

# Platinum–Nickel Electrocatalysts for the PEMFC Cathode: Their Synthesis, Acid Treatment, Microstructure and Electrochemical Behavior

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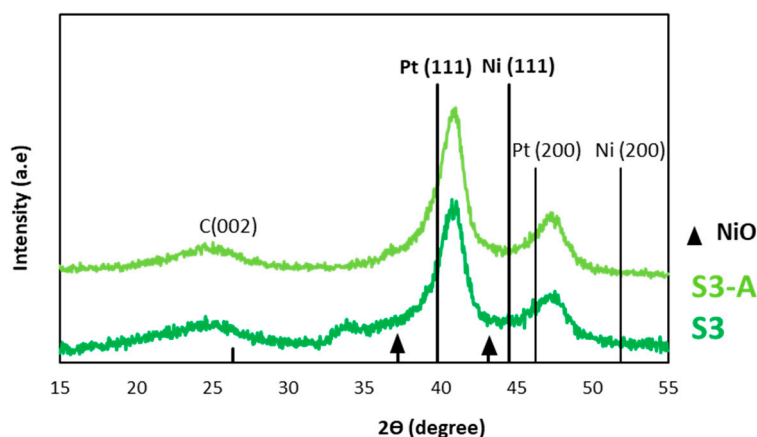
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Additionally, material S3 was obtained by using a double volume of triethylamine. The acid treatment was carried out to obtain sample S3–A. After the treatment, the mass fraction of metals, calculated by the gravimetric method, decreased due to the selective dissolution of the alloying metal that was not included in the crystallite structure (Table S1).

The X-ray patterns (Figure S1) show that the peaks are shifted from the standart positions of Pt and Ni, which confirms the formation of a bimetallic system. The composition calculated according to the Vegard's law is PtNi<sub>0.3</sub> and PtNi<sub>0.28</sub> for the initial and acid-treated samples, respectively. According to the XRD data, the average crystallite size is 4.8 nm for both S3 and S3–A.

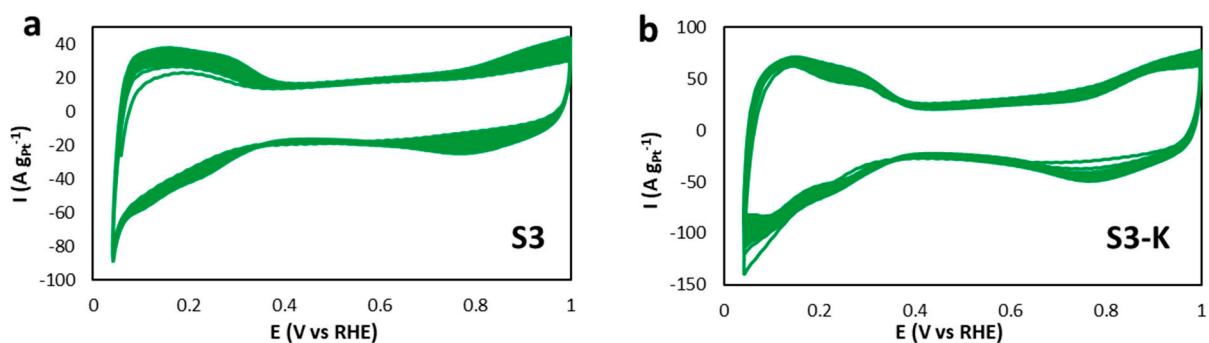


**Figure S1.** X-ray diffraction patterns of the obtained bimetallic catalysts. Positions of the standart reflections for Pt, Ni and NiO are indicated.

