

Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers
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Supplementary information

Nickel-based pectin coordination polymer as oxygen reduction reaction catalyst for proton-exchange membrane fuel cell

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S1. Experimental Details

IR. Infrared (IR) (Figure S1) spectra were recorded on IR-Fourier spectrophotometer IRS-113 (Bruker) with 1 cm⁻¹ resolution in the range 400–4000 cm⁻¹, the substance being pressed with KBr in tablets.

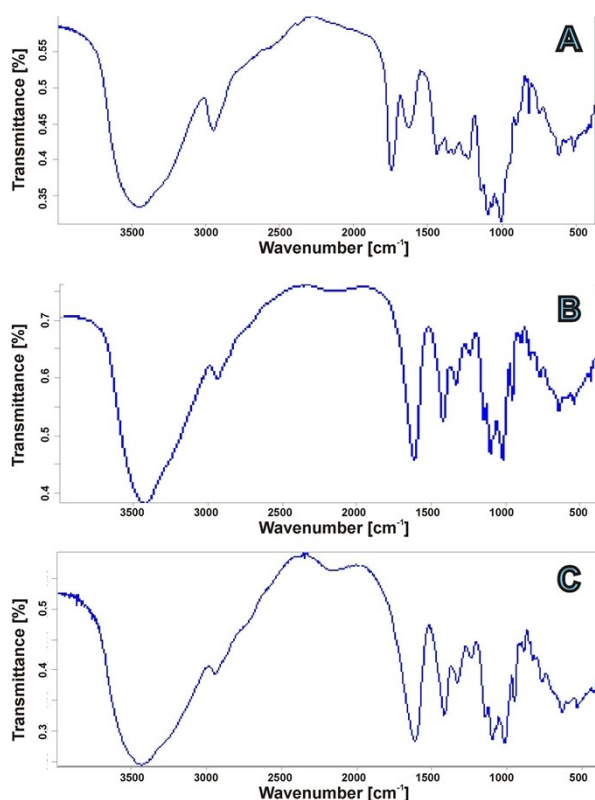


Figure S1. IR spectra (A) - pectin Herbstreith & Fox KG (Germany), (B) - sodium polygalacturonate (PG-Na), (C) - sodium polygalacturonate complex with nickel (PG-NaNi) with 25% sodium substitution for nickel.

The disappearance of the absorption band of the valence vibrations ν (C=O) of the carboxyl or ester groups at 1745-1750 cm^{-1} , characteristic for pectin (Figure S1A) and the appearance of the absorption band of valence vibrations ν (C=O) at 1600-1650 cm^{-1} , characteristic for the ionic form have been presented in the IR spectra of PG-Na (Figure S1B) and PG-NaNi (Figure S1C).

S2. ICP-OES. Na, Ni were identified in the samples using simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) model iCAP 6300 DUO by Varian Thermo Scientific Company equipped with a CID detector. This spectrometer enables the simultaneous measurement of peak heights within the 166 to 867 nm range. The optical resolution is less than 0.007 nm to 200 nm. The working frequency is 27.12 MHz. Together, the radial and axial view configurations enable optimal peak height measurements with suppressed spectral noises. Concentration of Na, Ni ions was determined, respectively, by the spectral lines: 589.592 nm, 231.604 nm.

Sample preparation was carried out as follows: 10 mg of sample was placed in 20 ml of 0.2 M sulfuric acid solution. After 1 month, the resulting solution was filtered. Content of elements in % of total mass on ICP-OES results are shown in the Table S1.

Table S1. Content of elements of PG-NaNi in % of total mass on ICP-OES results

Sample	Content of elements in % of total mass	
	Na (589.592)	Ni (231.604)
PG-NaNi	4.12	3.54

S3. DSC/TG/DTG. The thermal decomposition of sodium nickel polygalacturonate PG-NaNi was studied (Figure S2) by thermal analysis (differential scanning calorimetry / thermogravimetry / differential thermogravimetry - DSC/TG/DTG) in which the variation of the sample mass as a function of temperature and the corresponding heats are recorded. A NETZSCH STA449-F3 TG/DSC instrument was used. The sample (~15 mg) was placed in aluminum crucible with a perforated lid and heated from room temperature to 350°C together with an empty crucible as the reference. The TG/DSC measurement was carried out at a heating rate of 10 K/min in an argon flow of 50 mL/min.

