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Original scientific paper

On the stability of platinum-composite electrocatalysts prepared with different substrate materials^{*}

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Abstract

Cyclic voltammetry (CV) measurements were conducted and analyzed for a preliminary estimation of the stability of composite electrocatalysts based on Pt. The changes in CV currents of platinum nanoparticles supported on TiO₂ were compared to the changes of those supported on commercial carbon. TiO₂ was synthesized by sol-gel method and Pt was deposited from Pt colloidal dispersion synthesized by microwave-assisted polyol process. It was found that Pt component in both Pt/TiO₂ and Pt/C behaves similarly with respect to stability and activity during the cycling. The loss in activity with cycling was linear and strongly depended on sweep rate, i.e., the relative loss is higher at lower sweep rates. The steady state activities for both electrocatalysts were reached at the level of 65 % of initial activity and required more than 100 voltammetric cycles.

Keywords

Catalytic activity, Metal colloids, Pt supported on TiO₂, Sweep rate dependent stability

Introduction

Fuel cells-related investigations are nowadays in expansion, due to their promising application as alternative energy sources [1,2]. The main focus of current research activities are directed toward fuel cell reliability and durability [1]. Durability of polymer electrolyte membrane (PEM) fuel cell is considerably influenced on the electrocatalytic stability of electrode materials. Hence, a proper selection of nanoarchitecture and composition of membrane electrode assembly (MEA),

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and particularly the electrode material, is of extreme importance. Electrode material is required to be stable, economically suitable and nonpolluting [3]. Platinum nanoparticles supported on carbonaceous substrates (Pt/C) are widely envisaged as electrocatalysts in fuel cells [4], but carbon suffers from some disadvantages, such as low chemical inertness and modest potential window of stability [5]. Hence, the development of a support alternative to carbon could be of high importance. TiO_2 appears to be suitable replacement, because this oxide is of good mechanical and chemical resistance toward acidic and oxidative environments [6]. Pt nanoparticles could be deposited on TiO_2 by various methods, e.g., hydrothermal treatment [7,8], photo-assisted reduction [9] and underpotential deposition [10-12]. TiO_2 can influence catalytic activity of noble metal, e.g., platinum, due to hypo-d-electron configuration, which can interact with similar configuration of the noble metal [13]. There are studies showing better MEA stability and activity of Pt nanoparticles supported on mesoporous TiO_2 in comparison to commercial carbon as a support [14,15]. However, there are rather opposite findings for the influence of TiO_2 to Pt electrocatalysis; there are papers reporting the improvement for oxygen reduction kinetics [16,17] and the activity in H_2 evolution [18], but some results show that TiO_2 -supported Pt suffers from significantly lower activity in H_2 and O_2 reactions than Pt supported on carbon [19]. Hence, it could be of interest to take into consideration new approaches in composite catalyst synthesis and more detailed analysis of electrocatalytic properties of synthesized materials, able to mutually produce new findings and benefits for Pt catalysts supported on materials other than carbon of rather modest properties.

The aim of the present work was to synthesize TiO_2 as a supporting material for Pt and to estimate stability and activity of prepared composite at a glance, and to compare these properties with Pt supported on commercial carbon.

Experimental

TiO₂ synthesis. TiO_2 was synthesized by forced hydrolysis of TiCl_3 . TiCl_3 was added dropwise into the boiling 0.7 mol dm^{-3} HCl solution. During 90 min of boiling under reflux, TiO_2 was formed as a fine white precipitate. Obtained precipitate was centrifuged and washed with water, dried and thermally treated at $400 \text{ }^\circ\text{C}$ for 3 h in air, to remove residual chlorides [20].

Pt colloid synthesis. Pt colloid was synthesized by standard polyol process [21]. The mixture of ethylene glycol, which serves as reducing agent for PtCl_6^{2-} and stabilizing agent for produced Pt particles, and H_2PtCl_6 was stirred for 15 min. 0.1 M NaOH was added to increase pH to 12 and this mixture was placed in microwave at 70 W for 1 min.

Pt deposition onto TiO₂/C support from the colloidal dispersion. Pt was deposited onto TiO_2 , as well as on commercial carbon black (Vulcan XC72R, C) by following procedure. 20 mg of obtained TiO_2 powder (or C) was ultrasonically dispersed in 20 ml H_2O for 1 h and transferred into 150 ml of 2 M H_2SO_4 . The obtained suspension was stirred for 15 min before Pt colloidal dispersion was added. The stirring was continued for additional 3 h. Upon filtration and rinsing with water, the obtained Pt/ TiO_2 (or Pt/C) composite was thermally treated at $160 \text{ }^\circ\text{C}$ in N_2 atmosphere. The composite suspension for the preparation of thin layer electrode was formed by ultrasonic treatment (40 kHz, 70 W) of 3 mg of Pt/ TiO_2 (Pt/C) in 1 ml H_2O for 1 h. The suspension was pipetted onto glassy carbon electrode ($A = 0.196 \text{ cm}^2$) and room-dried to form 0.31 mg cm^{-2} composite thin layer.

