

Short communication

Evaluation of carbon-supported Pt and Pd nanoparticles for the hydrogen evolution reaction in PEM water electrolyzers

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Abstract

Carbon-supported Pt and Pd nanoparticles (CSNs) were synthesized and electrochemically characterized in view of potential application in proton exchange membrane (PEM) water electrolyzers. Electroactive metallic nanoparticles were obtained by chemical reduction of precursor salts adsorbed to the surface of Vulcan XC-72 carbon carrier, using ethylene glycol as initial reductant and with final addition of formaldehyde. CSNs were then coated over the surface of electron-conducting working electrodes using an alcoholic solution of perfluorinated polymer. Their electrocatalytic activities with regard to the hydrogen evolution reaction (HER) were measured in sulfuric acid solution using cyclic voltammetry, and in a PEM cell during water electrolysis. Results obtained show that palladium can be advantageously used as an alternative electrocatalyst to platinum for the HER in PEM water electrolyzers. Developed electrocatalysts could also be used in PEM fuel cells.

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1. Introduction

Proton exchange membrane (PEM) water electrolysis [1,2] is considered as an attractive process to accelerate the transition to the hydrogen economy and to develop a hydrogen infrastructure network (development of hydrogen re-filling stations for automotive applications using electric power stations at night hours and/or renewable energy sources). Compared to the more conventional alkaline process, PEM water electrolysis offers a number of significant technical advantages for the production of electrolytic-grade hydrogen: higher operating security offering the possibility of producing compressed gases (>200 bar) for direct storage with no compressor, higher gas purity (>99.99% for hydrogen) with no soda, and long time performance without maintenance. However, the main drawback of this technology, which still postpones applications in the industry, is its pro-

hibitive cost, which comes mainly from the use of noble metals as electrocatalysts. Typically, platinum is used at cathodes for the hydrogen evolution reaction (HER) and iridium (metal or oxides) is used at anodes for the oxygen evolution reaction (OER). These noble metals are required (i) because they yield the best catalytic activity for the HER and the OER in acidic media (typical conversion efficiencies >80% are commonly obtained at 1 A cm⁻²) and (ii) because of the strong acidity of the solid electrolyte, which would cause the corrosion of non-noble metals. To reduce the cost of PEM cells, different approaches can be followed: (i) a reduction in Pt and Ir loadings (in state-of-the-art electrolyzers, 2–5 mg cm⁻² black Pt and Ir are commonly used), (ii) the use of less expensive noble metals such as Pd and Ru or (iii) the development of alternative low-cost electrocatalysts based on non-noble metals and molecular chemistry [3].

Palladium, which is widespread in the Earth crust and less expensive than platinum, also exhibits interesting electrocatalytic properties for various reduction and oxidation electrode processes. Most applications reported in the literatures concern

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fuel cells, either in alkaline [4–8] or in acidic (PEM) [9–11] media. Palladium can be used as electrocatalyst for the oxidation of various fuels. Pd nanoparticles, electrochemically deposited onto glassy carbon [4] or on single-walled carbon nanotubes (SWNTs) [5], have been reported to exhibit a high electrochemical activity with regard to hydrazine oxidation. Highly dispersed Pd nanoparticles onto carbon have also been reported to promote the oxidation of methanol, formaldehyde and ethylene glycol [6]. Concerning the hydrogen oxidation reaction (HOR), the electrochemical activity of palladium has been investigated using Pd deposited onto glassy carbon in alkaline [7] and in acidic [9] media. Pd nanoparticles dispersed onto carbon have also been reported to promote the oxygen reduction reaction (ORR) in alkaline solutions [6]. Pd particles inserted into polythiophene films were studied with respect to their activity for the hydrogen oxidation and oxygen reduction in acidic media for fuel cell applications [10]. More recently, new types of bimetallic catalysts (in particular electrocatalysts based on Pt–Pd), have been developed and characterized for both the HOR and ORR [8,11].

Concerning water electrolysis applications, the possibility of using Pd (dispersed onto carbon electrodes) for the HER in alkaline medium has been reported by Ndzebet et al. [12]. But for PEM water electrolysis and the HER in acidic media, palladium has been less studied than platinum. The purpose of this paper is to report on the possibility of reducing noble metal contents for the HER in PEM water electrolysis cells by using carbon-supported nanoparticles (CSNs), and to investigate the possibility of using palladium in place of platinum.

