

Supporting information

Which insights can gas diffusion electrode half-cell experiments give into activity trends and transport phenomena of membrane electrode assemblies?

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All data presented in the main article and in the supporting information is available from an open access repository:

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- Figure 3 <https://doi.org/10.48328/tudatalib-1048>
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RDE measurements

RDE measurements were carried out on a Octostat5000 Multichannel Potentiostat by Ivium Technologies and controlled by IviumSoft software. A leak-free double-junction Ag/AgCl electrode (Aldrich) was used as reference electrode and a Pt wire (PINE) as counter electrode. All potentials shown in this work were calibrated against reversible hydrogen electrode (RHE) using hydrogen evolution-oxidation reaction on a Pt electrode. A glassy carbon rotating disk electrode (GC-RDE, 5 mm diameter, PINE) was used as working electrode. Before every measurement the RDE was cleaned by ultrasonication in ethanol, acetone and ultrapure water. In order to coat the RDE with catalyst at first a catalyst ink was prepared. Therefore, the catalyst powder was placed in an eppendorf tube together with 5 wt-% Nafion[®] solution and an ethanol/water-mixture as solvent. The amount of Nafion[®] solution was adapted to achieve an ionomer-to-carbon ratio (I/C ratio) of 0.5. The amount of solvent was chosen to achieve a Pt concentration in the catalyst ink of 0.393 mg mL⁻¹. The catalyst was finely dispersed in the solvent by ultrasonic treatment using an ultrasonic processor (Hielscher, UP200St). Afterwards 10 µL of the homogeneous catalyst ink were pipetted on the RDE to achieve a Pt loading on the electrode of 20 µg cm⁻². In order to ensure a uniform catalyst layer on the RDE the catalyst ink was dried under rotation at 700 rpm. The electrochemical measurements were conducted at room temperature in N₂-saturated 0.1 M HClO₄ solution. For determination of the electrochemically active surface area (ECSA), the catalyst was first electrochemically cleaned via potential cycling between 0.05 and 1.2 V (vs. RHE) at 500 mV s⁻¹ for at least 200 cycles until the hydrogen adsorption/desorption signal was stable. Thereafter, CV curves in N₂-saturated 0.1 M HClO₄ in a potential range between 0.05 and 1.2 V (vs. RHE) at 20 mV s⁻¹ were measured and the charges associated with the hydrogen desorption signals were used to calculate the final ECSA, assuming 210 µC cm⁻² for calibrating the desorption charge of a monolayer of hydrogen on a Pt surface.

For the determination of the catalyst activity for the ORR the electrolyte was saturated with O₂ for at least 20 min and O₂ bubbling was maintained during the measurement. Then 3 cycles were recorded under rotation of the RDE with 1600 rpm in a potential range of 1.05 - 0.05 V vs. RHE with a scan rate of 20 mV s⁻¹. The ORR activity was determined out of the resulting polarization curves regarding the anodic sweep of the third cycle. Therefore, the measured current was baseline corrected by a current recorded previously with the same settings in N₂ atmosphere. For the determination of the ORR activity the mass-transport corrected kinetic current $j_{kinetic}$ was calculated by using the *Koutecky-Levich* equation:

$$\frac{1}{j} = \frac{1}{j_{kinetic}} + \frac{1}{j_{diffusion}}$$

Equation 1

where J is the baseline corrected experimentally measured current and $J_{diffusion}$ is the diffusion limited current. The kinetic current was calculated at 0.90 and 0.95 V vs. RHE. The calculated values were then normalized to the Pt mass, to obtain the mass specific activity (MSA).

