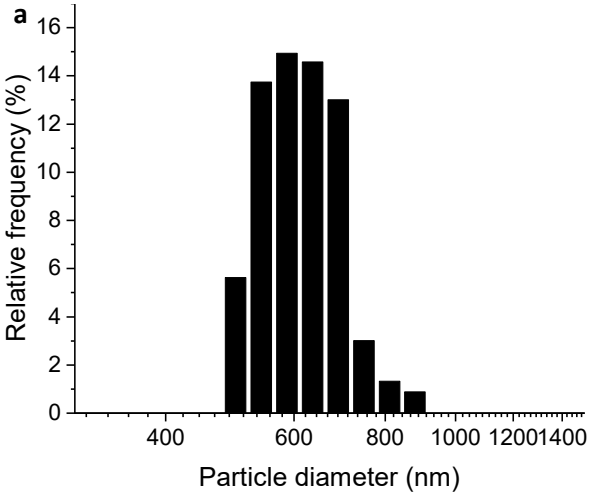
Supplementary Information for

Enhanced ORR Performance with Biomass-Derived Freestanding Catalyst Layers: Advancing Mass Transport in Gas Diffusion Electrodes

Mengnan Wang [a], Jiaguang Zhang [b], Simon Kellner [a], Ifan E. L. Stephens [c], Maria Magdalena Titirici *[a]

[a.] *Department of Chemical Engineering, Imperial College London, South Kensington Campus SW7 2AZ London, UK*
[b.] *School of Chemistry, University of Lincoln, Bayford Pool, Lincoln LN6 7TS, UK.*
[c.] *Department of Materials, Imperial College London. White City Campus, 80 Wood Ln, London, W12 7TA, UK*



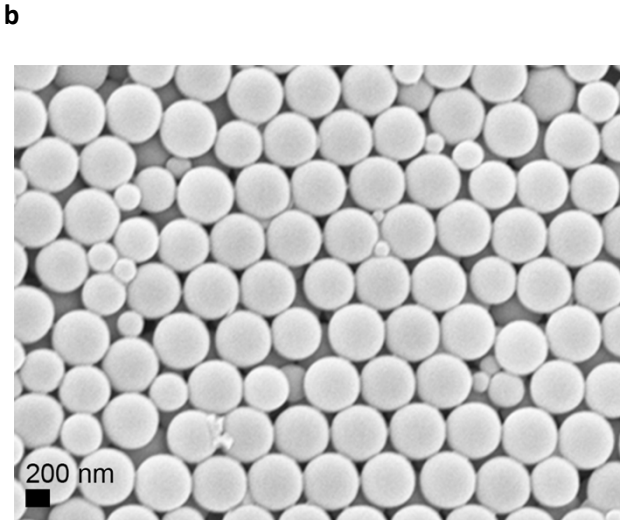


Figure S1. (a) DLS diameter distribution and (b) SEM images of the synthesised polystyrene particles showing particles size around 500nm.

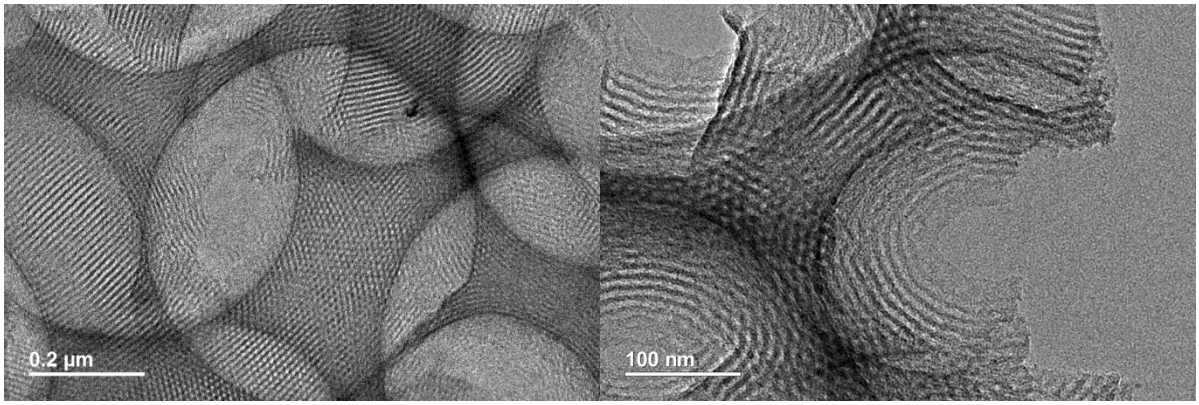


Figure S2. TEM images of hierarchical carbon.