2. Experimental section

2.1. Catalyst synthesis

An impregnation/reduction method described in detail elsewhere [13] was used in the present work to prepare working electrodes. Pt (Pd) nanoparticles were deposited directly at the surface of Vulcan XC-72 (a carbon carrier from Cabot Co. of large, $250\text{ m}^2\text{ g}^{-1}$, surface area) by chemical reduction of Pt (Pd) precursor salts using ethylene glycol and formaldehyde as reductants. Briefly, 135 mg of Vulcan were dispersed in 4.6 cm^3 of 0.1 M solutions of H_2PtCl_6 (H_2PdCl_4) in bi-distilled water and 8 vol.% of 2-propanol. Then the pH of the mixtures was set to a value of 8 using 0.1 M Na_2CO_3 . Dispersions were added to 60 cm^3 of ethylene glycol to initiate the reduction process. Finally, drop-wise amounts of formaldehyde were added to perform post-reduction of particles. After that, the temperature of the mixture was kept constant at $80\text{ }^\circ\text{C}$ for 2 h (until completion of reduction) and then the heating was switched off and the solution was cooled down to room temperature. After 12 h, the excess of liquid was poured out and the remaining deposits (Pt or Pd on Vulcan) were washed off (8–10 times) using bi-distilled water. Results reported in this paper were obtained using Pt40/Vulcan XC-72 and Pd40/Vulcan XC-72 catalysts, where 40 denotes the amount of metal expressed in wt.%.

2.2. Physical and electrochemical characterization of catalyst particles

The structure and morphology of the metal-carbon catalysts were investigated using a CM30 Philips (300 kV) TEM microscope. Cyclic voltammetry was used for the electrochemical characterization. Experiments were performed using a typical three-electrode cell. Working electrodes were prepared as follows. CSNs were mixed with 5 wt.% alcoholic solution of Nafion[®] (Aldrich Co.), the polymer acting as a binder, and the mixtures were sprayed over 1 cm^2 glassy carbon disks. Slurries were then air-dried at $75\text{ }^\circ\text{C}$ in a furnace, and typical loadings of ca. 0.7 mg cm^{-2} of noble metals were obtained. A KCl-saturated silver–silver chloride electrode (SSCE) and a platinum wire were used as reference and counter electrodes, respectively. Cyclic voltammograms were recorded in de-aerated 1 M H_2SO_4 using a Solartron 1285 potentiostat/galvanostat (Solartron Analytical). Electrode surfaces were first activated by cycling in the potential range -0.2 to $+1.1\text{ V}$ vs. SSCE, in order to obtain stable and reproducible voltammograms.

2.3. Preparation of PEM electrolysis cell

Electrolysis cells were prepared as follows, using Nafion[®]-115 (E.I. du Pont de Nemours Co.) as solid electrolyte. Membranes were repeatedly washed using 10 vol.% HNO_3 , then 1 M KOH and finally de-ionised water, in order to remove various surface and bulk impurities. Catalytic structures (Pt40/Vulcan XC-72 or Pd40/Vulcan XC-72 on cathodic sides and Ir-black powder on anodic sides) were mixed with 7 (cathodes) or 10 (anodes) wt.% of the ion-exchange polymer (wt.% values are expressed with respect to the weight of catalyst). These mixtures were then directly sprayed as an ink over the surface of 7 cm^2 current collectors made of 1.4 mm thick porous titanium sheets (45% porosity). Typical metal loadings of 0.7 and 2.4 mg cm^{-2} were obtained for cathodes and anodes, respectively. Finally, membrane-electrode assemblies (MEAs) were prepared by hot pressing the Ti-supported electrocatalytic layers against each side of the Nafion[®] membrane (Fig. 1).

Current–voltage and polarization curves were recorded in a 7-cm^2 single electrolysis cell at $90\text{ }^\circ\text{C}$ and atmospheric pressure of gases (water was supplied to the anode).

3. Results and discussion

3.1. Morphological characterization of catalyst particles

To reduce the amount of noble metal in the CSNs and to maintain at the same time the same level of electro-activity compared to black catalysts powders, it is necessary to optimize experimental parameters. First, metallic particles must be deposited as uniformly as possible over the entire surface of the carbon carrier, trying to obtain a coverage ratio close to unity and to benefit from its large surface area (typically $250\text{ m}^2\text{ g}^{-1}$ for Vulcan XC-72). Second, small particles of homogeneous size (in the nm range) must be obtained to increase the surface/volume atomic ratio. Experimentally, these two requirements are contradictory

