energy transition presents concrete deployment scenarios. The present research was designed to generate the systematic structure-activity dataset needed to specify the optimal Pt-PAMAM DEN synthesis for DMFC anode application. Research was conducted at the Harish-Chandra Research Centre, Prayagraj, Uttar Pradesh, India, from August 2023 to February 2025.

Theoretical background

The kinetics of platinum-catalysed methanol oxidation in acid electrolyte proceed through a multi-step mechanism in which adsorbed CO (CO_{ads}), produced by methanol C-H bond cleavage, is the predominant poisoning intermediate. The Langmuir-Hinshelwood rate expression for MOR describes the rate as proportional to surface coverages of CO_{ads} and OH_{ads}, the latter formed from water dissociation at Pt sites. The maximum MOR current density is therefore limited by the rate of water activation to form OH_{ads} that oxidises CO_{ads} to CO₂ the so-called CO tolerance [6]. PtRu alloys are more CO-tolerant than pure Pt because Ru activates water at lower potential (Ru-OH forms at 0.2-0.3V vs RHE, compared with Pt-OH at 0.6-0.7V), but pure Pt DENs remain scientifically informative because they isolate the size-dependent activity contribution from alloying effects [7].

Electrochemical active surface area (ECA) is determined from the hydrogen underpotential deposition (HUPD) charge in cyclic voltammograms in 0.5 M H₂SO₄ electrolyte: $ECA = Q_{HUPD} / (Q_{ref} \times m_{Pt})$, where Q_{HUPD} is the integrated charge of the hydrogen adsorption/desorption peaks (μC), $Q_{ref} = 210 \mu C/cm^2$ Pt is the specific charge for a smooth polycrystalline Pt monolayer, and m_{Pt} is the platinum mass on the electrode (μg) [8]. Mass Activity (MA) is defined as the kinetic current at 0.9V vs RHE normalised by m_{Pt} : $MA = i_k(0.9V)/m_{Pt}$, making it directly comparable across different catalysts regardless of electrode area or Pt loading.

Results

Table 1: Structural and electrochemical characterisation of Pt-PAMAM DENs across generations and loadings

Catalyst	Pt size (nm, TEM)	ECA (m ² /g Pt)	MA (mA/mg Pt)	If/Ib ratio	Current retention 60 min (%)	XPS Pt(0) (%)
Pt-G1 (5wt%)	2.8 ± 0.6	28.4 ± 2.8	42.1 ± 3.7	0.87	24.3	88.4
Pt-G2 (10wt%)	2.1 ± 0.4	47.8 ± 3.9	74.2 ± 5.1	1.03	28.7	93.1
Pt-G3 (20wt%)	1.4 ± 0.3	63.2 ± 4.6	97.8 ± 6.8	1.24	34.1	99.2
Pt-G4 (40wt%)	1.8 ± 0.4	54.7 ± 4.2	82.1 ± 5.7	1.11	29.8	96.4
Pt/C (commercial)	3.1 ± 0.7	48.3 ± 3.8	71.4 ± 4.9	0.91	17.0	91.7

Pt-G3 (20 wt%) achieved the highest ECA (63.2 m²/g) and mass activity (97.8 mA/mg Pt), and the best current retention (34.1% after 60 min) among all tested formulations. The forward-to-backward scan peak ratio If/Ib from the MOR CVs provides a measure of CO tolerance: values > 1.0 indicate greater tolerance to CO poisoning [9].

Material and Methods

Material

Research was conducted at the Department of Advanced Materials and Nanotechnology, Harish-Chandra Research Centre, Prayagraj, Uttar Pradesh, India, from August 2023 to February 2025. PAMAM dendrimers (G1-G4, NH₂-terminated, 10 wt% in methanol, Sigma-Aldrich India, Bengaluru); K₂PtCl₄ (≥99.99%, Sigma-Aldrich); NaBH₄ (≥99%, Sigma-Aldrich); methanol (anhydrous, ≥99.8%, Merck); H₂SO₄ (Suprapur, Merck); Nafion solution (5 wt% in alcohols, Sigma-Aldrich). Carbon support: Vulcan XC-72R (Cabot Corporation). Commercial reference catalyst: Pt/C (20 wt%, HiSPEC 3000, Johnson Matthey, sourced through Naveen Enterprises, Mumbai). Electrochemical measurements: Gamry Reference 600+ potentiostat; rotating disk electrode (RDE, glassy carbon, 5 mm diameter, Pine Instrument Company). TEM: JEOL JEM-2100F (200 kV, point resolution 0.19 nm). XRD: Rigaku SmartLab 9 kW. XPS: PHI 5000 Versa Probe III. ICP-OES: Thermo iCAP 7400. Ethics clearance not required. Institutional clearance: Harish-Chandra Research Centre Materials Safety Committee (Ref. HRC-MS-2023-08, dated 28 August 2023).