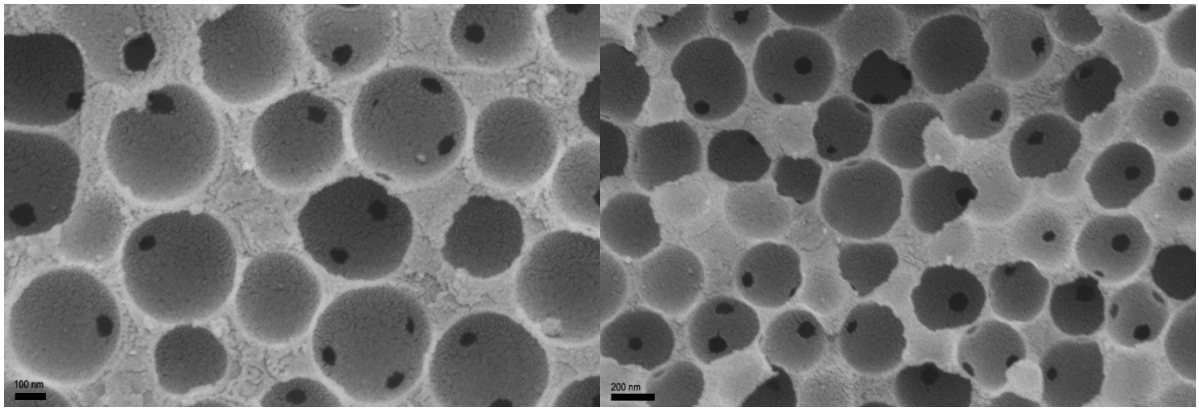


Figure S3. SEM images of hierarchical carbon.

