

Evaluation of polymer electrolyte fuel cell catalysts using gas diffusion electrodes in aqueous electrolytes

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Received October 17, 2007, Revised March 10, 2008

This work presents a new fast and reliable method for rapid screening and optimization of Pt/C electrocatalysts for polymer electrolyte fuel cell (PEFC). The approach is a combination of electrochemical and structural characterization. Catalysts with various Pt concentration and preparation conditions were synthesized and their structure and electrochemical performance is evaluated on real gas diffusion electrodes (GDE) in different electrolytes: proton exchange membrane (PEM), sulphuric acid, perchloric acid and potassium hydroxide solution. The results in KOH show very good similarity with those in PEM electrolytes. The results in KOH are comparable not only in the Tafel region, but reveal the same transport limitations in the active layer. The comparison between the catalysts in PEM and KOH is possible on the base of current densities per geometric area only and can be explained by low utilization of Pt in GDE. XRD data reveal that the electrocatalytic activity depends on the Pt crystallite size, type of support and processing conditions.

Key words: fuel cells, electrocatalysts, screening method.

INTRODUCTION

The selection of efficient catalysts for oxygen reduction is one of the main tasks in developing and commercialization of PEFC. Superior Micro Powders (SMP) has developed a new manufacturing approach for production of Pt/carbon electrocatalysts for fuel cell applications. This approach, based on a spray pyrolysis route, enables a high level of control over the microstructure and the composition of these catalysts. The evaluation of the catalytic activity in PEFC is a time-consuming and expensive process. The rate-determining step of the oxygen reduction reaction on platinum catalysts in different electrolytes is the same, according to the works of Damjanovic and Brusic [1], Appleby [2], Ross and Andricacos [3] and others. This is giving as a theoretical base for practical comparison of the Pt/carbon catalysts on real electrodes in different electrolytes. We chose KOH and HClO₄ as non-adsorbing electrolytes, as well as an adsorbing one – H₂SO₄. There are fast methods for pre-screening of fuel cells catalysts activity on small rotating disk electrodes [4, 5]. Half-cell measurements on real (10 cm²) gas diffusion electrodes (GDE) in aqueous

electrolytes are simple and fast. The objective of this work is to show experimentally a correlation in the electrochemical performance of real GDE in liquid electrolyte and in PEFC, using electrochemical and structural (XRD, SEM and TEM) characterization of Pt/C electrocatalysts.

EXPERIMENTAL

The catalysts are manufactured at SMP using its novel method and are evaluated at the Center for Electrochemical Systems and Hydrogen Research (CESHR). The catalysts are 20% Pt and 10% Pt on carbon blacks.

The simple scheme of three-electrode cell for testing of gas diffusion electrodes (GDE) is shown in Fig. 1. The GDE are double layered [6]. They consist of a gas diffusion layer (50 mg/cm² HCB-35 – hydrophobized carbon blacks with 35% PTFE [7]) and catalytic layer (mixture of catalyst and HCB-35). The current collector (Ni-gauze) is pressed into the gas layer. The electrodes are prepared by pressing with P = 300 atm at room temperature. The GDE are mounted on the cell by gas chamber. The GDE for liquid electrolytes have an area of 10 cm² and work with air (oxygen) at atmospheric pressure and room temperature. Simple DC power supplies and multimeters were used for galvanostatic, steady-

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state electrochemical characterization of GDE. At least three electrodes with every catalyst were tested, in order to have performance reproducibility. The electrolytes were water solutions of KOH (7N KOH), H₂SO₄ (1N H₂SO₄) and HClO₄ (1N HClO₄). The potentials were recorded vs. reference electrodes, suitable with the electrolyte (Zn or Hg/HgO for alkaline, Hg/Hg₂SO₄ for suitable sulphuric acid and hydrogen electrode in the same solution - "Hydroflex" from Gaskatel for perchloric acid. All the test results were referenced to RHE.