GDE measurements

Catalyst coating of gas diffusion layers

For GDE evaluation, at first gas diffusion electrodes were prepared by catalyst coating of Sigracet 25 BC gas diffusion media. For catalyst ink preparation 4 mg of the respective catalyst sample were mixed together with deionized water ($<1.1 \mu\text{S cm}^{-1}$, VWR chemicals), ultrapure ethanol and ionomer (Aquivion® D98-25BS, Sigma-Aldrich) in an Eppendorf tube and finely dispersed with the use of an ultrasonic processor (Hielscher, UP200St). The total volume of ethanol and water was chosen to achieve a Pt concentration in the catalyst ink of 0.393 mg mL^{-1} . The ionomer/carbon ratio was held at 0.5 g g^{-1} and the volume percentage of ethanol in the catalyst ink was set to a value of 45 %. For application of the catalyst on the GDL the prepared catalyst ink was further diluted with an ethanol/water (45 % EtOH) in the ratio 1:1 and, finally, a volume of the resulting catalyst ink corresponding to a theoretical loading of $100 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ was pipetted onto the GDL, which is fixed in an alumina body preheated to $125 \text{ }^\circ\text{C}$ on a heating plate. The coated area is restricted by a PTFE mask, that is mounted onto the alumina body and having a round hole of varying diameter. In the present work PTFE masks resulting in catalyst coated areas of 0.785 cm^2 for the IL modified samples and 0.5 cm^2 for the N-doped catalysts were utilized.

Electrochemical protocol for GDE evaluation

GDE measurements were carried out in an automated setup, that is controlled using a single self-developed LabVIEW-based software application. As the measurement cell, a commercially available half-cell (FlexCell® PTFE, Gaskatel GmbH) was utilized at room temperature using 2 M perchloric acid (ROTIPURAN®Ultra 70 %, Carl-Roth), that was diluted with ultrapure water, serving as the electrolyte.

The electrochemical active surface area (ECSA) was determined by integrating the hydrogen desorption area (H_{UPD}) of the CVs in N_2 -atmosphere at a scan rate 100 mV s^{-1} , carried out after 200 activation cycles between 0.05 and 1.2 V vs. RHE at 500 mV s^{-1} . Additionally, CO-Stripping was carried out at a scan rate of 20 mV s^{-1} for determination of the ECSA. For ORR activity evaluation a galvanostatic step protocol is utilized, which is summarized in Table S1. For constructing the ORR polarization curves, the last 3 s of each current step were used, considering only the anodic sweep. The uncompensated resistance (iR drop) in the utilized GDE setup was determined using electrochemical impedance spectroscopy (EIS) and was used for post-correction of all measured potentials. In order to avoid any overcorrection of the iR drop due to heating of the electrolyte, for the

two highest measured current densities, the iR drop was determined separately during the course of the polarization curve measurement via EIS and used for post-correction of the potentials measured at these currents. All lower currents were corrected by using a uniform value determined at the beginning of the electrochemical evaluation (Step 1 in Table S1). For each experiment at least two samples have been tested. During the course of the measurement, the electrolyte chamber is constantly purged with $50 \text{ mL min}^{-1} \text{ N}_2$, while the gas flow to the gas chamber is adapted for the respective method.

Table S1: Protocol for the electrochemical characterization for 0.785 cm^2 catalyst spot size.

Step	Method	Parameter		
1	Determination of iR drop	EIS galvanostatic	Gas flow	N_2 ($\sim 300 \text{ mL min}^{-1}$)
			EIS frequency range	10000-1 Hz
			EIS amplitude	0.05 A
			Current	0 mA
2	Electrochemical cleaning	Cyclic voltammetry (CV)	Gas flow	N_2 ($\sim 300 \text{ mL min}^{-1}$)
			Potential limits	0.05 – 1.2 V
			Scan rate	500 mV s^{-1}
			Number of cycles	~ 200 (until CV constant)
3	ECSA (N_2)	CV	Gas flow	N_2 ($\sim 300 \text{ mL min}^{-1}$)
			Potential limits	0.05 – 1.2 V
			Scan rate	100 mV s^{-1}
			Number of cycles	3
4	Formation of CO-monolayer	Chronoamperometry (CA)	Gas flow	First 2 min: CO ($\sim 200 \text{ mL min}^{-1}$) Remaining time: N_2 ($\sim 500 \text{ mL min}^{-1}$)
			Potential	0.1 V
			Time	60 min
5	ECSA (CO)	CV	Gas flow	N_2 ($\sim 300 \text{ mL min}^{-1}$)
			Potential limits	0.1 – 1.0 V
			Scan rate	20 mV s^{-1}
			Number of cycles	3
6	ORR (O_2)	Galvanostatic staircase	Gas flow	O_2 ($\sim 200 \text{ mL min}^{-1}$)
			Pt-reduction step	0.1 V for 300 s in N_2 ($\sim 300 \text{ mL min}^{-1}$) OCV (600 s);
			Current steps* (holding time)	-0.04 mA; -0.08 mA (90 s); -0.20 mA; -0.40 mA (60 s); -0.80 mA; -2.00 mA; -4.00 mA; -8.00 mA (30 s) -20 mA; -40 mA; -80 mA; -200 mA; -400 mA; -800 mA; -1200 mA (5 s) →in negative and positive direction
7	ORR (Synthetic air)			See 6

*for 0.5 cm² catalyst spot size, the applied currents were adapted to reach identical geometric current densities compared to 0.785 cm² catalyst spot size. Additionally, a measurement point at a current density of -2500 mA cm⁻²_{geo} was added.

