Supplement

Autothermal Polarization of Membrane Electrode Assemblies – Effect of the Pt Content of the Catalyst and the Thickness of Fuel Cell Catalyst Layer

Balázs Kereszty[1], Gábor Pál Szijjártó[1*], Emese Lévai[2], Luka Szerb[1], Richárd Kunstár[1,3], András Tompos[1]

[1] Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, POB 17, 1525 Budapest, Hungary
[2] Department of Energy Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3., H-1111, Budapest, Hungary
[3] ArtTECHNICS Bt., Telepy street 5., 2nd floor / Nr.3, H-1096, Budapest, Hungary
[*] Corresponding author, e-mail: szijjarto.gabor@ttk.hu

1 Explanation of Nyquist diagram components in case of fuel cells

The abbreviations R_1, R_2, and $C2$ can be interpreted not only textually but also graphically on the Nyquist plots generated from impedance spectra (Fig. S1).

2 The differentiation of catalyst layer thickness and platinum content effects on temperature behavior

Catalyst layers in PEM fuel cells are comprised of nanoscale carbon supports, platinum particles, ionomer binders, and pore volume, forming a porous, irregular microstructure rather than a monolithic slab with a uniform thickness. Established surface characterization techniques such as SEM, TEM, AFM, or even highresolution optical profilometry cannot reliably quantify a single unambiguous thickness parameter for these coatings, because the surface exhibits significant micro and nanoscale roughness with pore opening and closing across the surface, leading to ambiguous height definitions. On the other hand porosity and ionomer distribution vary spatially, so a

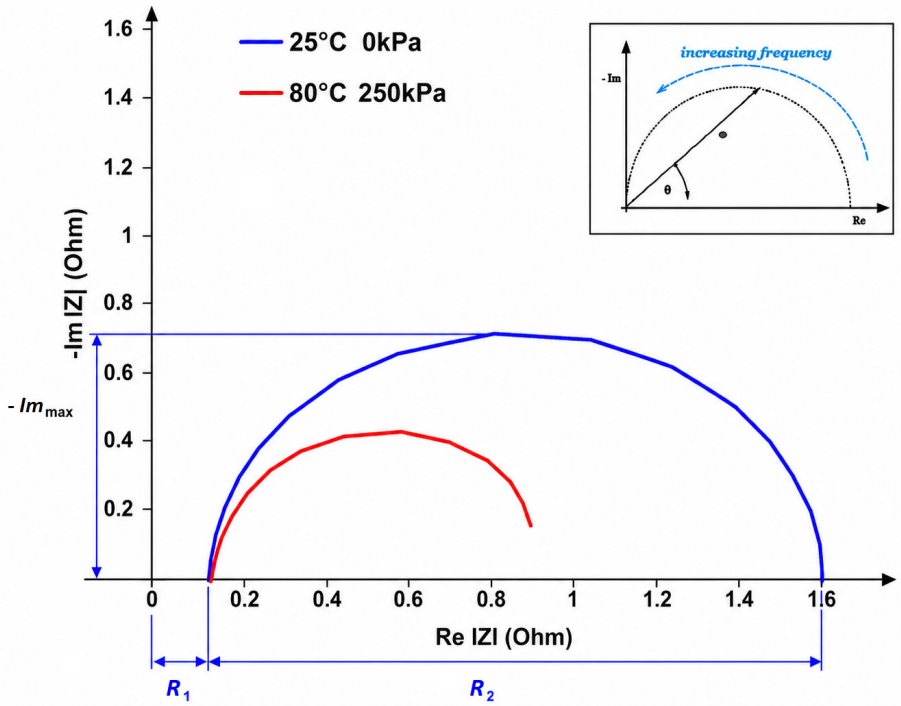


Fig. S1 Graphical explanation of R_1, R_2 and $C2$ parameters

single geometric distance between substrate and top surface does not capture the functional reaction interface. Last but not least the measurements on flat surrogate substrates (e.g., catalyst layers on glass) may approximate an average elevation, but these surrogate geometries do not faithfully represent MEA structures and water transport pathways in actual cells.