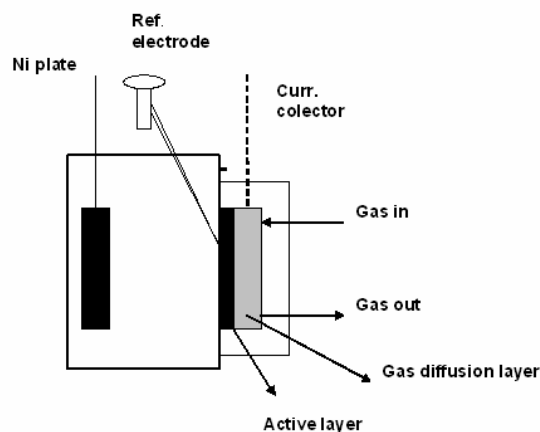


Fig. 1. Scheme of three-electrode cell for testing of gas diffusion electrodes.

The PEFC electrodes are prepared by the technology developed in CESH [8]. The platinum loading is 0.2 mgPt/cm² on air (oxygen) side and 0.1 mgPt/cm² on hydrogen side. The electrodes have an area of $S = 50 \text{ cm}^2$. The membrane and electrode assembly (MEA) were fabricated by hot-pressing a Nafion 112 membrane between the electrodes at 155°C and $P = 70 \text{ atm}$. The MEA was mounted in a single cell and was tested by fuel cell test stations equipped with controls for the current density, cell voltage, gas pressures, and cell temperature, as well as gas humidification bottles. The cell potential/current density characteristics were determined with externally humidified gases air (oxygen) and hydrogen, at atmospheric pressure, and $t^\circ = 60^\circ\text{C}$. The gas stoichiometry was maintained constant during measurements at 1.1 times for hydrogen and 2.2 times for oxygen in air.

The XRD spectra for the catalysts were recorded on a BRUKER AXS D8 Advance, SEM on Hitachi S-3500N and TEM on JEOL 2010.EM.

RESULTS

Composition and characterization data of SMP electrocatalysts

The composition and characterization data of SMP electrocatalysts are summarized in Table 1.

The electrocatalysts have 20 and 10 % Pt on two types of carbon blacks; Vulcan XC-72 (Support 1) and Shawinigan black (Support 2). They are produced at four processing conditions. The crystallite size varies between 5 and 12 nm. The last column in Table 1 presents the electrocatalytic activity of the catalysts in PEFC, expressed as a current density at the same potential – $E = 0.7 \text{ V}$ in oxygen. From the data is clear that the catalytic activity depends on: (i) size of the crystallites, which optimum is about 5 nm – catalysts C, E, G and F; (ii) type of support (carbon black) – compare catalysts G and F; and (iii) processing conditions – compare catalysts E and C.

Table 1. Composition and characterization data of SMP electrocatalysts.

Catalyst	Pt %	Type of support	Pt crystallite size (XRD), nm	$i (E = 0.7 \text{ V}), \text{ PEM, oxygen, mA/cm}^2$
A	20	1	11.4	90
B	20	1	9.8	200
C	20	2	5.7	355
D	20	1	11.5	10
E	20	2	5.2	240
F	10	1	4.6	180
G	10	2	6.3	120

Optimization of the gas diffusion electrodes

The electrodes with working area $S = 10 \text{ cm}^2$ were double-structured. The gas diffusion layer contained 50 mg/cm² HCB-35, based on previous experience. The macro-structure of the catalytic layer (mixture of catalyst and HCB-35) was optimized. The following parameters were changed, keeping all others constant: (i) the ratio r between catalyst and HCB-35; and (ii) the amount of the catalytic mixture (catalyst + HCB-35), i.e., the thickness of the catalytic layer. A criterion in the optimization of the structure of the catalytic layer with respect to the ratio catalyst:HCB-35 was the mechanical stability of the GDE. Keeping the thickness constant (20 mg/cm²), we found that the ratio equal to $r = 1:1$ (by weight) gives stable enough electrodes. The optimization with respect to the catalyst content (amount of catalyst + HCB-35) was carried out at a constant ratio between the catalyst and HCB-35 equal to $r = 1:1$ by weight. Figure 2 shows the relationship between the potential of the electrode and the amount of the catalytic mixture, i.e., the thickness of the catalytic layer at different current densities. At least three GDE were tested for every amount of the catalytic mixture. The reproducibility between the GDE is shown in Fig. 2 for the amount of the catalytic mixture equal to 10 mg/cm², and it is between 4 mV at $i = 6 \text{ mA/cm}^2$ and