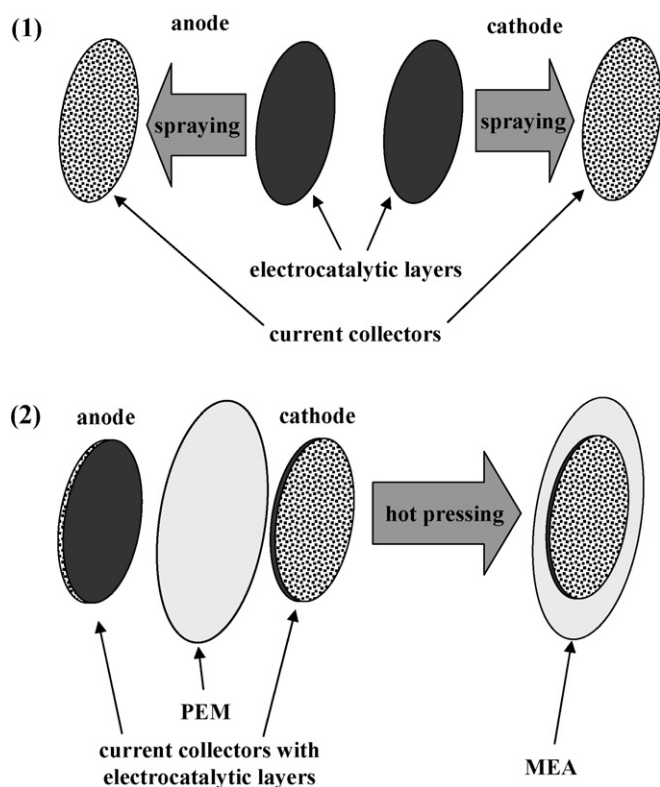


Fig. 1. Schematic diagram of the two-step process used in the present study to prepare the MEAs: (1) anodic and cathodic electrocatalytic compositions are sprayed onto the surface of current collectors; (2) the catalyst-covered current collectors are hot-pressed against the solid polymer membrane.

since uniform coatings require higher concentration of precursor salts during the impregnation step, which in turn yields, in general, larger particles. Figs. 2 and 3 show two TEM pictures obtained using two different magnifications, with respectively Pt-Vulcan XC-72 and Pd-Vulcan XC-72 CSNs. As can be seen

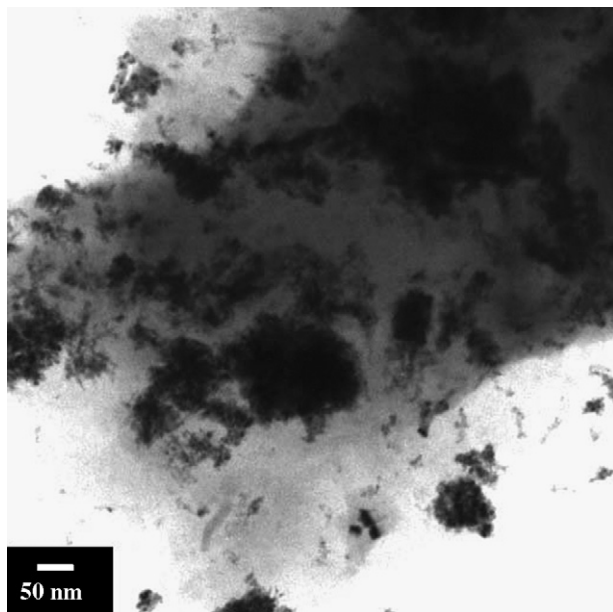


Fig. 2. TEM picture of a Pt/Vulcan XC-72 catalyst.

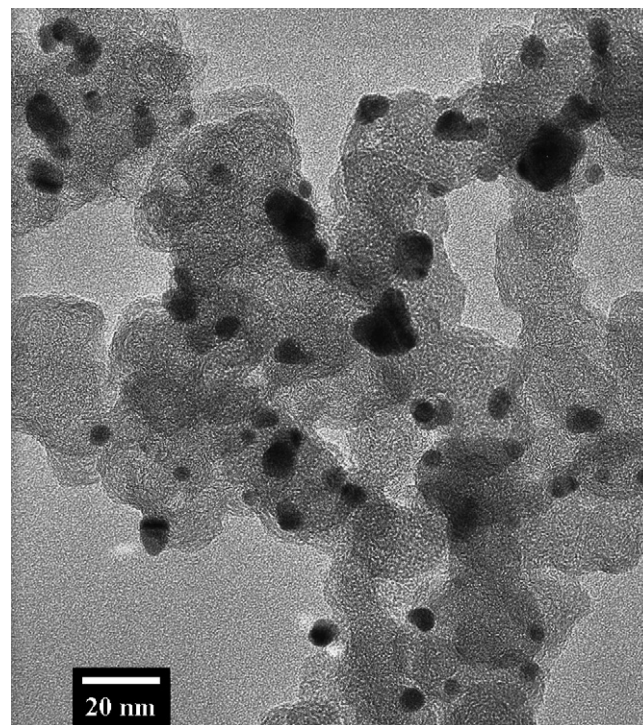


Fig. 3. TEM picture of a Pd/Vulcan XC-72 catalyst.