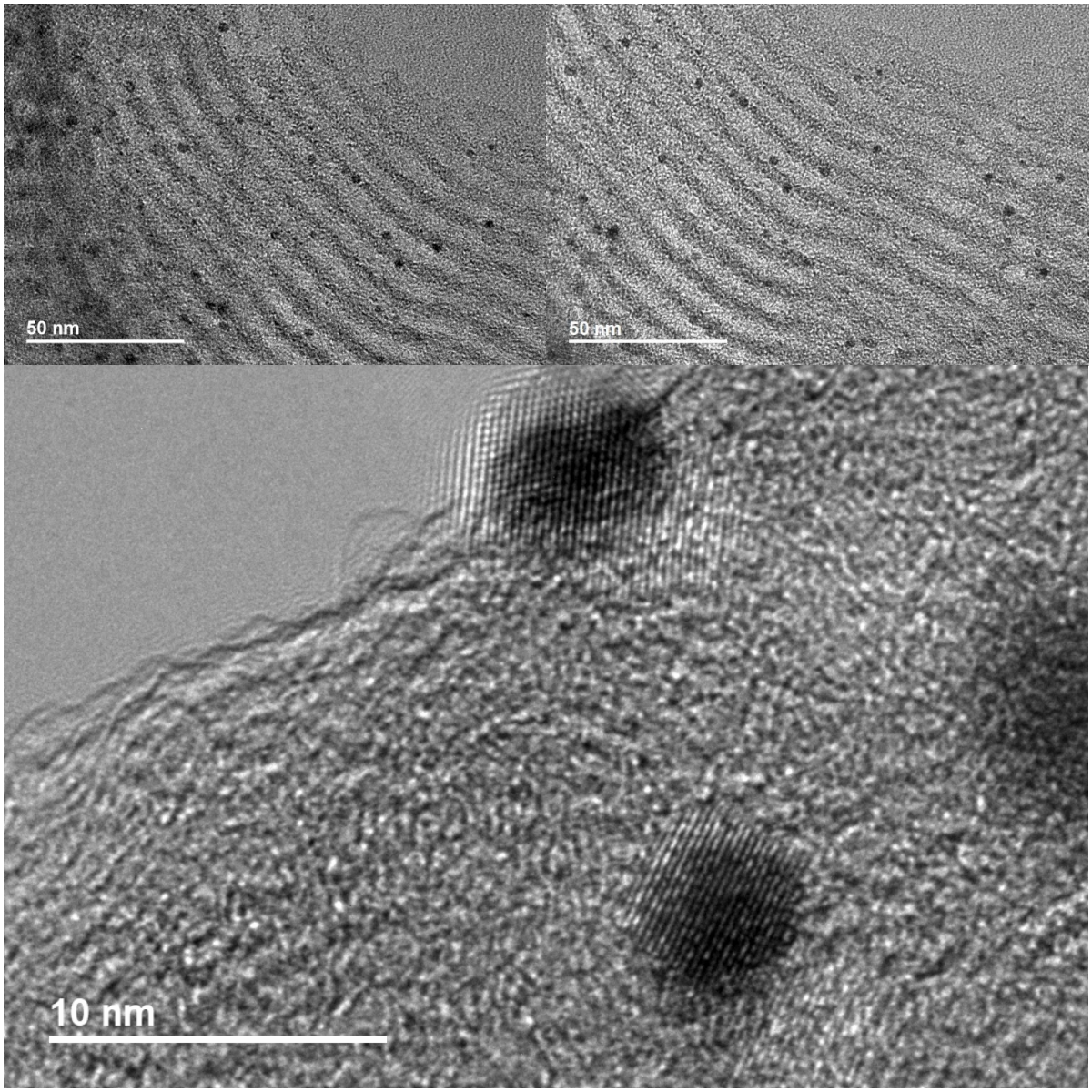


Figure S4. TEM images of Pt loading on hierarchical carbon.

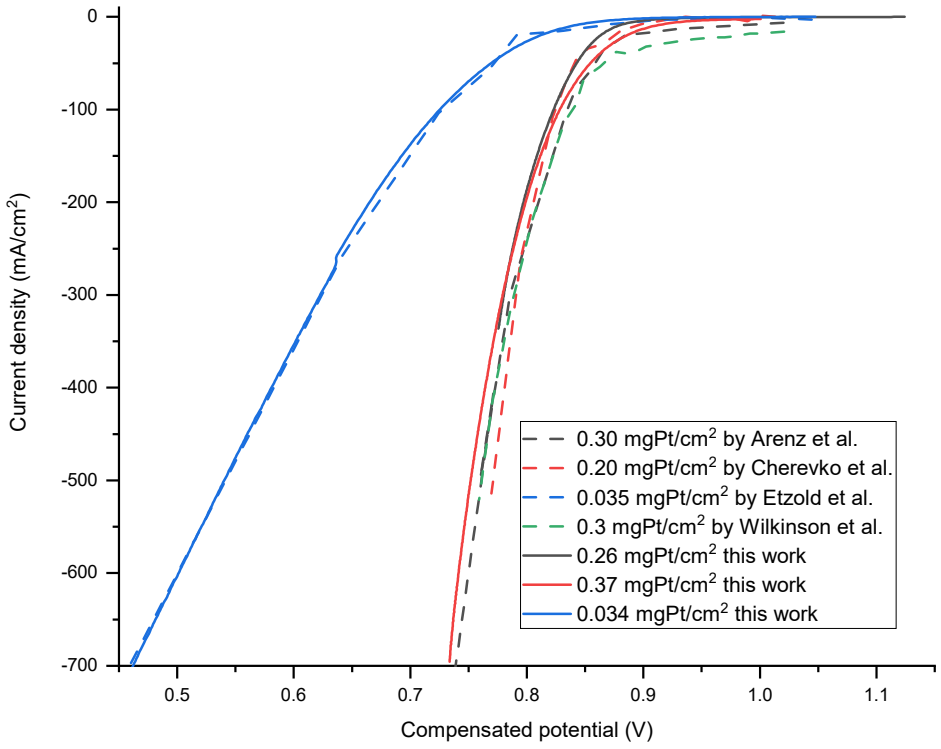


Figure S5. ORR polarisation benchmarking of the half -cell using the same Pt/C catalysts HiSPEC4000 (Johnson Matthey). Our measurements were done in 1M $HClO_4$ electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s scanning rate. Literature results were extracted from respective publications.[123]