Thermodynamic and kinetic correction of GDE data for comparison with MEA data

In order to compare GDE and MEA results for the N-modified samples, the GDE data was corrected for the differing reaction conditions (temperature + partial pressure of oxygen reactant). Therefore, following [1], a kinetic and a thermodynamic correction of the GDE data was carried out. Thermodynamic correction was carried out using Nernst equation, whereby the influence of oxygen partial pressure and temperature on the Redox potential can be taken into account (see equation 2+3). For this comparison only MEA data collected at 100 %RH in oxygen atmosphere and GDE data measured in oxygen atmosphere was considered.

$$E(a_i, T) = E^0(T) - \frac{RT}{zF} \ln \left(\frac{a_{H_2O}}{a_{H_2} a_{O_2}^{0.5}} \right) = E^0(T) + \Delta E^{conc}(a_i, T) \quad \text{Equation 2}$$

With

$$E^0(T) = E^0(T^0) + \frac{\Delta s^0(T^0)}{zF} (T - T^0)$$

$$T^0 = 298.15 \text{ K} \rightarrow E^0(T^0) = 1.229 \text{ V}; z = 2, F = 96485 \frac{\text{C}}{\text{mol}}; R = 8,314 \frac{\text{J}}{\text{K mol}}$$

$$\Delta s^0(T^0) = s_{H_2O}^0 - s_{H_2}^0 + 0.5 s_{O_2}^0 = -163.3 \frac{\text{J}}{\text{K mol}}$$

$$a_{H_2O} = 1; a_{O_2} = \frac{p_{system} - p_{H_2O}(T_{Humidifier})}{p^0}; p^0 = 1.013 \text{ bar}$$

$$MEA: T = 80^\circ\text{C}, p_{H_2O} = 0.476 \text{ bar} \quad GDE: T = 20^\circ\text{C}, p_{H_2O} = 0.023 \text{ bar (assuming 100 \%RH)}$$

$$E_{GDE, corr} = E_{GDE} + [E(a_{MEA}, T_{MEA}) - E(a_{GDE}, T_{GDE})] = E_{GDE} - 65 \text{ mV} \quad \text{Equation 3}$$

For kinetic correction, the concentration effect on the kinetics is taken into account following equation 4:

$$j_{GDE, corr} = j_{GDE} \frac{p_{O_2, MEA}}{p_{O_2, GDE}} = 0.54 j_{GDE} \quad \text{Equation 4}$$

Inductively coupled plasma optical emission spectrometry

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000DV) was used to determine the platinum loading on the prepared N-doped and undoped Pt/KB catalyst samples. From each sample approximately 5 mg was taken and weighed into a vial. The vials were heated up in a muffle oven (Nabertherm® N7) to a temperature of 800 °C. The temperature was kept for four hours to eliminate the entire carbon from the catalyst. After cooling down, 5 mL of fresh aqua regia were added to the remaining residue. Afterwards, the samples were let stand for five days for full dissolution of platinum and then diluted with deionized water to a total volume of 50 mL. These samples were finally used for ICP-OES analysis.

Table S2: Pt content of the with and without N-doped via ICP-OES.

Sample	Pt-content / wt.%
Pt/C	30
N-mod Pt/C	38

synthesized Pt/C catalysts carbon support determined

Nitrogen Physisorption

Nitrogen physisorption was used to determine the specific surface area and the pore volume of the N-doped and undoped Ketjenblack carbon support. For all measurements the measuring device Quadrasorb evo (Quantachrome Instruments) was used.