8 mV at $i = 50 \text{ mA/cm}^2$. In order to not complicate the figures, the reproducibility is not shown further, but it is the same for all tested GDE. The experiments were done with 20% Pt/carbon catalyst A. The curves are going through a maximum, which is obvious for this kind of measurements and can be explained by the influence of two opposite effects. The increase of catalyst loading leads to higher currents generated. From the other side, the diffusion hindrance in the catalytic layer increases with their thickness and decrease the current density. A clear maximum is observed at 10 mg/cm^2 . As a result of this optimization the GDE have the following structure: (i) gas diffusion layer – $50 \text{ mg HCB-35/cm}^2$; (ii) ratio between the catalyst and HCB-35 in the catalytic layer equal to 1:1; (iii) amount of catalyst mixture (catalyst + HCB-35) equal to 10 mg/cm^2 , which gives as a Pt catalyst loading of about 1 mg Pt/cm^2 for catalysts with 20% Pt/carbon or 0.5 mgPt/cm^2 for catalysts with 10% Pt/carbon.

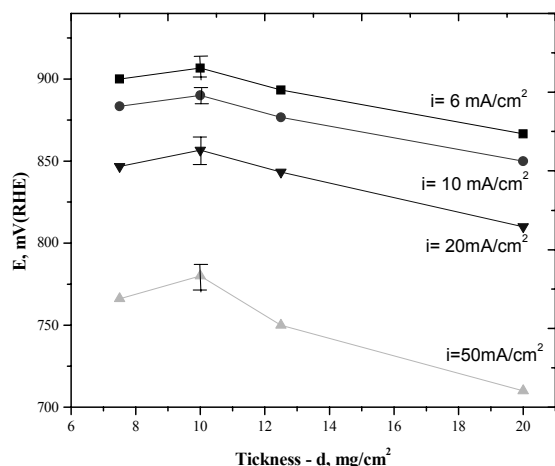


Fig. 2. Relationship between the electrode potential and the amount of the catalytic mixture, i.e., the thickness of the catalytic layer at different current densities; GDE – $S = 10 \text{ cm}^2$; catalyst - 20% Pt/carbon; 7 N KOH;

Characterization of Pt/carbon catalysts in PEM

The polarization curves for three catalysts (20% Pt/Vulcan XC-72, B, A and 20% Pt/Shawinigan black, C) are shown in Figure 3 (with oxygen) and Figure 4 (with air). The catalyst C has the best characteristics both in oxygen and in air. The order of performance of the tested catalysts in PEM with oxygen is: $C > B > A$. The characteristics of B in air becomes almost equal to A. This can be explained by the ΔE measurements, presenting the relationships between the difference in performance in oxygen and in air ($\Delta E = E_{O_2} - E_{air}$) and current density – Fig. 5. According to Kaisheva *et al.* [9], these measurements provide information for the transport limitations in gaseous phase. It is clear

from Fig. 5 that the electrodes with catalyst B display more severe transport limitations.