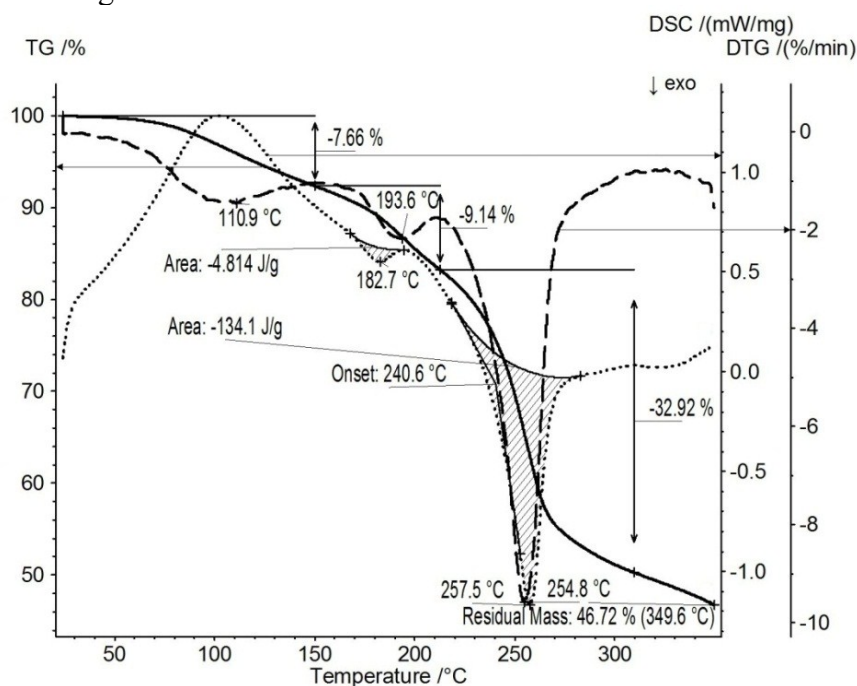


Figure S2. DSC/TG/DTG curves of PG-NaNi.

S4. AFM. An atomic force microscope MultiMode V has been used to reveal the morphology of the particles. The 250-350 kHz cantilevers (Veeco, USA) with silicone tips (tip curvature radius is of 10-12 nm) have been used in all measurements. The microscopic images were obtained with 512×512 resolution. The scanning rate was 1 Hz.

S5. TEM. The transmission electron microscopy (TEM) images were obtained with Hitachi HT7700, Japan. The images were acquired at an accelerating voltage of 100 kV. Samples were ultrasonicated in water for 10 min and then dispersed on 300 mesh copper grid with continuous carbon-formvar support film. Figure S3 shows an additional TEM-image of PG-NaNi.

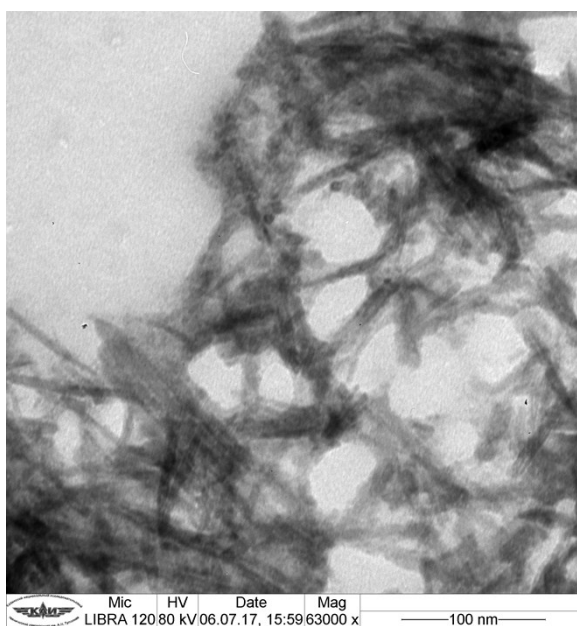


Figure S3. TEM-image of PG-NaNi.

S6. SEM. The investigation by SEM (Figure S4) were carried out on an information from reflected electrons from InLens and SE2 modes. Mainly the InLens mode was chosen which allows to provide high resolution about 10 nanometers. The magnification was up to 150000 at the electron's accelerated voltage 5 KV. The pectin powder were applied on a plain surface of a special substrate for SEM on air. As a covering of a substrate the carbon adhesive tape was used.