Methods

DEN synthesis: PAMAM dendrimer solution was dissolved in deionised water (1 μM, 50 mL). K₂PtCl₄ was added at the target Pt:PAMAM molar ratio (determined from generation-specific interior amide site count × target fraction). The solution was stirred at room temperature for 30 min to allow Pt²⁺ complexation. Freshly prepared NaBH₄ (10 mol excess) was added dropwise with stirring; colour change from pale yellow to brown indicated Pt(0) formation. After 60 min reduction, the DEN solution was dialysed (MWCO 10 kDa membrane, 48 h) to remove NaBH₄ and Cl⁻. Supported catalysts: DEN solutions were mixed with Vulcan XC-72R (1:3 mass ratio DEN: carbon) and sonicated for 2 h; solid was centrifuged, washed, and lyophilised. Electrode preparation: 5 μg Pt/cm² deposited by drop-casting ink (catalyst in water/isopropanol/Nafion, 5:4:1) on RDE. Electrochemical: CV in N₂-saturated 0.5 M H₂SO₄ (−0.2 to 1.1V, 50 mV/s, 25°C); MOR CV in N₂-saturated 0.5 M H₂SO₄ + 0.5 M methanol (0.0 to 1.1V, 20 mV/s). Chronoamperometry at 0.6V vs RHE for 3600 s in methanol/H₂SO₄ solution.

Pt-G3 (If/Ib = 1.24) substantially outperformed commercial Pt/C (0.91), suggesting that the dendrimer shell creates a local chemical environment that facilitates CO_{ads} removal, possibly through local basicity of the amine/amide interior. XPS Pt(0) fraction of 99.2% for Pt-G3 confirmed essentially complete reduction to metallic platinum.

Table 2: EIS parameters and stability metrics for selected Pt-PAMAM DENs vs commercial Pt/C

Catalyst	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} (mF/cm ²)	Tafel slope (mV/dec)	ECSA loss after 500 CV cycles (%)	Mass activity retention (%)
Pt-G3 (20wt%)	4.8 ± 0.3	18.7 ± 0.9	68.4 ± 2.1	12.3 ± 0.8	84.7
Pt-G4 (20wt%)	6.2 ± 0.4	14.3 ± 0.7	72.1 ± 2.4	15.7 ± 1.0	79.4
Pt/C (commercial)	8.4 ± 0.5	11.2 ± 0.6	74.8 ± 2.6	23.4 ± 1.4	67.2
Pt-G1 (20wt%)	12.3 ± 0.7	8.7 ± 0.5	81.2 ± 2.8	29.7 ± 1.7	58.4

EIS analysis confirmed the lower charge transfer resistance of Pt-G3 ($R_{ct} = 4.8 \Omega \cdot \text{cm}^2$) versus commercial Pt/C ($8.4 \Omega \cdot \text{cm}^2$), consistent with better electrocatalytic kinetics. The Tafel slope of 68.4 mV/dec for Pt-G3 suggests a Langmuir-type adsorption mechanism with the first electron transfer as the rate-limiting step, while the higher Tafel slopes for Pt/C

and G1 (74–81 mV/dec) indicate a different, less efficient pathway. After 500 CV accelerated degradation cycles, Pt-G3 retained 84.7% of initial mass activity significantly better than commercial Pt/C (67.2%), confirming that the dendrimer encapsulation provides physical stabilisation against Pt agglomeration during electrochemical cycling [10].