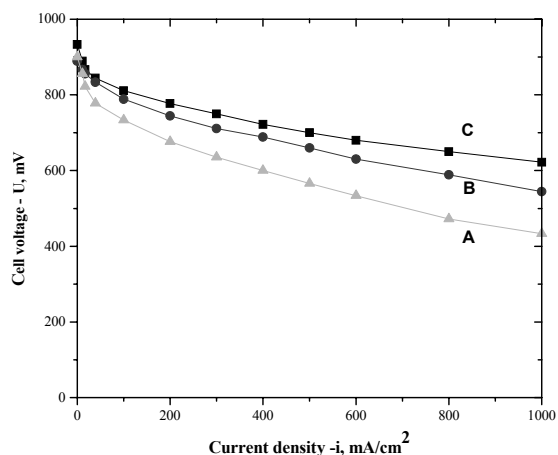


Fig. 3. Polarization curves for three catalysts (20% Pt/Vulcan XC-72, B, A and 20% Pt/Shawinigan black, C); PEM; oxygen.

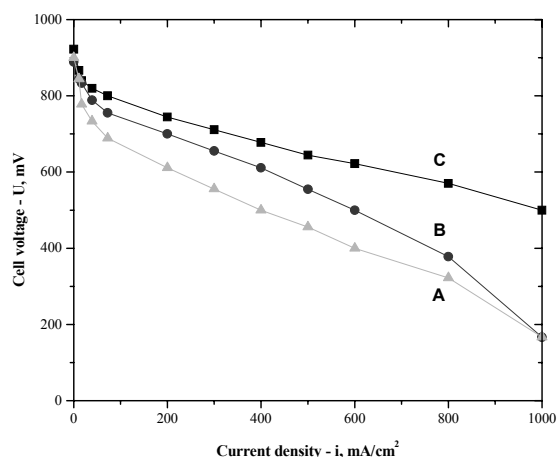


Fig. 4. Polarization curves for three catalysts (20% Pt/Vulcan XC-72, B, A and 20% Pt/Shawinigan black, C); PEM; air.

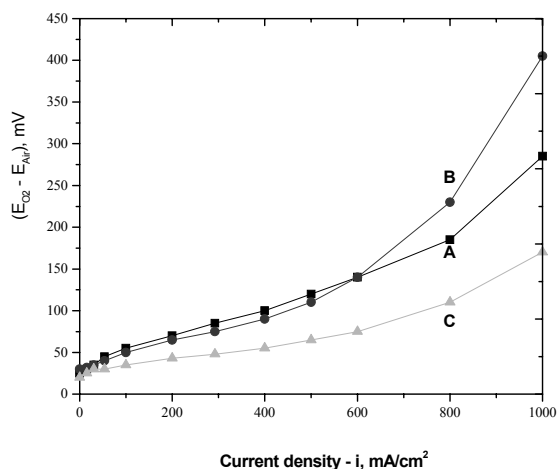


Fig. 5. Relationships between the difference in performance in oxygen and in air ($\Delta E = E_{O_2} - E_{air}$) and current density; PEM.

Characterization of Pt/carbon catalysts in sulphuric acid

The electrochemical characteristics of the above three catalysts (B, A and C) in air and in oxygen are shown in Fig. 6. The Tafel slopes for oxygen are shown in Fig. 7. The GDE in 1N H₂SO₄ are not able to reach high current densities and there is not a definite linearity in the Tafel region, especially for the catalysts with lower catalytic activity, such as A and B. Despite this, from the figures is clear that the order in performance is the same as in PEM: C > B > A. The results show that we can use the measurements in 1 N H₂SO₄ for fast pre-screening of catalysts for PEFC.

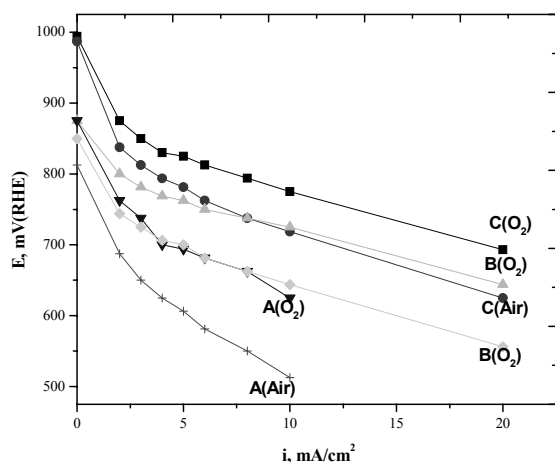


Fig. 6. Electrochemical characteristics of three catalysts in sulphuric acid (B, A and C) in air and in oxygen; GDE – S = 10 cm²; catalyst 20% Pt/carbon; 1 N H₂SO₄.