from Fig. 2, it is possible to obtain uniform coatings although a significant part of the carrier surface remains uncovered. Pt and Pd catalyst particles were found similar in shape and size. As can be seen from Fig. 3, particle sizes in the 5–10 nm range, with a roughly bimodal distribution of size, are obtained.

3.2. Electrochemical characterization

Typical cyclic voltammograms recorded using 1 cm² working electrodes made of Pt40/Vulcan XC-72 and Pd40/Vulcan XC-72 CSNs, respectively are shown in Fig. 4. It can be seen from this figure that the potentiodynamic curves are similar in shape to those obtained with bulk metals (see for example Ref. [14]).

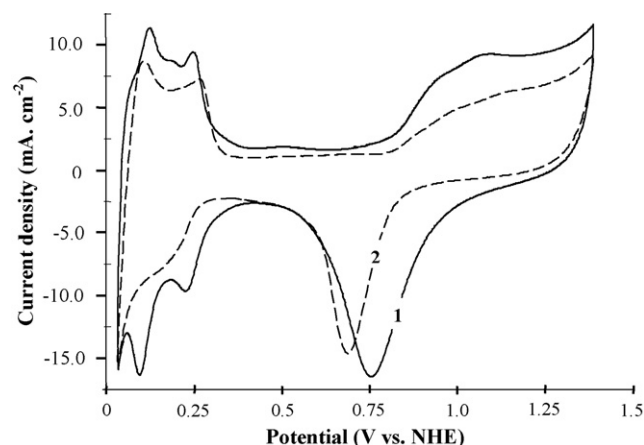


Fig. 4. Cyclic voltammograms of (1) Pt40/Vulcan XC-72 and (2) Pd40/Vulcan XC-72 electrodes recorded in 1 M H₂SO₄ (scan rate 20 mV s⁻¹).

Electrochemical active surface areas (EAS) of the catalysts were estimated from the voltamperograms of Fig. 4. The EAS of the Pt catalyst was obtained from the coulombic charge associated with hydrogen-adsorbents desorption (Q_H)

$$EAS = \frac{Q_H}{Q_{Ho}G_{Me}},$$

where Q_{Ho} is the amount of electricity per unit surface area, corresponding to the full coverage of the metal surface by one monolayer of hydrogen (for polycrystalline platinum $Q_{Ho} = 0.21 \text{ mC cm}^{-2}$ [15,16]); G_{Me} is the weight, corresponding to the metal fraction in the catalyst.

The charge Q_H for Pt catalysts was calculated using the method described in the literatures [16–18], i.e. by integrating the potentiodynamic curve in the hydrogen desorption region (Q_Σ) and by subtracting the contribution of the carbon carrier (Q_C)

$$Q_H = Q_\Sigma - Q_C.$$

The EAS of the Pd electrode was estimated likewise but this time using the reduction peak of chemisorbed oxygen [19]. To calculate the EAS value, the specific amount of electricity corresponding to the full coverage of the Pd surface by one monolayer of oxygen was taken as 0.42 mC cm^{-2} [19,20]. Results are compiled in Table 1 where average sizes of metal particles were estimated from TEM analysis.

In spite of identical concentration of precursor salts, it was repeatedly observed that Pd-CSNs present significantly lower EAS values compared to Pt-CSNs. This difference can be attributed to the larger size of Pd particles reported in Table 1. This is a general trend, which can be ascribed to faster reduction kinetics. For the HER, this negative effect can be partly counter-balanced by a 30% higher exchange current density: according to Ref. [21], $\log i_0 (\text{A cm}^{-2}) = -3$ for Pd and $\log i_0 (\text{A cm}^{-2}) = -3.1$ for Pt at 298 K.