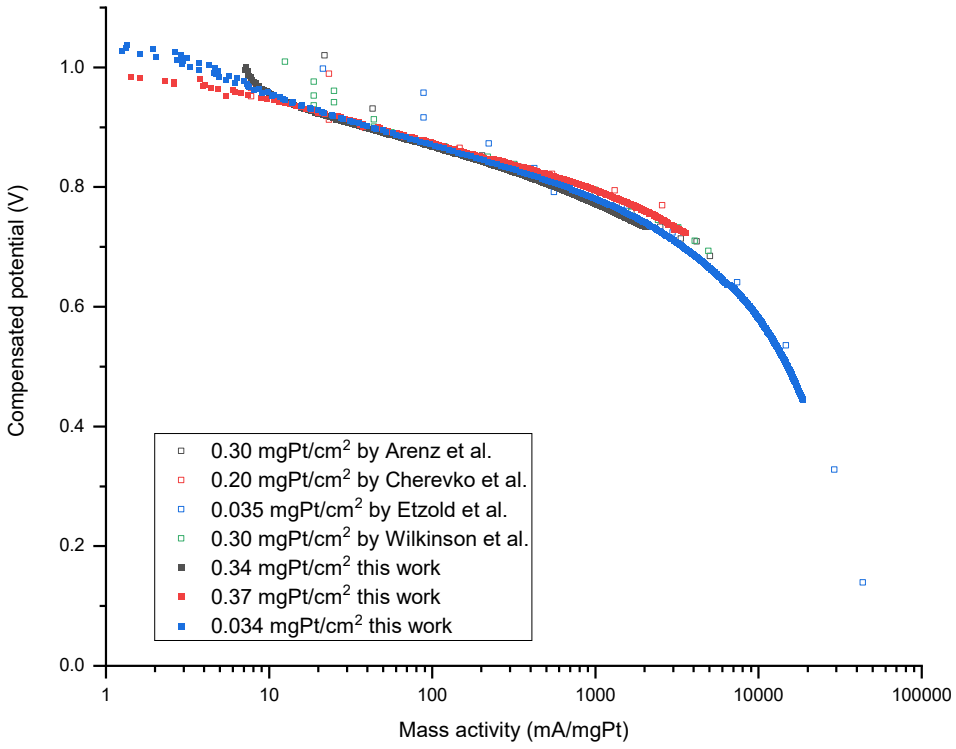


Figure S6. Mass specific activity of the same Pt/C catalysts HiSPEC4000 (Johnson Matthey) benchmarked in GDE half -cell. Home measurements were done in 1M $HClO_4$ electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s scanning rate. Literature results were extracted from respective publications.[123]