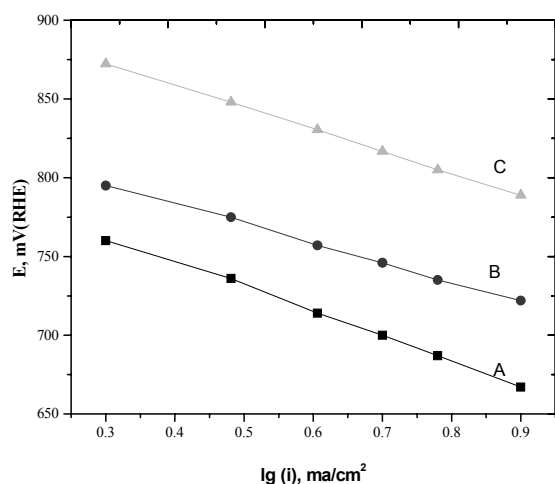


Fig. 7. Tafel plots of three catalysts in sulphuric acid (B, A and C) in oxygen; GDE – S = 10 cm²; catalyst 20% Pt/carbon; 1 N H₂SO₄;

Characterization of Pt/carbon catalysts in perchloric acid

The tests of real GDE in perchloric acid reveal that during the measurements HClO₄ changes its

colour to yellow, which means that the acid is not stable at these conditions, possibly attacked by the produced in GDE H₂O₂. Some data at low current density can be recorded fast, but they are not reproducible enough.

Characterization of Pt/carbon catalysts in alkaline electrolyte

The potential/current densities relationships for GDE with the tested catalysts in 7 N KOH are shown in Fig. 8 (oxygen) and Fig. 9 (air). The electrodes can reach relatively high current densities. The curves reveal the same order in performance for GDE with Pt/carbon catalysts in 7N KOH as in PEM: C > B > A. The Tafel plots with oxygen are presented in Fig. 10. The catalytic activities, expressed as a current density (mA/cm²) at the same potential – E = 930 mV (RHE) are in the same order: i_c = 8.2 > i_B = 5.9 > i_A = 3.1. The catalytic activity of B is close to C, but its performance in air is almost equal to A. The results for ΔE = E_{O₂} – E_{air} measurements are represented in Fig. 11 and they show that the electrodes with catalyst B display more severe transport limitations.

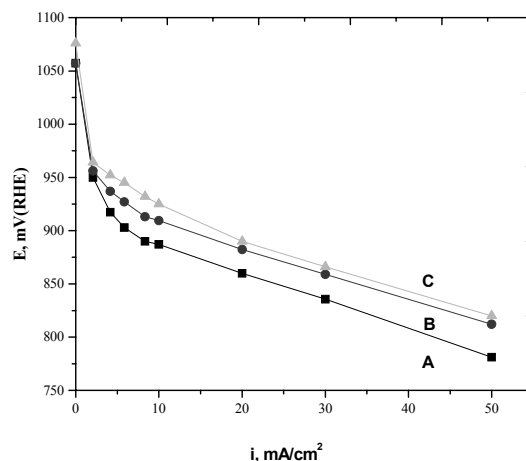


Fig. 8. Potential/current densities relationships for GDE with the tested catalysts in 7 N KOH in oxygen; GDE – S = 10 cm²; catalyst 20% Pt/carbon.