3.3. Water electrolysis performances in MEA configuration

Typical current–voltage curves recorded at 90°C during PEM water electrolysis are plotted in Fig. 5. It can be seen that cell voltages of ca. 1.68 V were obtained at a current density of 1 A cm^{-2} . Results obtained with Pd40/Vulcan XC-72 cathodes are slightly less efficient than those obtained with Pt40/Vulcan XC-72. More precisely, at the current density of 1 A cm^{-2} , the operating voltage of the cell with Pd-CSNs is ca. 20 mV higher compared to that with Pt-CSNs. The difference between the two catalysts can be interpreted in terms of EAS and exchange current density as discussed above.

Stability tests performed at constant current density over more than 100 h of continuous electrolysis have shown stable

Table 1
Characteristics of Pt- and Pd-CSNs

No.	Electrocatalysts	EAS ($\text{m}^2 \text{ g}^{-1}$)	Particle mean size (nm)
1	Pt40/Vulcan XC-72	40 ± 4	7.1 ± 0.7
2	Pd40/Vulcan XC-72	33 ± 3	14.9 ± 1.6

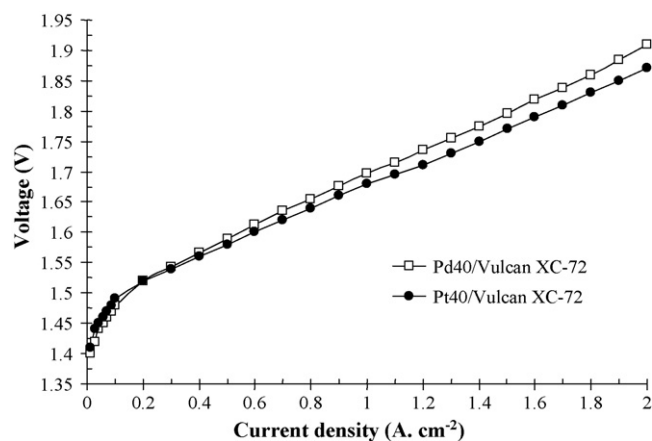


Fig. 5. Current–voltage relationships measured using 7 cm^2 single electrolysis cell at 90°C and atmospheric pressure of gases; cathodic catalyst: Pt40/Vulcan XC-72, Pd40/Vulcan XC-72 (0.7 mg cm^{-2} of metal); anodic catalyst: black Ir (2.4 mg cm^{-2}); Nafion®-115 membrane.

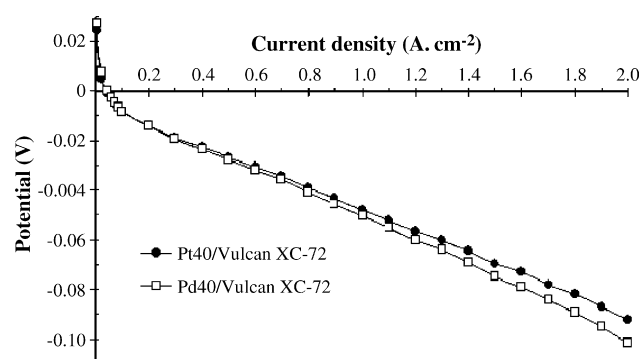


Fig. 6. Cathodic overvoltages measured at 90°C and atmospheric pressure on Pt40/Vulcan XC-72 and Pd40/Vulcan XC-72 (0.7 mg cm^{-2} of metal) during PEM water electrolysis experiments.

results and it can be concluded that Pd can be advantageously used in place of Pt on cathodes in PEM water electrolyzers.

To make a more direct comparison of Pd and Pt electrodes, individual cathodic overvoltages were also measured during PEM water electrolysis. Since no reference electrode can be placed directly against the working electrode, the membranes were equipped with a narrow strip acting as an ionic bridge, the end of which was immersed in a $0.5 \text{ M H}_2\text{SO}_4$ solution [22]. A saturated KCl electrode was used as reference electrode. First, the ohmic drop across the whole membrane thickness was measured by ac impedance spectroscopy. Then, it was assumed that the potential at the end of the membrane strip was the same as the potential value in the middle of the membrane. Therefore, raw measurements of individual electrode potentials were corrected by half the value of the ohmic drop across the solid polymer membrane. Results are plotted in Fig. 6. It is concluded that the slight difference in cell voltage reported in Fig. 5 is not due to the anode but to the difference between the Pd and Pt cathodes.