Therefore, around 30 mg of the respective carbon support were measured into the glass tubes and then degassed in vacuum. For degassing, the samples were heated to 200 °C with a heating ramp of 2.5 K min⁻¹ and held at this temperature for 15 h. After cooling down, the samples were transferred to the sample room, evacuated and cooled down to 77 K with liquid nitrogen. The adsorption and desorption isotherms were recorded in a range of $10^{-5} \leq p/p_0 \leq 0.995$ with p_0 as the saturation pressure and p as gas pressure. The BET method was applied to evaluate the overall surface area by using a multipoint fit in the range of $0.04 \leq p/p_0 \leq 0.2$. Additionally, a DFT model was applied for determination of the specific surface area and for determination of the specific pore volume. The evaluation is carried out by using the software VersaWin.

Sample	BET surface area / $m^2 g^{-1}$	QSDFT surface area / $m^2 g^{-1}$	QSDFT specific pore volume / $cm^3 g^{-1}$
KB EC300-J	774	744	1.404
N-mod KB	792	760	1.445

Table S3: Results of the physisorption analysis of the unmodified and the N-doped Ketjenblack carbon support.

Elementary analysis

Elementary analysis was used to analyze the content of nitrogen, hydrogen and carbon of the N-doped and undoped Ketjenblack carbon support. The oxygen content was further calculated from the remaining difference after combustion of the sample. The measurements were carried out on the measuring device VarioEL III CHN (Company Elementar).

Table S4: Results of the elemental analysis of the unmodified and the N-doped Ketjenblack carbon support.

Sample	C / at%	N / at%	H / at%	O / at%
KB EC300-J	98.92 ± 0.01	-	-	1.08
N-mod KB	98.21 ± 0.01	0.23 ± 0.01	0.36 ± 0.00	1.18

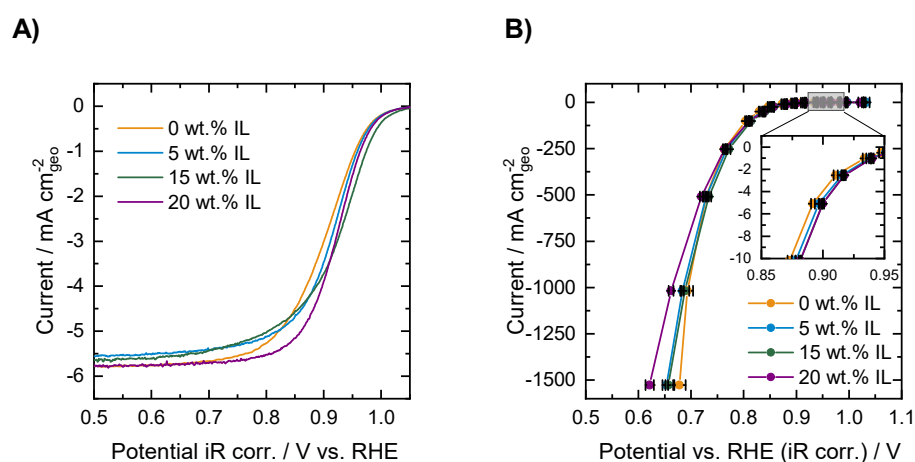


Figure S1: ORR activity of Pt/C catalyst modified with [BMIM][beti]. A) ORR polarization curves obtained in RDE measurements at room temperature in oxygen saturated 0.1 M HClO₄ and 1600 rpm at a catalyst loading of 20 µg_{Pt} cm⁻². B) ORR polarization curves obtained in GDE measurements at room temperature in oxygen atmosphere in 2 M HClO₄ at a catalyst loading of 100 µg_{Pt} cm⁻².