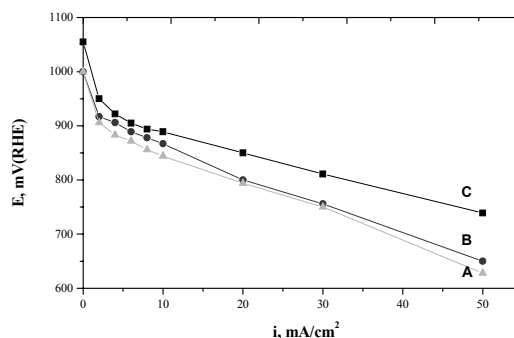


Fig. 9. Potential/current densities relationships for GDE with the tested catalysts in 7 N KOH in air; GDE – S = 10 cm²; catalyst 20% Pt/carbon.

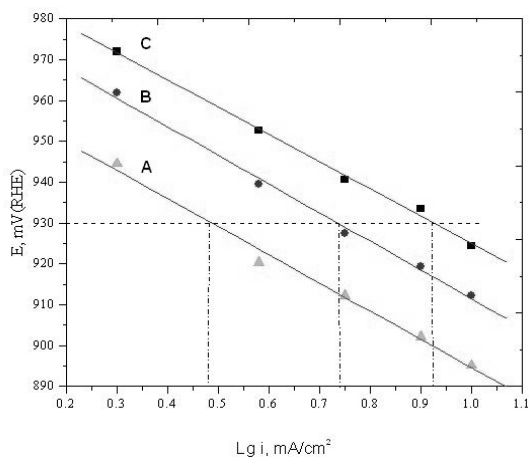


Fig. 10. Tafel plots of three catalysts in alkaline electrolyte (B, A and C) in oxygen; GDE – S = 10 cm²; catalytic 20% Pt/carbon; 7 N KOH.

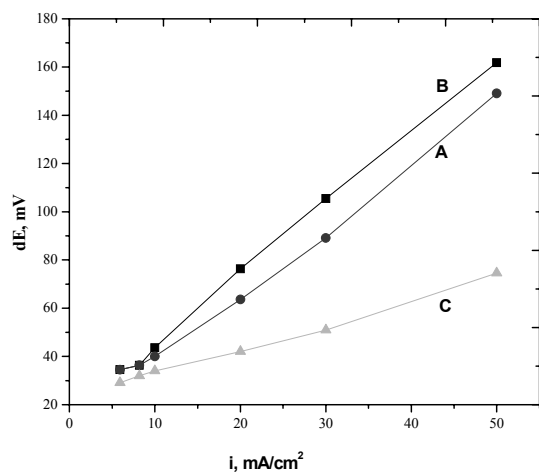


Fig. 11. Relationships between the difference in performance in oxygen and in air ($\Delta E = E_{O_2} - E_{air}$) and current density; GDE – S = 10 cm²; catalytic 20% Pt/carbon; 7 N KOH.

From these results is clear that the GDE with Pt/carbon catalysts in 7 N KOH have comparable performance with the electrodes in PEM, promoted with the same catalysts. From the measurements in 7 N KOH we can evaluate the comparable catalytic activity of the tested catalysts, as well as their gas transport limitations.

All the three catalysts presented above consist of 20% Pt on carbon black. In practice we have to evaluate catalysts with different catalysts loading. Figure 12 represents the oxygen polarization curves in PEM for four catalysts: two with 20 % Pt/carbon (E – 20% Pt/Shawinigan black, D – 20% Pt/Vulcan XC-72) and two with 10% Pt/carbon (G – 10% Pt/Shawinigan, F – 10% Pt/Vulcan XC-72). The Pt loading is the same for the four electrodes – 0.2 mgPt/cm². In order to achieve the same loading the catalytic layer of the electrodes with 10% Pt/carbon are twice thicker. Figure 13 shows the potential/current

densities relationships for GDE with the same catalysts in 7 N KOH with oxygen. The thickness of the catalytic layer of the four electrodes is the same 20 mg/cm², but the Pt loading is different, because of the various optimal ratios between the catalyst and HCB-35 in their catalytic layers. GDE with E has a Pt loading of 2.66 mgPt/cm²; GDE with D – 2.95 mgPt/cm²; GDE with G – 1.43 mgPt/cm²; GDE with F – 1.23 mgPt/cm². Despite that, the current densities for GDE in 7 N KOH in Fig. 13 are estimated per geometric area, not per mg Pt. Comparing the last two figures it is clear that the order in performance for Pt/carbon catalysts on electrodes in PEM and in 7 N KOH is the same: (i) for catalytic activity at low current density – E > G > F > D; and (ii) for gas transport limitations – E > F > G > D.