For these reasons, the community generally uses catalyst layer composition (Pt loading, ionomer content) and electrochemically active surface area (ECSA) as meaningful metrics, rather than attempting to define an exact physical thickness. The present dataset controls Pt loading symmetrically across samples, and the observed thermal and impedance responses can be directly attributed to catalyst layer structural and compositional differences, without relying on a poorly defined thickness parameter.

3 Tafel slope calculation

The Tafel slope characterizes the voltage drop occurring in the activation region when the current density increases by one order of magnitude (Table S1). The Tafel equation in the activation-controlled region is given by:

$$E_a = a + b \times \log_{10}(j), \quad \text{(S1)}$$

where:

- E_a = activation overpotential [V]
- j = current density [mA/cm²]
- b = Tafel slope [V/decade]

The fitted slope (reported in absolute value) is obtained from a near-linear regression of the activation region of the polarization curve. The extrapolated intercept corresponds to the open circuit voltage (OCV) observed at the initial point of the curve.

4 Why are the back pressures of the anode and cathode different during the autothermal activation

An international standard had be followed during the fuel cell testing process, which provides more objective and exact comparison to results of other researchers. The New European Driving Cycle (NEDC) protocol [1] was the method, which was chosen by us. NEDC defines exactly the most important measurement parameters: cell temperature (80 °C), relative humidity (anode: 50%, cathode: 30%), back pressures (anode: 250 kPa, cathode: 230 kPa). In case of polarizations at fixed temperature, just this protocol was followed. Method had to be modified in autothermal activation and polarization, because in that case temperature and humidity ratio is continously changing, but back pressure can be fixed, and pressure difference between anode and cathode also can be kept. That was the reason, that the back pressures of the anode and cathode were different during the autothermal activation. Anode pressure is usually higher than anode pressure, because by this way water crossover can be avoided. Higher anode back pressure makes hurdle for the water, which is produced on the cathode side because of the working of the fuel cell.

During the autothermal activation applied pressures were smaller, than in case of polarization at fixed temperature (150–130 kPa *vs.* 250–230 kPa). Most important reason is the material of the gaskets. They were made of polyethylene (PE). Advantages of that material are availability, cheapness and chemically inertness. In case of a simple measurement (with NEDC conditions) firstly temperature is risen to 80 °C and then, after 10 min waiting / temperation, back pressure is set to 250 kPa (anode) or 230 kPa (cathode). Temperation helps PE gaskets to take the shape of O-ring sealings, which provides better gas tightness of the cell. In case of autothermal activation, temperation is missing, because process starts at room temperature. That was taken into account, and applied back pressure was decreased, but 20 kPa pressure difference between anode and cathode was kept for avoiding the water crossover.

Table S1 Tafel slope in case of different samples

Sample	Tafel slope (mV/decade)
C-40-Pt loading = 0.57 mg/cm²	156.8
C-60-Pt loading = 0.57 mg/cm²	174.6
C-60-Pt loading = 0.13 mg/cm²	84.2

5 $R1$, R_2, C_2 values obtained in autothermal polarization case and in NEDC measurements

When measuring various samples using different protocols, we may obtain different results. The figures below illustrate this in an expanded form (Fig. S2).

6 GEIS curves from autothermal polarization and GEIS curves at constant 80 °C temperature

In autothermal case: frequency: 1–10,000 Hz; amplitude: 500 mA; Anode: 150 kPa H_2; Cathode: 130 kPa O_2; 16 cm² GDEs. In the GEIS measurement: Frequency: 1–10,000 Hz; amplitude: 500 mA; T = 80 °C; Anode: 250 kPa H_2 50% relative humidity; Cathode: 230 kPa O_2 50% RH; 16 cm² GDEs (Fig. S3).