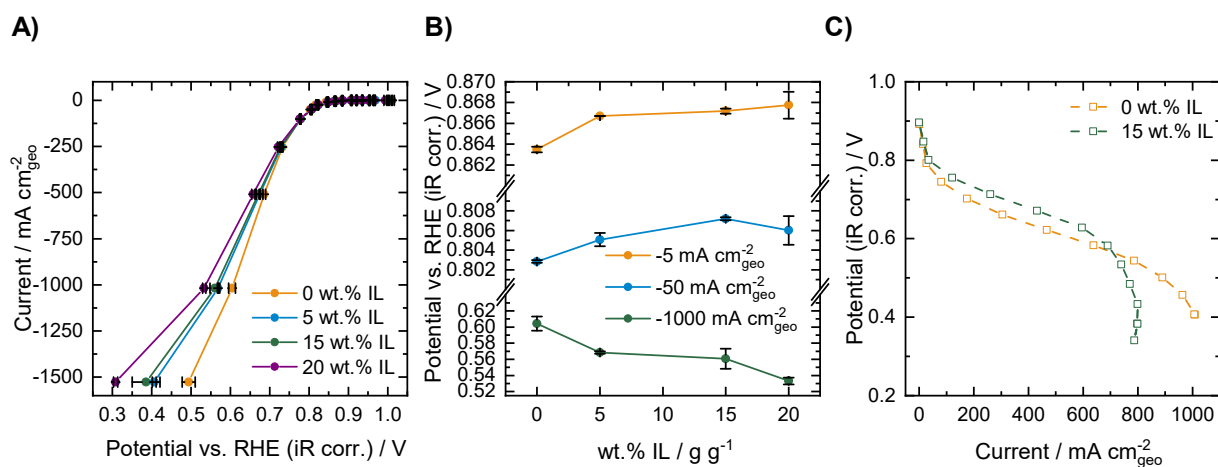


Figure S2: ORR activity of Pt/C catalyst modified with [BMIM][beti] in synthetic air. A) ORR polarization curves obtained in GDE measurements at room temperature in synthetic air in 2 M HClO₄ at a catalyst loading of 100 µg_{Pt} cm⁻². B) ORR potentials at different current densities depending on the amount of IL obtained in GDE measurements. C) ORR polarization curve of Pt/C catalyst modified with [BMIM][beti] in synthetic air.

unmodified Pt/C and Pt/C modified with 15 wt.% of IL measured in a MEA at 80 °C, and 100%RH synthetic air (1 atm) at a catalyst loading of $100 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$.

Table S5: Pt loadings of the gas diffusion layers coated with the synthesized Pt/C catalysts with and without N-doped carbon support and analyzed in GDE half-cell and in MEA measurements.

Sample	GDE half-cell loading / $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$	MEA cathode loading / $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$
Pt/C I/C 0.1 #1	75	172
Pt/C I/C 0.1 #2	75	163
N mod. Pt/C I/C 0.1 #1	99	215
N mod. Pt/C I/C 0.1 #2	99	219
Pt/C I/C 0.5 #1	75	194
Pt/C I/C 0.5 #2	75	204
N mod. Pt/C I/C 0.5 #1	101	253
N mod. Pt/C I/C 0.5 #2	101	237
Pt/C I/C 1.7 #1	75	187
Pt/C I/C 1.7 #2	75	173
N mod. Pt/C I/C 1.7 #1	102	270
N mod. Pt/C I/C 1.7 #2	102	250

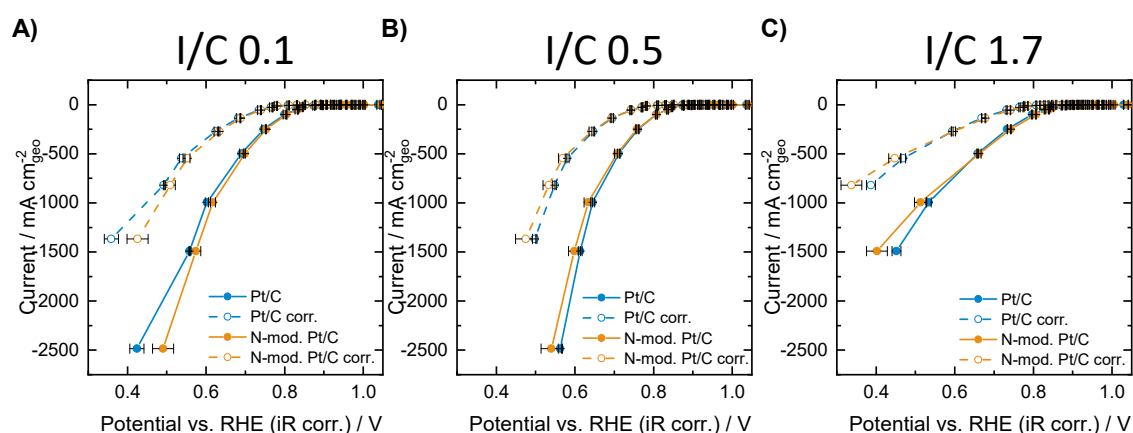


Figure S3: ORR polarization curves of the unmodified and N-doped Pt/C catalysts obtained in the GDE half-cell (data collected at room temperature in 2 M HClO_4 in oxygen atmosphere) before and after thermodynamic and kinetic correction for MEA conditions (80 °C, 100 %RH). A) I/C ratio = 0.1 B) I/C ratio = 0.5 C) I/C ratio = 1.7.