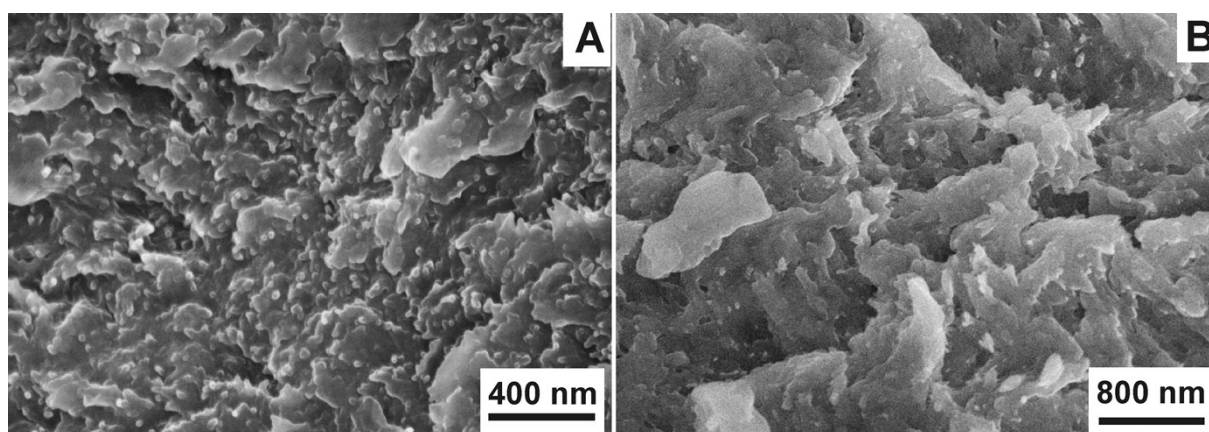


Figure S4. SEM images of PG-Na (A) and PG-NaNi (B).

S7. XRD. Powder X-ray diffraction patterns were obtained (Figure S5) on an automatic X-ray diffractometer Bruker D8 Advance, equipped with a Vario attachment and a linear coordinate detector Vantec. Cu K α radiation (λ 1.54063 Å), monochromatized by the curved Johanson monochromator, operating mode of the X-ray tube 40 kV, 40 mA was used. The experiments were performed at room temperature in the Bragg-Brentano geometry with a flat sample.

The sample was preliminarily ground and applied a thin layer on the surface of a single-crystal silicon plate (standard holder with minimal background scattering), or filled into a cavity of a standard cell of polymethylmethacrylate. The diffraction patterns were recorded in the range of scattering angles 2θ 3 - 80 °, step 0.008 °, the time of spectrum collection at the point 0.1 - 3.0 sec. Several diffractograms were obtained with different dataset time. The processing of the obtained data was carried out using the EVA software package [DIFFRAC Plus Evaluation package EVA, Version 11 (2005). User's Manual, Bruker AXS, Karlsruhe. Germany. - 258 p].