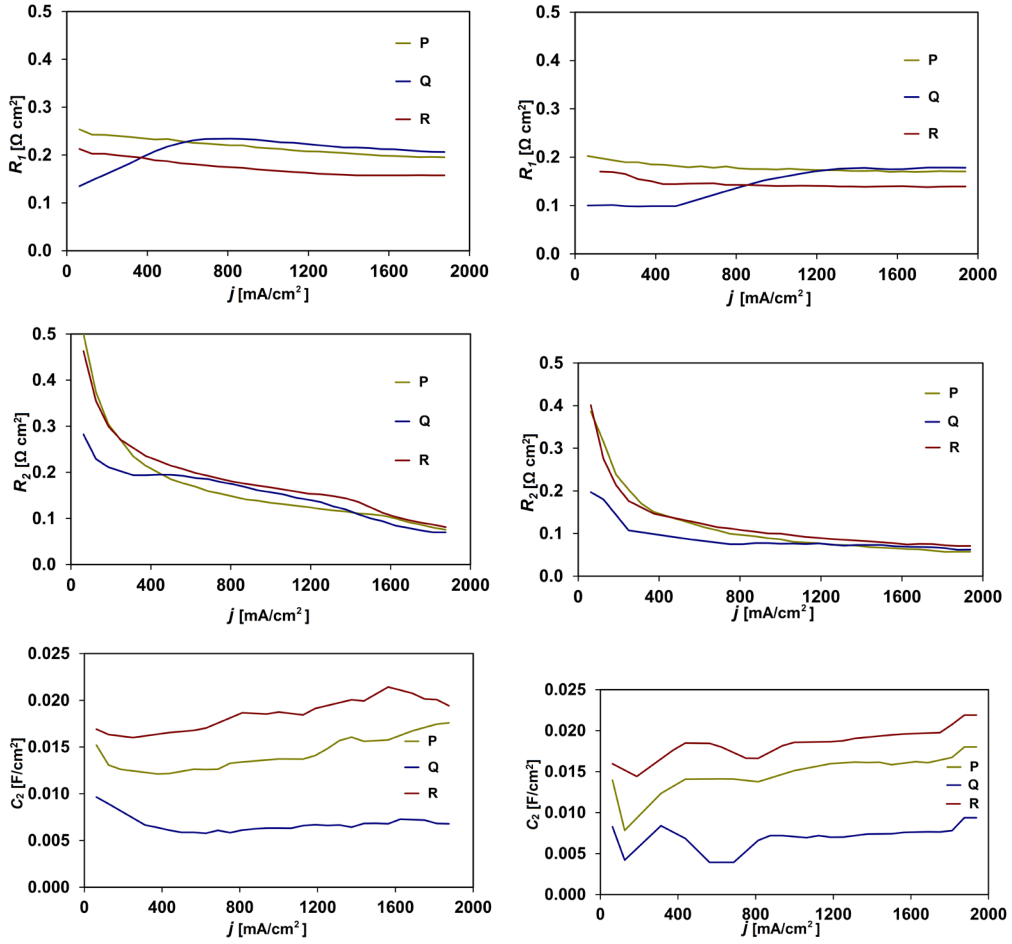


Fig. S2 R_1, R_2 and $C2$ values obtained in (a) autothermal polarization and (b) in NEDC measurements