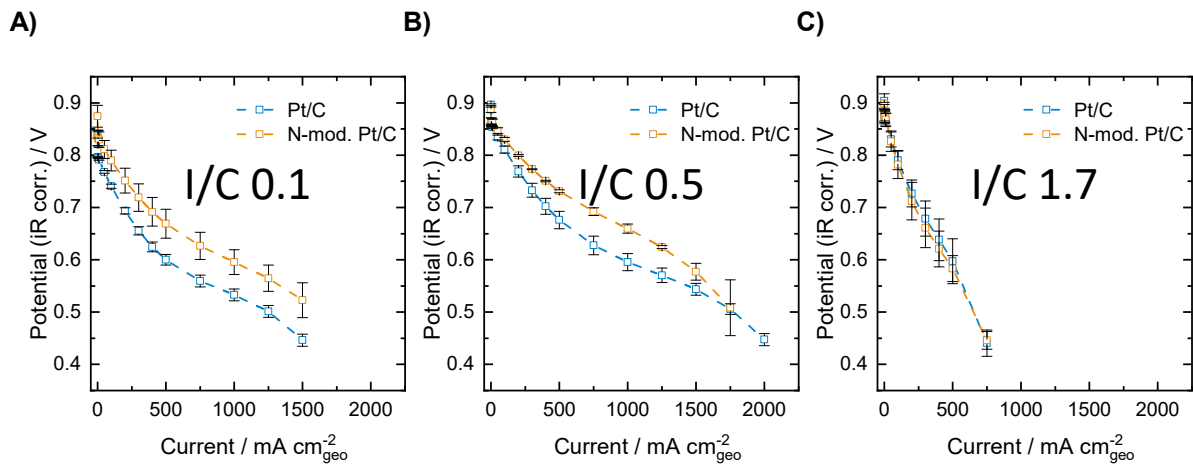


Figure S4: ORR polarization curves of the unmodified and N-doped Pt/C catalysts obtained in MEA measurements at 80 °C and 100 %RH in oxygen atmosphere (1 atm) A) I/C ratio = 0.1 B) I/C ratio = 0.5 C) I/C ratio = 1.7.

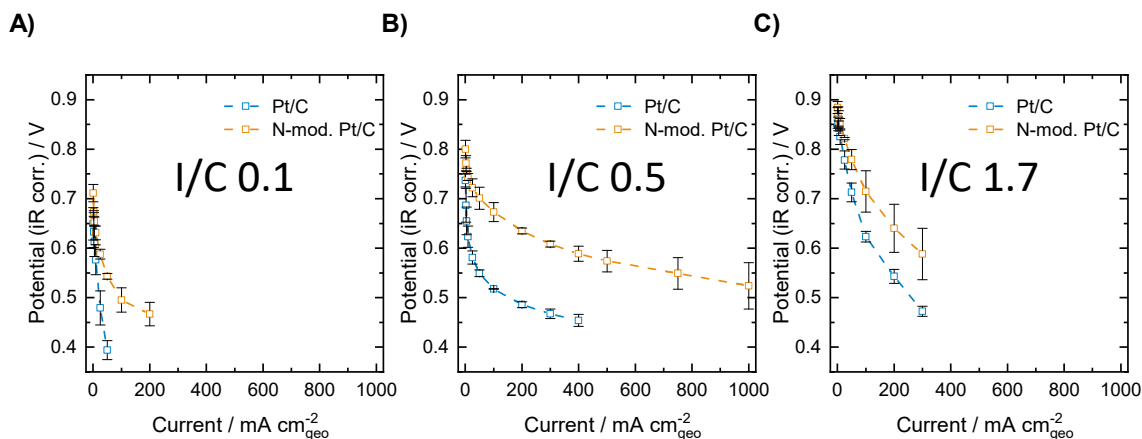


Figure S5: ORR polarization curves of the unmodified and N-doped Pt/C catalysts obtained in MEA measurements at 80 °C and 17 %RH in oxygen atmosphere (1 atm) A) I/C ratio = 0.1 B) I/C ratio = 0.5 C) I/C ratio = 1.7.