4. Conclusions

An impregnation/reduction method was used to prepare Vulcan XC-72-supported Pt and Pd nanoparticles. These

carbon-supported catalysts have been characterized using TEM analysis and cyclic voltammetry. Results show that Pd-CSNs have a lower electrochemical active surface than Pt-CSNs. These catalysts have been used as cathodes in PEM cells with metal loadings of ca. 0.7 mg cm^{-2} , that is a value three times lower than those usually found with metal-black loadings (typically ca. 2 mg cm^{-2}). Water electrolysis using 7 cm^2 single cells have demonstrated good performances, with conversion efficiencies of ca. 88% at 1 A cm^{-2} . Electrochemical performances measured with Pd catalysts are slightly lower than those obtained with Pt. These results lead to the conclusion that the impregnation/reduction method is a promising way for preparing carbon-supported electrocatalytic structures for PEM water electrolysis applications. Palladium can be considered as an alternative catalyst to platinum with regard to the HER in PEM water electrolysis cells. Developed electrocatalysts could be used in PEM fuel cells.

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References

- [1] P. Millet, F. Andolfatto, R. Durand, *Int. J. Hydrogen Energy* 21 (1996) 87–93.
- [2] S.A. Grigoriev, V.I. Poremsky, V.N. Fateev, *Int. J. Hydrogen Energy* 31 (2006) 171–175.
- [3] O. Pantani, E. Anxolabéhère-Mallart, A. Aukauloo, P. Millet, *Electrochem. Commun.* 9 (2007) 54–58.
- [4] F. Li, B. Zhang, S. Dong, E. Wang, *Electrochim. Acta* 42 (1997) 2563–2568.
- [5] D.-J. Guo, H.-L. Li, *J. Colloid Interface Sci.* 286 (2005) 274–279.
- [6] R. Pattabiraman, *Appl. Catal. A* 153 (1997) 9–20.
- [7] N. Tateishi, K. Yahikozawa, K. Nishimura, Y. Takasu, *Electrochim. Acta* 37 (1992) 2427–2432.
- [8] Y. Kiros, S. Schwartz, *J. Power Sources* 87 (2000) 101–105.
- [9] J. Moreira, P. del Angel, A.L. Ocampo, P.J. Sebastian, J.A. Montoya, R.H. Castellanos, *Int. J. Hydrogen Energy* 29 (2004) 915–920.
- [10] M.T. Giacomini, M. Balasubramanian, S. Khalid, J. McBreen, E.A. Ticianelli, *J. Electrochem. Soc.* 150 (2003) A588–A593.
- [11] M.J. Escudero, E. Hontanón, S. Schwartz, M. Boutonnet, L. Daza, *J. Power Sources* 106 (2002) 206–214.
- [12] E. Ndzebet, O. Savadogo, *Int. J. Hydrogen Energy* 20 (1995) 635–640.
- [13] S.A. Grigor'ev, E.K. Lyutikova, E.G. Pritulenko, D.P. Samsonov, V.N. Fateev, *Russ. J. Electrochem.* 42 (2006) 1251–1254.
- [14] A.J. Bard, L.R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, John Wiley & Sons, Inc., New York, 1980 (Chapter 12).
- [15] M.R. Tarasevich, V.A. Bogdanovskaya, B.M. Grafov, N.M. Zagudaeva, K.V. Rybalka, A.V. Kapustin, Y.A. Kolbanovskii, *Russ. J. Electrochem.* 41 (2005) 746–757.
- [16] B.B. Damaskin, O.A. Petrii, *Introduction to Electrochemical Kinetics*, Vysshaya Shkola, Moscow, 1975, p. 70.
- [17] F. Gloaguen, J.-M. Leger, C. Lamy, *J. Appl. Electrochem.* 27 (1997) 1052–1060.
- [18] Y. Verde, G. Alonso-Nunez, M. Miki-Yoshida, M. Jose-Yacaman, V.H. Ramos, A. Keer, *Catal. Today* 107–108 (2005) 826–830.
- [19] N.V. Korovin, *Corrosive and Electrochemical Properties of Palladium*, Metallurgy, Moscow, 1976, p. 257.
- [20] G.A. Tsirlina, S.B. Baronov, F.M. Spiridonov, M.Y. Rusanova, T.Y. Safonova, O.A. Petrii, *Russ. J. Electrochem.* 36 (2000) 1179–1185.
- [21] J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 2, Plenum Press, New York, 1970, p. 1238.
- [22] S.F. Chernyshov, A.G. Pshenichnikov, V.N. Zhuravleva, *Voprosy atomnoi nauki i tekhniki (Problems of Atomic Science and Technology)*, Institut Atomnoi Energii, Moscow, 1985, p. 36.