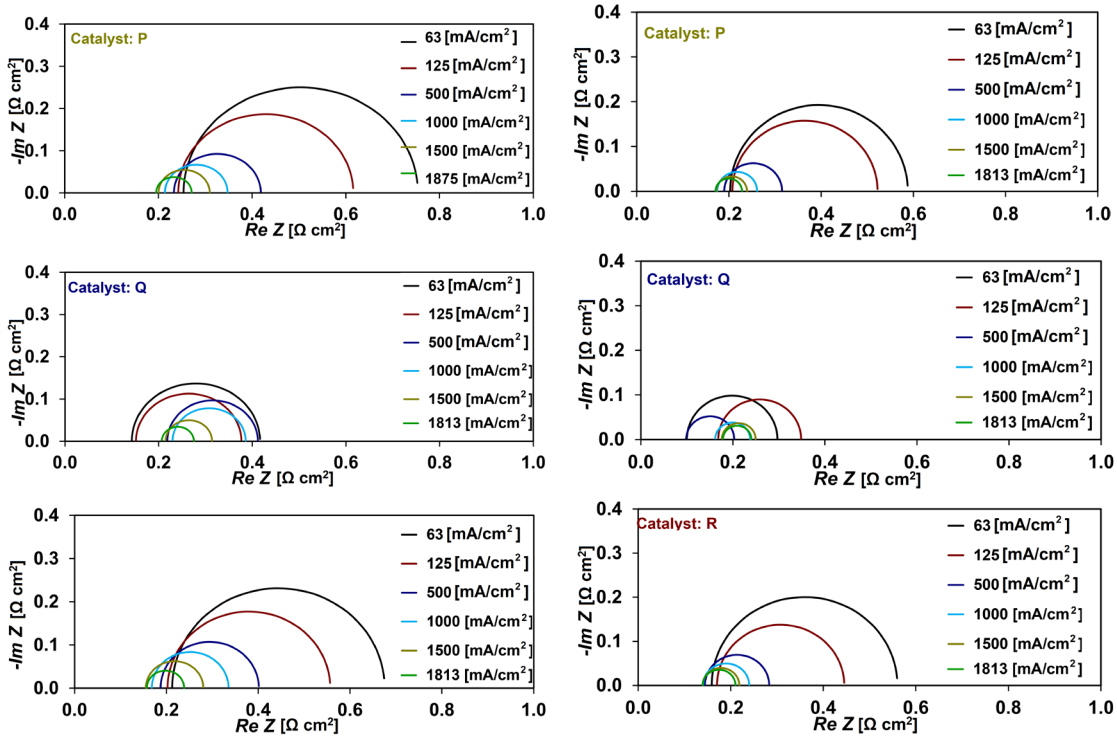
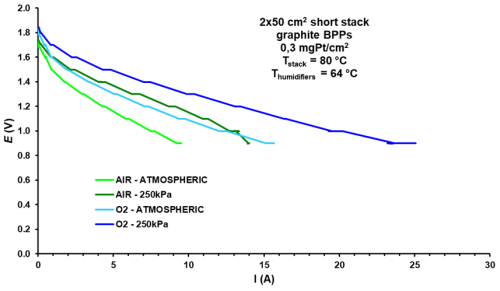


Fig. S3 (a) GEIS curves from autothermal polarization and (b) at 80 °C constant temperature.

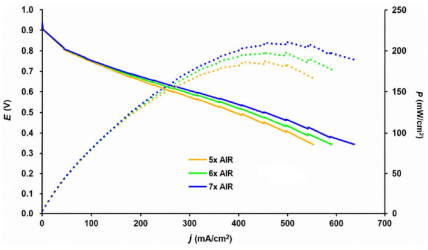
7 A comprehensive review of the factors influencing the autothermal polarization behavior of the MEA

First of all it is necessary to clarify, that what are those phisical factors, which has influence generally on the polarization itself. NEDC protocol [1], which was also used by us, have a detailed recommendation for different parameter settings Reaction temperature, ratio of humidity, back pressure, flow rate of anode gas and cathode gas, oxygen content of cathode gas (pure O_2 vs. air); they are those factors, which has important role in increasing or decreasing of the cell performance. Following examples, which were previously measured by us in other projects, will demonstrate the effect of different phisical parameters. Fig. S4 shows polarizations in case of different back pressures, in air and in pure O_2. This is clearly visible, that larger back pressure and larger oxygen content of cathode gas have positive effect on polarization.

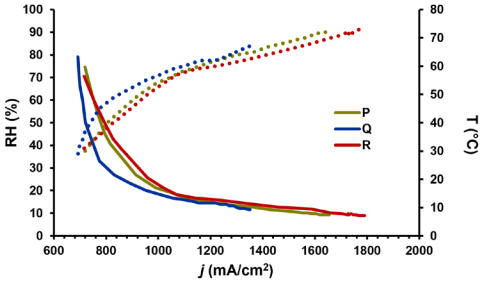
Increasing of the reaction temperature and ratio of humidity also increase the performance of the cell. That was our experience and the conclusion of the review of Ozen et al. [2]. Fig. S4(b) shows polarizations, in which H2 flow is fixed and air flow is increased, for demonstration of the effect of the flow ratio of hydrogen and cathode gas. It is vizible, that larger amount of oxygen increases the performance of the cell.



(a)



(b)



(c)

Fig. S4 (a) Polarization of a 2 × 50 cm² short stack for testing of the effect of back pressure and the oxygen content of cathode gas. (b) Polarizations with diffent air flow rates. Hydrogen flow was 200 mL/min, air flow was 1000 mL/min (yellow line), 1200 mL/min (green line) and 1400 mL/min (blue line). (c) Shows the changing of humidity and temperature as a function of current density. Largest decrement in ratio of humidity appears in the beginning of the process.