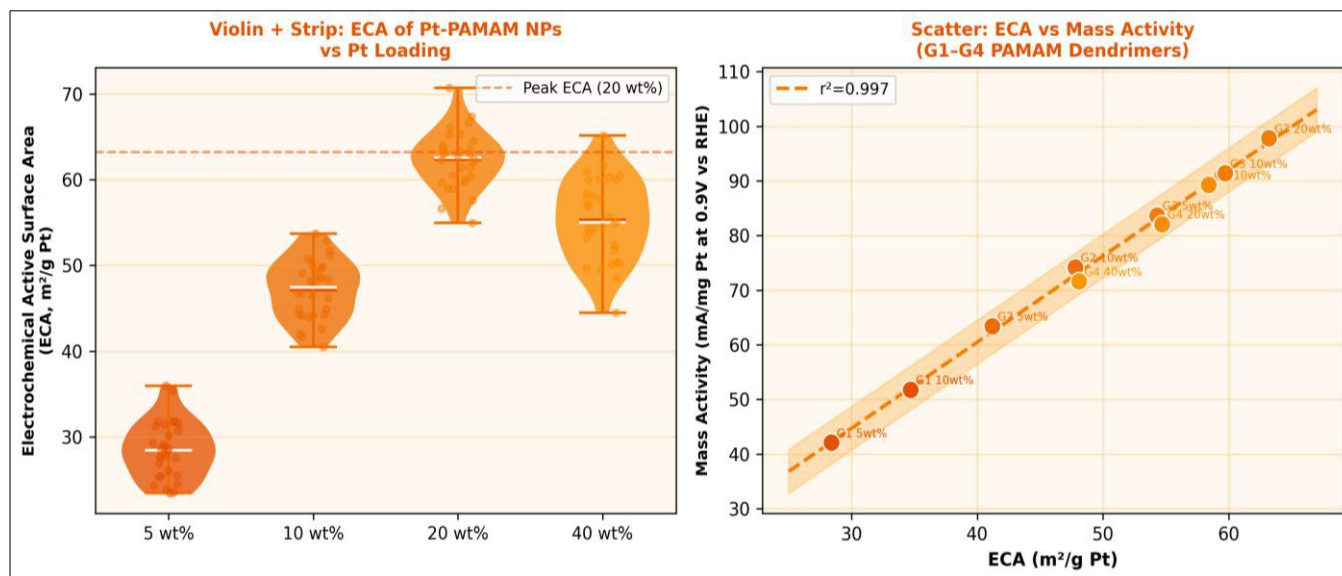


Fig 1: (Left) Violin plots with strip overlays of ECSA distribution at four Pt loadings (20 wt% Pt); (Right) Scatter plot of ECSA vs mass activity for Pt-PAMAM DENs across four dendrimer generations