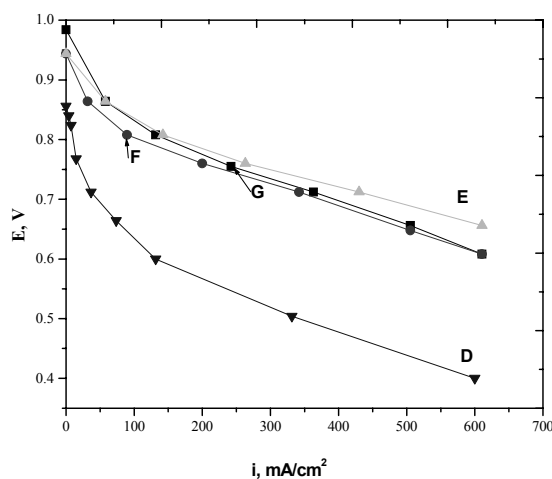


Fig. 12. Polarization curves in PEM with oxygen for four catalysts: E - 20% Pt/Shawinigan black; D - 20% Pt/Vulcan XC-72; G - 10% Pt/Vulcan XC-72; F - 10% Pt/Vulcan XC-72; Pt loading 0.2 mgPt/cm².

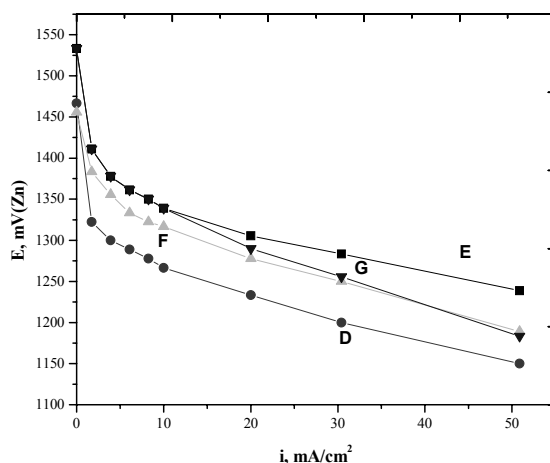


Fig. 13. Polarization curves in alkaline solution with oxygen for four catalysts: E - 20% Pt/Shawinigan black, D - 20% Pt/Vulcan XC-72, G - 10%Pt/Vulcan XC-72, F - 10% Pt/Vulcan XC-72; GDE – 10 cm²; 7 N KOH; oxygen; catalytic layer 20 mg/cm².

The Tafel slopes for GDE with the four catalysts in 7 N KOH, shown in Fig. 14, reveal the same order in catalytic activity. Figure 15 shows the same Tafel plots, but the current densities are estimated per platinum loading – i (mA/mgPt). It is clear that the order of activity is different and does not represent the order found in PEM. Thus, the comparison between the catalysts in PEM and KOH is possible on the base of current densities per geometric area only and can be explained by low utilization of Pt in GDE.

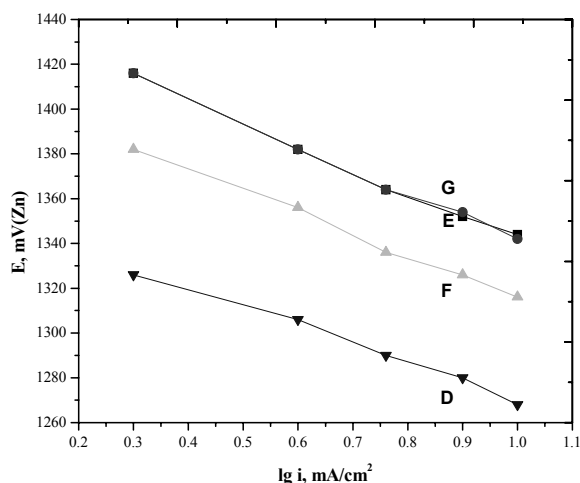


Fig. 14. Tafel slopes for GDE with the four catalysts as in Fig. 13 in 7 N KOH.

