### **Supporting information**

## Probing of complex carbon nanofiber paper as gas-diffusion electrode for high temperature polymer electrolyte membrane fuel cell

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#### **Table of contents**

Cyclic voltammetry (CV)	2
BET specific surface area data	4
Electrochemical impedance spectroscopy (EIS)	5

#### Cyclic voltammetry (CV) of the catalyst Pt/PAN/Vulcan/Ni/Zr-350-1000

#### Catalytic ink preparation

2 mg of the catalyst in 300  $\mu$ L of bidistilled water in fitst Eppendorf tube and 1  $\mu$ L of 5% Nafion solution in 300  $\mu$ L of bidistilled water in second Eppendorf tube were homogenized in ultrasonic bath during 10 min. Then, 200  $\mu$ L from the second tube were moved to the first tube (total resulting volume in the first tube is 500  $\mu$ L), and the fitst tube was sonicated in ultrasonic bath during 40 min).

#### Catalytic ink deposition

5  $\mu$ L of Pt-containing catalytic ink were deposited on isotropic pyrocarbon working electrode (surface area 0.196 cm<sup>2</sup>), which corresponds to 102  $\mu$ g cm<sup>-2</sup> of catalyst. Then, the electrode was dried.

#### CV

Usually CV is used for study and control of the catalyst surface state on a catalyst/electrolyte border. CV was registered in the potential range -0.2 - 1.1 V with silver chloride Ag/AgCl reference electrode (0.04 – 1.34 V respective to SHE) at 0.05 V s<sup>-1</sup> rate, under inert atmospere (Ar) at 50 °C. All electrochemical measurements were conducted using IPC-Pro potentiostat.

*Surface area assessment of electrochemically active surface (Sel-a) of platinum catalyst* 

For  $S_{el-a}$  calculation of platinum component of the catalyst, the value of charge which is necessary for one hydrogen atom adsorption on the surface (Q<sub>H</sub>) is used. For polycrystalline platinum,  $Q_H = 0.210$  mC cm<sup>-2</sup>.

Electrical charge spent for hydrogen desorption was determined by CV curve integration in the range 0.04 - 0.16 V (related to SHE) or -0.200 - 0.16 V (Ag/AgCl) using formula:

# $Q_{S1} \;=\; \int i \partial E$

where  $Q_{S1}$  – charge required for hydrogen desorption

i – current density, mA cm<sup>-2</sup>,

E – potential (related to SHE), V, where E is a function of time.

Correction for double layer charge was introduced according to:

$$Q_S = Q_{S1} - Q_{S2}$$

where  $Q_S$  – charge required for hydrogen desorption, considering double layer charge, mA V cm<sup>-2</sup>,

 $Q_{S1}$  – charge required for hydrogen desorption, mA V cm<sup>-2</sup>,

 $Q_{S2}$  – charge required for double layer charging, mA V cm<sup>-2</sup>,



Fig. S1. CV of the catalyst in the range -0.2 - 1.1 V respective Ag/AgCl with two different catalyst depositions (a) and (b) on pyrographitic electrode. 0.5 M H<sub>2</sub>SO<sub>4</sub>, Ar, 50 °C, rate 0.05 V s<sup>-1</sup>.

The calculation of electrochemically active surface  $(S_{el-a})$  of platinum component was performed according to

$$S_{el-a}\left[\frac{\mathrm{m}^2}{\mathrm{g}_{Pt}}\right] = \frac{Q_s\left[\frac{\mathrm{mA}\,\mathrm{V}}{\mathrm{cm}^2}\right]}{\nu\left[\frac{\mathrm{V}}{\mathrm{s}}\right] \times 0.210\left[\frac{\mathrm{mC}}{\mathrm{cm}^2}\right] \times m\left[\frac{\mathrm{g}_{Pt}}{\mathrm{cm}^2}\right]}$$

where  $Q_s$  – charge required for hydrogen desorption considering double layer charging, mA V cm<sup>-2</sup>,

v – potential rate, V s<sup>-1</sup>,

m – mass of Pt per unit of electrode surface,  $g_{Pt}$  cm<sup>-2</sup>.

Electrochemically active surface of platinum component was calculated from CV curves and is  $25 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ .

#### BET specific surface area data



Fig. S2. Multi-point BET for 1 (PAN/Vulcan/Zr/Ni-350-1000).

Calculated data from BET: Slope 54.255 Intercept 3.263 Correlation coefficient, r 0.995401 C constant 17.626 Specific Surface Area 60.546 m<sup>2</sup> g<sup>-1</sup>

To compare, Specific Surface Area for carbon black Vulcan $\mathbb{R}XC$ -72 is 213 m<sup>2</sup> g<sup>-1</sup> according to T. Chen, et al. Sci. Rep., 2016, 6, 23289.



Fig. S3. EIS Nyquist plot for PAN-CB-250-900 (black) and for commercial electrode Celtec $\mathbb{R}$  P1000 (red) recorded at 160 °C; 0.2 A cm<sup>-2</sup>.

PAN-CB-250-900 is an alternative material which is obtained by the electrospinning from a solution of polyacrylonitrile, polyvinylpyrrolidone and carbon black Ketjenblack® EC-600, oxidized at 250 °C (air), and pyrolyzed at 900 °C (vacuum). "Irregular" shape of the Nyquist plot on Fig. S5 suggests lack of proton conductivity under conditions of fuel cell operation.



Fig. S4. EIS Nyquist plot for the composite electrode **1a** Pt/PAN/Vulcan/Ni/Zr-350-1000, recorded at  $180 \,^{\circ}$ C; 0.4 A cm<sup>-2</sup>.

It is assumed that the discussed improvement in proton conductivity for the composite electrode is due to Zr incorporation resulting in  $ZrO_x$  after pyrolysis.