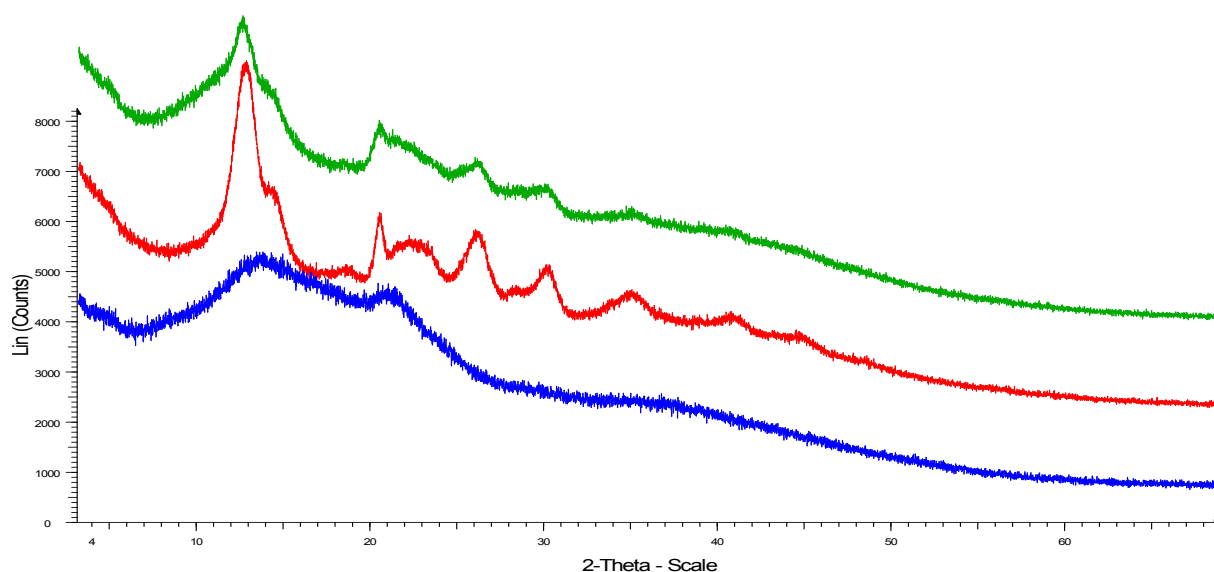


Figure 5 Experimental diffraction patterns of pectin (blue), PG-Na (red) and PG-NaNi (green).

S8. Electrochemistry. Electrochemical measurements were performed on a BASiEpsilonE2P electrochemical analyzer (USA). The program handles wave Epsilon-EC-USB-V200. A conventional three-electrode system was used with glassy carbon for solutions or carbon paste electrode (CPE) for powder samples as the working electrode, the Ag/AgCl (0.01M) electrode as the reference electrode and a Pt wire as the counter electrode. 0.1 M Et₄NBF₄ was used as the supporting electrolyte for the determination of current–voltage characteristics. Acetonitrile was distilled over P₂O₅ and KMnO₄, and then over molecular sieves. After purification, the solvent was stored under dry argon. Used as a base salt, Et₄NBF₄ was recrystallized from ethanol and dried in a vacuum chamber at 100 °C for 2 days. To study powder samples, a modified CPE working electrode was used. Its preparation was as follows: the carbon particles/ phosphonium salt (dodecyl(tri-tert-butyl)phosphoniumtetrafluoroborate) composite electrode was prepared by grinding a mixture of graphite powder and phosphonium salt in a ratio of 90/10 (w/w) in a mortar to give the homogeneous mass.¹⁻⁴ A modified electrode was made in a similar manner except that a part (ca. 5%) of graphite powder was replaced by the complex Ni_x[C₆H₃O₆]_y under investigation. A portion of the resulting paste was packed firmly into the cavity (3 mm in diameter) of a Teflon holder.

[1] Khrizanforov M.N., Arkhipova D.M., Shekurov R.P., Gerasimova T.P., Ermolaev V.V., Islamov D.R., Miluykov V.A., Kataeva O.N., Khrizanforova V.V., Sinyashin O.G., Budnikova Y.H. *Novel paste electrodes based on phosphonium salt room temperature ionic liquids for studying the redox properties of insoluble compounds*// J. Solid State Electrochem. –2015. – **19(9)**.–2883-2890.

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S9. Preparative solid-phase oxidation and reduction. To confirm the fact that the first peaks of the oxidation and reduction waves are of a metal-centered nature, solid phase preparative syntheses were carried out at the potentials observed in the CV (Figure S6), for the purpose of further studying them by ESR- spectroscopy.

To do this, a gel based on the phosphonium salt and the test substance of the CH₃CN (PG-NaNi in it is insoluble) were applied to the platinum plate, the counter electrode was separated by a glass ceramic membrane and the potential was exposed relative to the reference electrode. (Figure S7). After the powder was generated, the gel was broken by ultrasound to clean it, after which the powder was centrifuged. The solution was then removed, and the wet powder was dried on a Schlenk vacuum system. As a result, different powders were obtained that differed in color (Figure S6A).

To perform a potentiostatic stability test a modified carbon paste electrode working electrode was used. Its preparation was as follows: the carbon particles/phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) composite electrode was prepared by grinding a mixture of graphite powder and phosphonium salt in a ratio of 90/10 (w/w) in a mortar to give the homogeneous mass. A modified electrode was made in a similar manner except that a part (ca. 40%) of graphite powder was replaced by the PG-NaNi complex under investigation. A portion of the resulting paste was packed firmly into the cavity (3 mm in diameter) of a Teflon holder.