8 The descriptions regarding porosity and electrochemical active surface area are lacking in corresponding characterization data

8.1 Experimental for nitrogen physisorption measurement

Nitrogen physisorption measurements were carried out at temperature of liquid nitrogen (−196 °C) using a Surfer automatic volumetric adsorption analyzer (Thermo Fischer Scientific, Berlin, Germany). The specific surface area was calculated by the Brunauer-Emett-Teller (BET) method in the range of relative pressures from 0.05 to 0.30 [2]. Surface area of C-60-Pt was 110 $m^2/g \pm 1.47$; surface area of C-40-Pt was 120 $m^2/g \pm 0.72$.

8.2 Cyclic voltammetry on fuel cell

Cyclic voltammetry (CV) was applied for quick testing of the cell composition and for determinaton of the electrochemically active surface area (ECSA). Our experience showed, that if CV is able to run, and H-adsorption and desorption peaks appear, in that case polarization of the MEA is usually possible (Fig. S5, Table S2). Theory of CV in case of the three electrode system in electrochemical cell and liqiud electrolyte (0.5 M H_2SO_4) is almost the same, as in case of a PEMFC MEA. In fuel cell hydrogen is the anode gas and nitrogen is the cathode gas. Cathode is the working electrode and anode is the

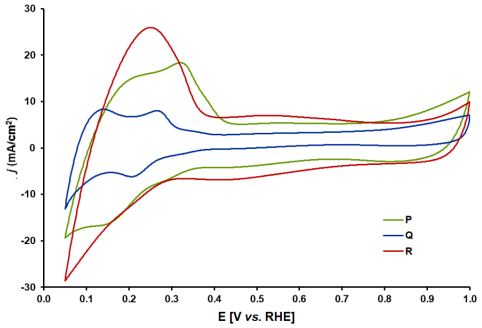


Fig. S5 MEA CVs of the examined samples

Table S2 ECSA loading in different samples

Sample name/abbreviation	ECSA [m^2/g Pt]
P	20.47
Q	35.59
R	26.77

counter and reference electrode. Speed of cyclization was 100 mV/s and measurements were carried out at room temperature to decrease the resistance of the cell. 100% RH was applied, without back pressure, which is in accordance with the offered CV settings of the manufacturer of our FC tester [3].

For calculation of ECSA (on fuel cell), size of the GDE (in cm^2) and its Pt loading (in mg Pt/cm^2) are necerrary parameters. The electrochemically active surface area of the catalysts can be determined by the following equations [4]:

$$\mathrm{ECSA}_{\mathrm{H_{upd}}}\left(\mathrm{cm^2}\right)=\mathrm{Q}_{\mathrm{OX_{H_{upd}}}}\left(\mu\mathrm{C}\right)/210\left(\mu\mathrm{C/cm^2}\right) \quad \text{(S2)}$$

$$\mathrm{ECSA}_{\mathrm{CO}}\left(\mathrm{cm^2}\right)=\mathrm{Q}_{\mathrm{OX_{CO}}}\left(\mu\mathrm{C}\right)/420\left(\mu\mathrm{C/cm^2}\right) \quad \text{(S3)}$$

where:

- ECSA: Electrochemically active area,
- Q: Electryc charge,
- OX: Oxidation,
- H_{upd}: abscorption,
- LPt: Platinum loading.

The real surface area of Pt catalysts is frequently investigated by in situ electrochemical methods, where currents associated with adsorption and desorption of a (sub)monolayer of species like hydrogen or carbon monoxide from the nanoparticle surface are measured [5]. Underpotential deposition of hydrogen (H_{upd}) and CO_{ads}-stripping voltammetry are the most frequently used electrochemical method for the real surface area determination of Pt. The surface area is then calculated from the charge that originates from the adsorption and desorption of these test species. In case of fuel cell, electrochemical testing with CO is technically more difficult, than in case of classic 3 electrode electrochemical cell with liquid electrolyte, and because of that reason, underpotential deposition of hydrogen (H_{upd}) was only analysed by CV on PEMFC.