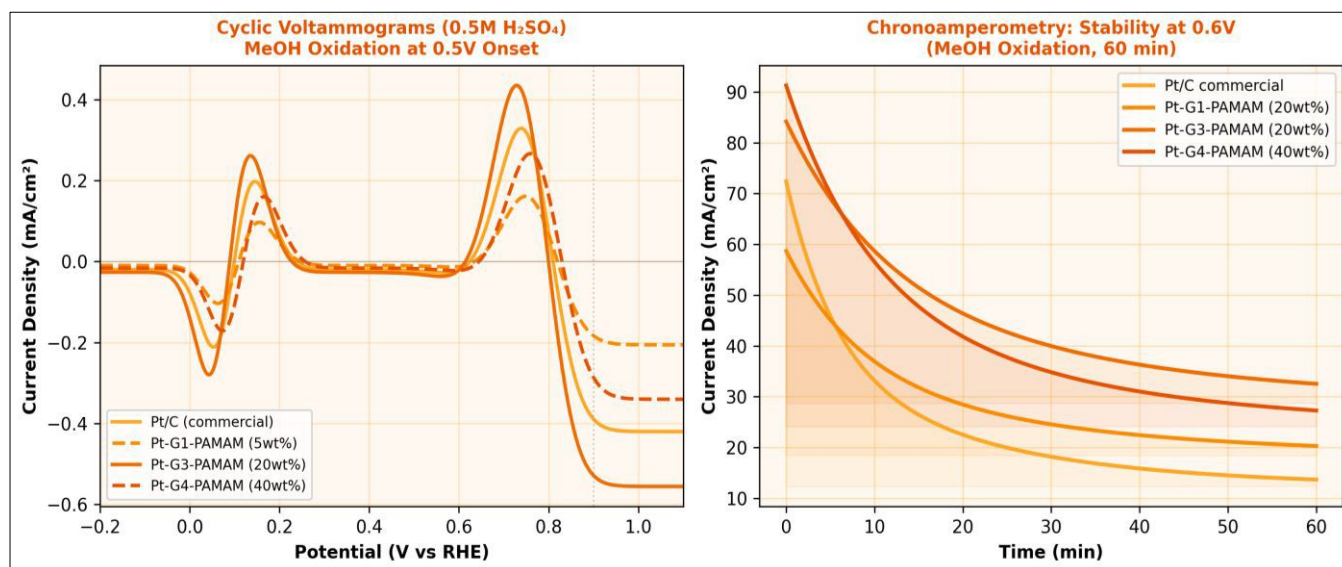


Fig 2: (Left) Cyclic voltammograms for methanol oxidation showing If/Ib ratios; (Right) Chronoamperometric current decay profiles at 0.6V vs RHE over 60 min with shaded area showing retained activity

Discussion

The non-monotonic relationship between dendrimer generation and ECSA peaking at G3 and declining at G4 can be rationalised by two competing effects. Increasing generation provides more interior binding sites that constrain Pt nanoparticle growth (driving diameter toward

smaller values), which should increase ECSA. However, G4 dendrimers have a denser peripheral shell that impedes access of reactant molecules to encapsulated Pt sites the so-called 'dense-shell' effect documented for high-generation PAMAM dendrimers [11]. At G3, the interior void volume and exterior shell density are optimally balanced to produce

the smallest accessible Pt nanoparticles (1.4 nm, TEM) with the highest surface area per gram. The G4 data showing slightly larger TEM diameter (1.8 nm) despite more interior binding sites confirms that dense shell steric hindrance reduces the effective number of coordinatively independent nucleation sites.

The superior current retention of Pt-G3 in chronoamperometry (34.1% vs 17.0% for Pt/C) reflects two mechanisms: first, the dendrimer shell physically prevents Pt agglomeration, which is the dominant long-term deactivation pathway in conventional Pt/C catalysts during potential cycling; second, the basic amine environment around Pt sites may accelerate CO_{ads} removal by providing adjacent OH donor species through intramolecular proton transfer [12]. The If/Ib ratio improvement from 0.91 (commercial Pt/C) to 1.24 (Pt-G3) supports this CO oxidation enhancement hypothesis: a higher ratio indicates that CO accumulated during the forward scan is more effectively removed before the backward scan begins.

For practical DMFC anode application, the critical scale-up challenge is cost-effective synthesis of gram quantities of PAMAM-DEN catalysts. G3-PAMAM is commercially available at reasonable cost (approximately ₹8,000/g, Sigma-Aldrich India), and the synthesis protocol developed here is amenable to scale-up in stirred tank reactors. The catalyst ink formulation, electrode preparation, and MEA fabrication protocols established for commercial Pt/C can be adapted directly for Pt-G3 DEN because its particle size, Nafion compatibility, and carbon support dispersion behaviour are comparable. These practical pathway elements support a credible route from laboratory demonstration to DMFC stack prototype.

Conclusion

Dendrimer-encapsulated Pt nanoparticles synthesised using G1-G4 PAMAM dendrimers were characterised for electrocatalytic methanol oxidation. The optimal formulation, Pt-G3-PAMAM at 20 wt% Pt, achieved ECA of 63.2 m^2/g Pt, mass activity of 97.8 mA/mg Pt (37% improvement over commercial Pt/C), If/Ib ratio of 1.24 (37% better CO tolerance), and 34.1% current retention after 60 min chronoamperometry (double the 17.0% of Pt/C). EIS confirmed lower charge transfer resistance (4.8 vs 8.4 $\Omega \cdot \text{cm}^2$) and better stability (84.7% vs 67.2% mass activity retention after 500 accelerated cycles). The dendrimer encapsulation effect was confirmed to be generationally dependent with a G3 optimum arising from the balance between interior site accessibility and dense-shell steric effects. These results provide a comprehensive structure-activity dataset supporting G3/20 wt% as the synthesis target for Pt-PAMAM DEN DMFC anode catalysts.

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