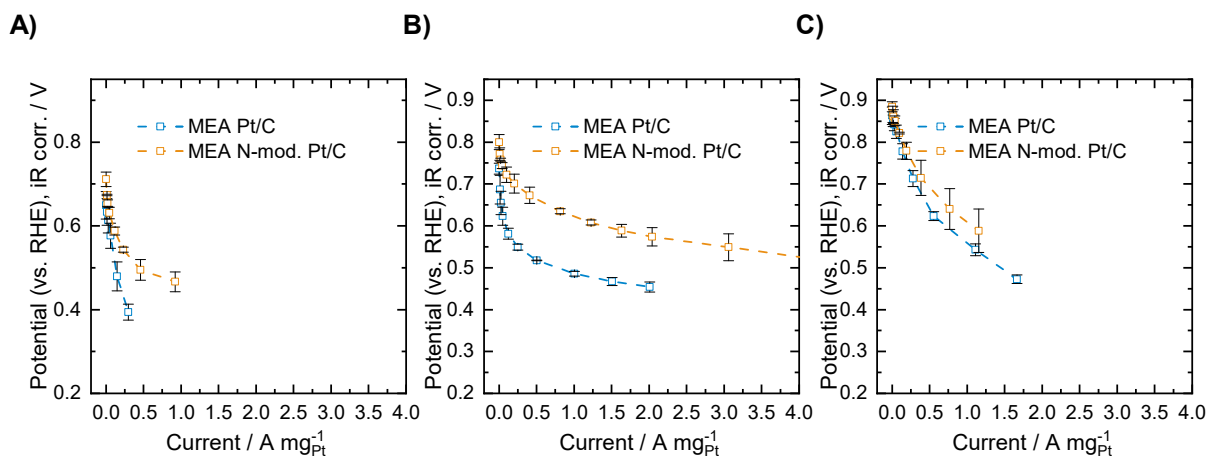


Figure S6: Mass specific ORR polarization curves of the unmodified and N-doped Pt/C catalysts obtained in MEA measurements at 80 °C and 17 %RH in oxygen atmosphere (1 atm) A) I/C ratio = 0.1 B) I/C ratio = 0.5 C) I/C ratio = 1.7.

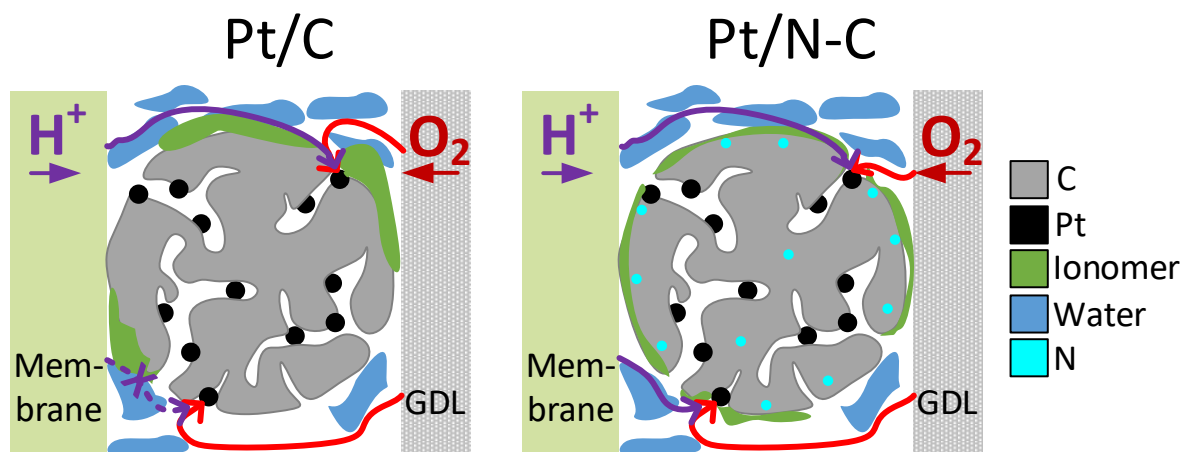


Figure S7: Schematic illustration of oxygen and proton transport pathways being affected by N-doping of Pt/C for low I/C ratio in MEA measurements.

References

- [1] K. Ehelebe, D. Seeberger, M.T.Y. Paul, S. Thiele, K.J.J. Mayrhofer, S. Cherevko, Journal of the Electrochemical Society 166 (2019) F1259.