The electrocatalytically active platinum surface area (ECSA) on which electrochemical reaction occurs can be determined by Eq. (S4):

$$\mathrm{ECSA}=Q_{ox_i}/Q^{s}_{ox_i}, \quad \text{(S4)}$$

where Q_{ox_i} is the charge accompanying the oxidation of the test species chemisorbed on the Pt surface, while $Q^{s}_{ox_i}$ is the transferred charge while a complete monolayer of test species i (i: H_{upd} or CO) is oxidized on 1 cm^2 of the Pt surface. The transferred charge of the oxidation of chemisorbed test species (Q_{ox_i}) can be calculated by the Eq. (S5) [6]:

$$Q^{s}_{ox_i}=n_i\times e\times N_A\times\Gamma_i, \quad \text{(S5)}$$

where n is the number of the transferred electrons, e is the elementary charge 1.6022×10^{-19} C, N_A is the Avogadro constant 6.022×10^{23} mol^{-1} and Γ_i is the surface concentration of adsorbed species. Assuming that $N_A\times\Gamma_i$ is equal to the surface density of the metal atoms (N_M) per unit surface area, the Eq. (S6) can be obtained as a simplified version of Eq. (S5):

$$Q^{s}_{ox_i}=n_i\times e\times N_M \quad \text{(S6)}$$

In the predominance of the (100) plane face or in case of equal distribution of the three low index planes on polycrystalline Pt, the number of surface atoms in 1 cm^2 of the platinum is 1.31×10^{15} cm^{-2} [7]. Assuming that the surface is covered with the monolayer of chemisorbed species, i.e., one H atom per surface Pt atom [6], the $Q^{s}_{ox_i}$ can be calculated.

Since, in case of hydrogen oxidation, the number of the transferred electrons is equal to 1 (n = 1), the transferred charge while underpotentially deposited hydrogen oxidized on 1 cm^2 Pt surface, ($Q^{s}_{oxH_{upd}}$) will be equal to Eq. (S7):

$$\begin{aligned}Q^{s}_{ox_{H_{upd}}}&=1\times1.6022\times10^{-19}\,\mathrm{C}\times1.31\times10^{15}\,\mathrm{cm^{-2}}\\&=210\ \mu\mathrm{C/cm^2}\end{aligned} \quad \text{(S7)}$$

References

[1] European Commission "Scientific, Technical and Economic Committee for Fisheries (STECF) – FDI methods (STECF-25-05)", JRC Publications Repository, 2025. https://doi.org/10.2760/7393752

[2] Nur, O., Timurkutluk, B., Altinisik, K. "Effects of operation temperature and reactant gas humidity levels on performance of PEM fuel cells", Renewable and Sustainable Energy Reviews, 59, pp. 1298–1306, 2016. https://doi.org/10.1016/j.rser.2016.01.040

[3] Ayyubov, I., Tálas, E., Borbáth, I., Pászti, Z., Trif, L., ..., Tompos, A. "Linking Structure to Electrocatalytic Performance: Graphene Nanoplatelets-Derived Novel Mixed Oxide–Carbon Composites as Supports for Pt Electrocatalysts with Enhanced Stability", Nanomaterials, 15(23), 1753, 2025. https://doi.org/10.3390/nano15231753

[4] Cooper, K. R. "In Situ PEM Fuel Cell Electrochemical Surface Area And Catalyst Utilization Measurement", Fuel Cell, 2009, pp. 28–30, 2009.

[5] Bard, A. J., Rubenstein, I. (eds.) "Electroanalytical Chemistry", CRC Press, 1996. ISBN 9780824793791

[6] Schulenburg, H., Durst, J., Müller, E., Wokaun, A., Scherer, G. "Real surface area measurements of Pt_3Co/C catalysts", Journal of Electroanalytical Chemistry, 642(1), pp. 52–60, 2010. https://doi.org/10.1016/j.jelechem.2010.02.005

[7] Trasatti, S., Petrii, O. "Real Surface Area Measurements in Electrochemistry", Pure and Applied Chemistry, 63(5), pp. 711–734, 1991. https://doi.org/10.1351/pac199163050711