S10. ESR–spectroscopy. ESR (Figure S6C, D) measurements were carried out on the Bruker Elexsys E-500 spectrometer utilizing a 100-kHz field modulation and X-band microwaves.

S11. FC tests. The catalytic ink was prepared according to the following procedure: 4 mg of organometallic catalyst and 40 mg of Vulcan XC-72 were added to 1.5 mL of IPA and 1.5 mL of deionized water. The ink was first sonicated for 15 min; then 320 µL of 10 wt% Nafion® solution (Aldrich) was added to the ink and sonicated again for 1 hour. The E-TEK (Pt₂₀/C) catalytic ink was prepared according to the almost similar procedure: 20 mg of E-TEK were added to 8.4 mL of IPA, then ink was sonicated for 15 min, and then 81 µL of 10 wt% Nafion® solution was added to the ink and sonicated again. The inks were deposited on carbon paper gas diffusion layer (GDL) Sigracet® 25CC. MEA was obtained by hot-pressing of GDLs on both sides of the Nafion® 115 membrane at 90°C with the load of about 300 lbs during 4 min. Polarization curves were obtained using the mechanical test station ElectroChem (United States) with the gas flow and pressure control system MTS-A-150 and the electronic load unit ECL-150.

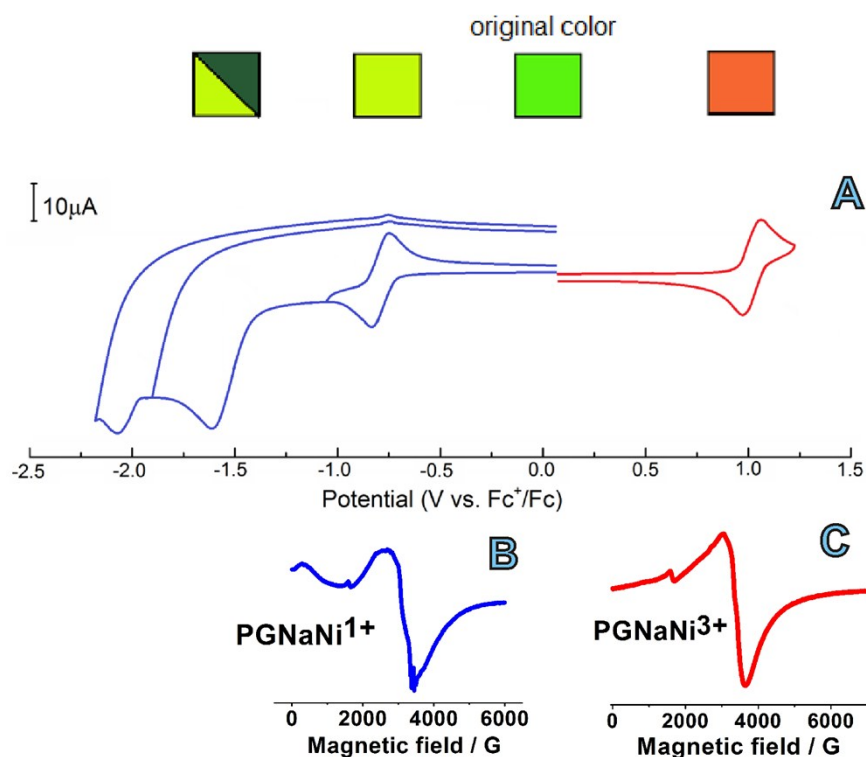


Figure S6. The color matching of PG-NaNi with respect to its redox properties (A), cyclic voltammograms (CVs) of PG-NaNi (B) with scan rate 100 mV/s, the ESR spectra of the PG-NaNi powder, reduced in the solid state at $E = -0.75$ V (C) and oxidized in the solid state at $E = +1.05$ V (D). Detailed conditions for these experiments are described in S8-S10.