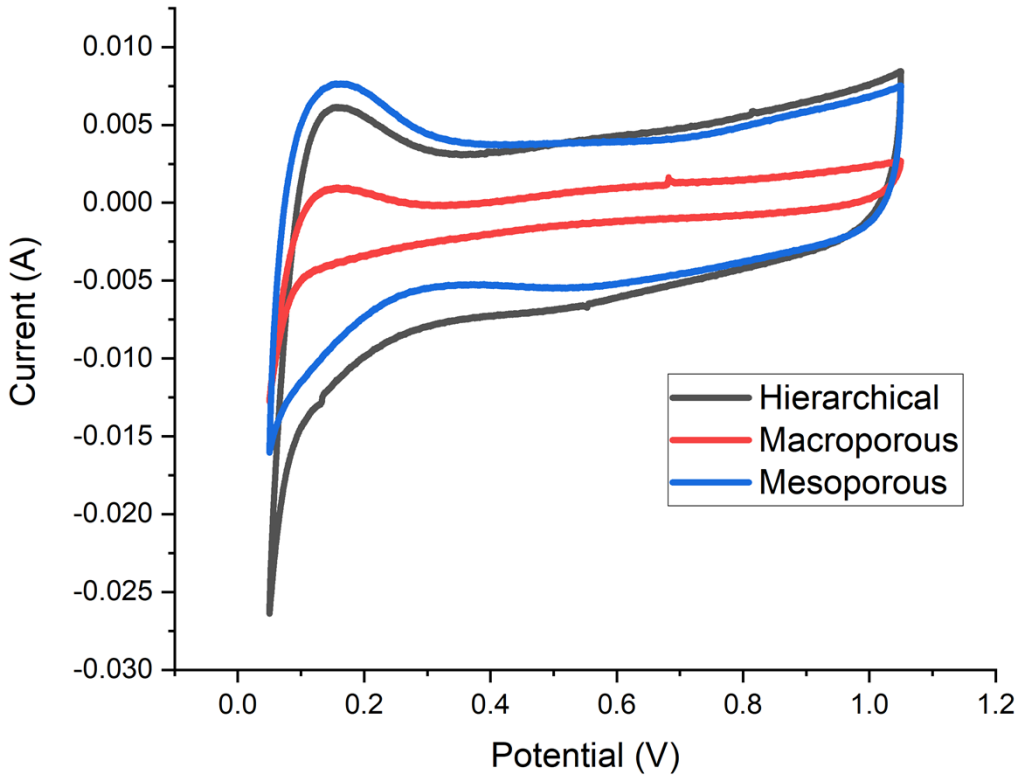


Figure S7. CV for all three catalyst layers under N_2 measured in gas diffusion electrode half-cell. Measurements were done in 1M $HClO_4$ electrolyte at room temperature with 200 mL/min N_2 flow and 100 mV/s scanning rate. Pt wire was used as the counter electrode in the same electrolyte chamber without membrane separation, RHE was used as the reference electrode in a different electrolyte chamber connected with Luggin capillary. Potential was corrected for IR compensation after measurements.

Table S1. ECSA determination via hydrogen underpotential deposition for all three catalysts in N_2-saturated 1 M $HClO_4$ at scan rate of 10 mV/s. The H_{UPD} current was converted to a corresponding Pt surface area using a specific capacity of 210 $\mu C \cdot cm Pt^{-2}$.

	Area under H_{UPD}	Charge (C)	Pt Area (m^2)	ECSA (m^2_{Pt}/g_{Pt})
Hierarchical	0.000644	0.00644	0.003067	48.81
Mesoporous	0.000574	0.00574	0.002733	43.51
Macroporous	0.000289	0.00289	0.001376	21.91

Table S2. Double layer capacitance (at 100mV/s) comparison of all three catalysts layer before and after the introduction of Pt NPs.

.

	Specific Capacitance (F/g)	
	Bare Carbon	Pt/Carbon
Hierarchical	80	83
Mesoporous	48	42
Macroporous	15	16

References:

1 B. A. Pinaud, A. Bonakdarpour, L. Daniel, J. Sharman and D. P. Wilkinson, Key Considerations for High Current Fuel Cell Catalyst Testing in an Electrochemical Half-Cell, *J. Electrochem. Soc.*, 2017, **164**, F321–F327.

2 K. Ehelebe, D. Seeberger, M. T. Y. Paul, S. Thiele, K. J. J. Mayrhofer and S. Cherevko, Evaluating Electrocatalysts at Relevant Currents in a Half-Cell: The Impact of Pt Loading on Oxygen Reduction Reaction, *J. Electrochem. Soc.*, 2019, **166**, F1259–F1268.

3 N. Schmitt, M. Schmidt, G. Hübner and B. J. M. Etzold, Oxygen reduction reaction measurements on platinum electrocatalysts in gas diffusion electrode half-cells: Influence of electrode preparation, measurement protocols and common pitfalls, *J. Power Sources*, 2022, **539**, 231530.