**Table S1.** Composition and structural parameter of obtained PtNi/C catalysts

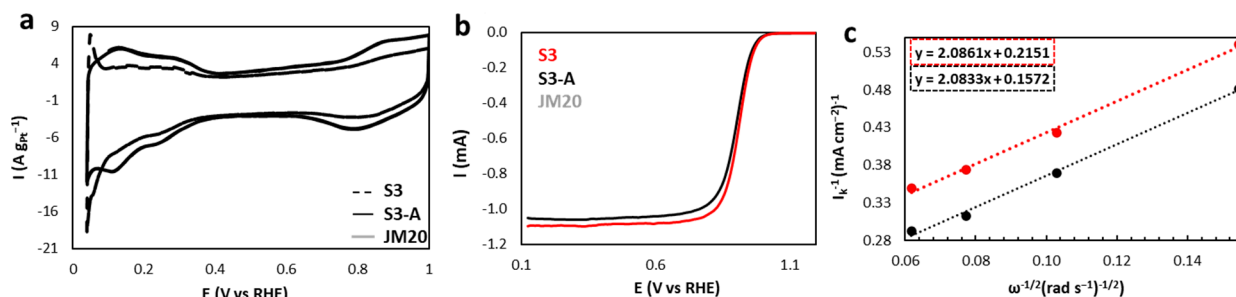
| Sample | $\omega(\text{Pt}+\text{NiO})$ ,<br>% mass. | ECSA<br>$\text{m}^2/\text{g}_{\text{Pt}} (\text{H}_{\text{ads}})$ | $I_{\text{mass}}$ , A/g (Pt) | $E_{1/2}$ , V |
|--------|---|---|------------------------------|---------------|
| S3     | 44.5  | 17  | 210                          | 0.91          |
| S3-A   | 27.5  | 26  | 301                          | 0.91          |

The electrochemical behavior of the resulting catalysts was studied after the standardization stage (Figure S2).



**Figure S2.** CVs of the activation stage for the PtNi/C catalysts. 100 cycles in the potential range of 0.04–1.00 V: S3 (a), S3-A (b). Potential sweep rate is 200 mV/s. Atmosphere of Ar, 0.1 M HClO<sub>4</sub>.

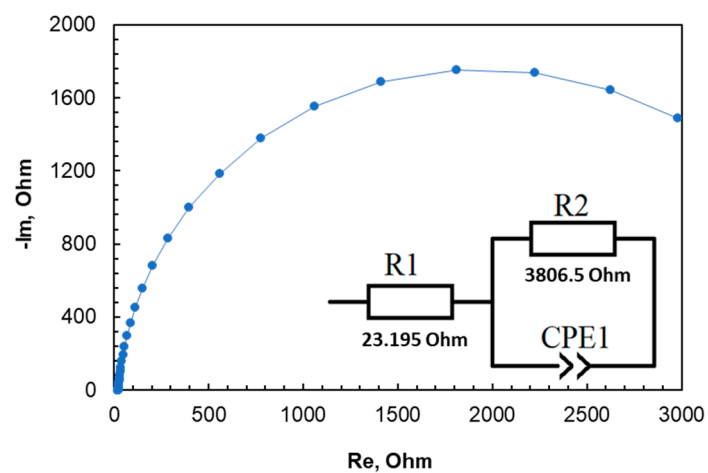
After acid treatment of sample S3, an increase in the ECSA value by 53% for S3-A was observed (Table S1).



**Figure S3.** Cyclic voltammograms at the potential sweep rate of 20 mV/s (a) for the samples activated in the potential range of 0.04–1.00 V and in an Ar atmosphere. Linear sweep voltammograms of the oxygen electroreduction in the studied catalysts at the RDE rotation speed of 1600 rpm, at the potential sweep rate of 20 mV s<sup>-1</sup> and in an O<sub>2</sub> atmosphere (b). 0.1 M HClO<sub>4</sub>. Dependence 1/j of  $\omega^{-1/2}$  at the potential of 0.90 V (c).

Based on the results of the polarization curves and the Koutecky-Levich dependence, it can be concluded that after acid treatment, the activity of the S3-A material increased by 43%. It should be noted that acid treatment contributed to additional purification of the catalyst surface, which also had a positive effect on its functional characteristics.

The oxygen reduction reaction impedance of the S2-A material was estimated on RDE. The study was carried out in 0.1 M perchloric acid while maintaining a potential of 0.9 V (vs. RHE) at a rotation of 1600 rpm to ensure a constant thickness of the diffusion layer in the frequency range from 20 kHz to 50 MHz. Figure S4 shows the impedance hodograph in Nyquist coordinates. The impedance hodographs were calculated according to the equivalent circuit shown in Figure S4, since there are no areas characterizing diffusion problems. According to the data obtained, it was found that the electrolyte resistance was 23.2 Ohm, and the resistance of the electrochemical reaction was 3806.5 Ohm.



**Figure S4.** Impedance hodograph and equivalent circuit of electrocatalyst S2-A for the oxygen reduction reaction on RDE (1600 rpm) at 0.9 V (vs. RHE). 0.1M  $\text{HClO}_4$ .