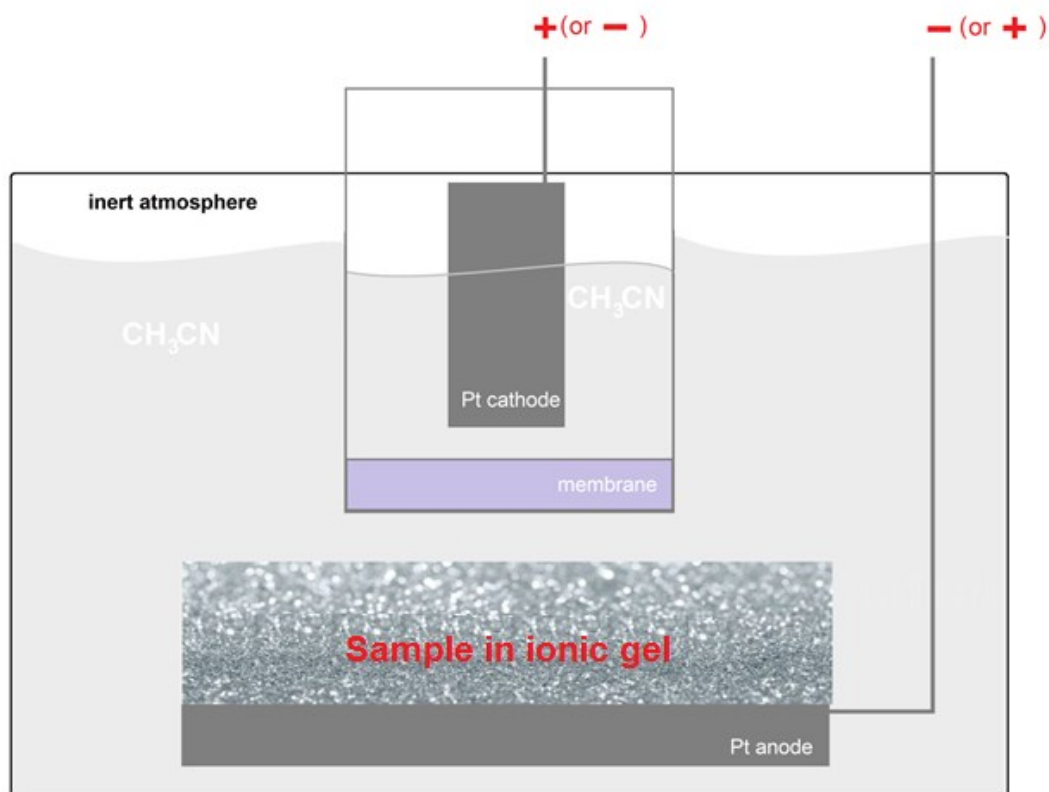


Figure S7. Scheme of installation for solid-phase reduction-oxidation of PG-NaNi

The surface concentration of nickel catalyst was 1 mg/cm^2 . The surface concentration of Pt was 1 mg/cm^2 ($5 \text{ mg Pt}_{20}/\text{C}$ on 1 cm^2). The area of the MEA was 1 cm^2 . The MEA was tested in standard 1 cm^2 PEMFC (Figure S8) of ElectroChem Ink. (US, catalogue number—FC-01-02). During the measuring the polarization curves the load was gradually increased till the maximum voltage (open-circuit voltage).

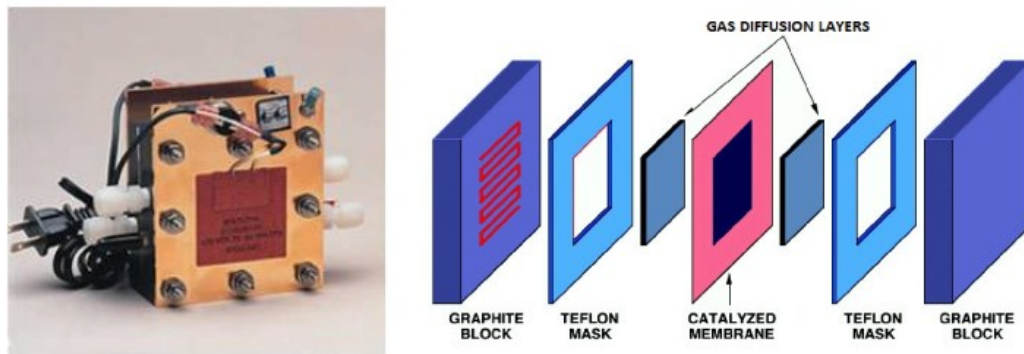


Figure S8. Scheme and appearance of the standard PEMFC used in the tests.