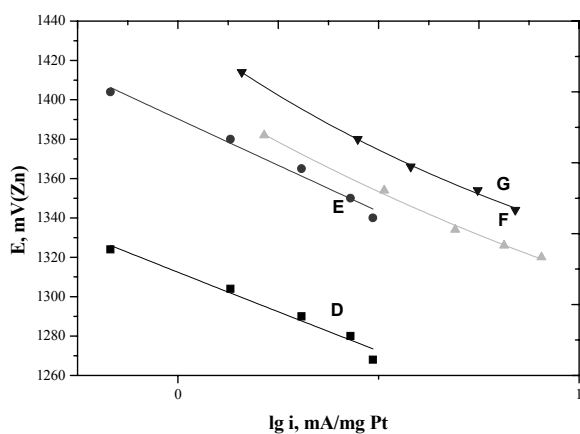


Fig. 15. Tafel slopes for GDE with the four catalysts as in Fig. 13 in 7 N KOH; current densities are estimated per platinum loading – i (mA/mgPt).

CONCLUSIONS

A number of catalysts with various Pt concentration and preparation conditions were synthesized and their structure and electrochemical performance were evaluated in different electrolytes.

The electrochemical measurements of the catalysts in PEFC and on GDE in sulphuric acid show the same order in performance. The perchloric acid is not stable at the conditions of electrochemical tests on real GDE.

The results in 7 N KOH show very good similarity in both electrolytes. The results in KOH are comparable not only in the Tafel region, but reveal the same transport limitations in the active layer. The comparison between the catalysts in PEM and KOH is possible on the base of current densities per geometric area only and can be explained by low utilization of Pt in GDE.

XRD data reveal that the electrocatalytic activity depends on the Pt crystallite size, type of support and processing conditions.

Fast and reliable approach, a combination of electrochemical and structural characterization, has been developed for rapid screening and optimization of Pt/C electrocatalysts for PEFC.

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ИЗПОЛЗВАНЕ НА ГАЗОДИФУЗИОННИ ЕЛЕКТРОДИ В АЛКАЛЕН ЕЛЕКТРОЛИТ ЗА ОПРЕДЕЛЯНЕ АКТИВНОСТТА НА КАТАЛИЗАТОРИ В ПОЛИМЕРЕН ЕЛЕКТРОЛИТ

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Постъпила на 17 октомври 2007 г., Преработена на 10 март 2008 г.

(Резюме)

Тази работа представя нов, бърз и надежден метод за предварително определяне на каталитичната активност и оптимизиране на платинови катализатори отложени върху активен въглен или сажди (Pt/C) за горивни елементи с протон-обменна мембрана (PEMFC). Подходът е съчетание от електрохимични и структурни характеристики. Катализаторите са синтезирани при различни условия, като е варирано съдържанието на платината. Тяхната структура и електрохимични характеристики е измервана за реални газодифузионни електроди (ГДЕ) в различни електролити: протон-обменна мембрана (PEM), сярна киселина, перхлорна киселина и калиев хидроокис. Резултатите в калиевата основа са подобни на тези в PEM електролити. Те показват подобни транспортни ограничения в активния слой и са сравними в Тафеловата област. Съпоставянето на катализаторите в PEM и КОН е възможно само на база на плътността на тока за геометрична площ, което вероятно се дължи на ниската им използваемост в ГДЕ. Рентгеноструктурният анализ показва, че електролитната активност зависи от размера на Pt кристали, типа на подложката и условията на получаване.