Electrochemical measurements were conducted in three-electrode cell using BioLogic SP-200 potentiostat. Saturated calomel electrode (SCE) was used as a reference electrode and platinum

mesh as a counter electrode in 0.1 M HClO₄ electrolyte. All potentials in the paper are given in SCE scale. Before measurements, the cell was deaerated by bubbling the nitrogen for 15 min. Stability of the samples was analyzed as a function of cycling and sweep rate.

Loss of activity was quantified by the relative change of voltammetric charge ($q / \%$) in a given cycle with respect to initial one, which has been spent for hydrogen adsorption/desorption processes [22]. The charge was averaged from the data of the well-developed first peak in cathodic direction and its anodic counterpart.

The particle size characterization of the TiO₂ was performed by dynamic light scattering (DLS) on Zetasizer Ver. 6.20 instrument Malvern Instruments Ltd., England. The sample for DLS analysis was prepared to mimic the Pt-free mixture for composite synthesis.

Results and discussion

Figures 1 and 2 show CV curves for Pt/TiO₂ and Pt/C, respectively, registered in 0.1 M HClO₄ at different sweep rates. The CV currents for both Pt/TiO₂ and Pt/C decrease during cycling in a different degree, indicating the continuous loss of the activity. The loss appears differently pronounced in different potential regions and at different sweep rates. In case of Pt/TiO₂ (Fig. 1), the CV response related to hydrogen adsorption/desorption and oxide formation is better resolved at higher sweep rate (Fig. 1b), which indicates more defined structure of Pt particles more easily accessible to the electrolyte (those located at the outer parts of the composite catalyst layer). The loss of activity upon cycling is more pronounced for Pt/TiO₂ than for Pt/C (Fig. 2), although in both cases the substantial loss takes place during the first 50-80 cycles (Figs. 1a and 2, respectively). In addition, the decrease in CV currents of Pt/TiO₂ is visible in whole region between potential CV limits (with the smallest decrease related to narrow double region), whereas the oxide formation (up to 0.6 V) and reduction in Pt/C appears almost insensitive to the cycling (Fig. 2). Similarly, the oxide reduction region (down to 0.6 V) for Pt/TiO₂ negligibly depends on cycling at higher sweep rate (Fig. 1b). If the charge spent for hydrogen adsorption/desorption is taken as a measure of Pt activity (see Experimental), the overall loss of the activity in Fig. 1a is 35 %, which is quite larger than the loss found in Fig. 1b - 20 %. This indicates also the different structure of outer-layer Pt particles in comparison to those located in most inner, loose parts of composite layer. The corresponding loss for Pt/C is a bit lower (Fig. 2), 12 %, although the number of cycles spent is considerably lower. Hence, it could be stated that Pt/TiO₂ and Pt/C are of similar characteristics upon cycling at higher sweep rates, or that outer-layer Pt in Pt/TiO₂ reaches the finely tuned structure upon *ca.* 150 cycles.

Although the two composite catalysts are prepared by the same procedure, the CV currents of Pt/TiO₂ are considerably lower than those of Pt/C. The Pt loading was projected to 20 mass %. According to the Pt/C CV response, the Pt nanoparticles diameter, calculated on the basis of standard procedure [21], is around 7 nm. In order to check Pt loading in Pt/TiO₂ composite, spectrophotometric measurements were employed. In this procedure, composite was dissolved in the *aqua regia* and obtained solutions were analyzed on the UV-Vis spectrophotometer and compared to the standards. It was found that Pt loading is almost the same as in the Pt/C composite, *i.e.* 19 mass %. However, the calculation of Pt content from Pt/TiO₂ CV response returns the value of *ca.* 3 mass %, with the assumption that Pt particles of similar size are formed in Pt/TiO₂ and Pt/C due to identical preparation procedure. It follows that considerable amount of Pt in Pt/TiO₂ is not involved in CV response. This could be due to semiconductive nature of TiO₂.

Namely, if there are some distinct heaps of Pt particles on TiO₂ surface, there will not be conductive pathways toward external circuit as it is in the case carbon support.

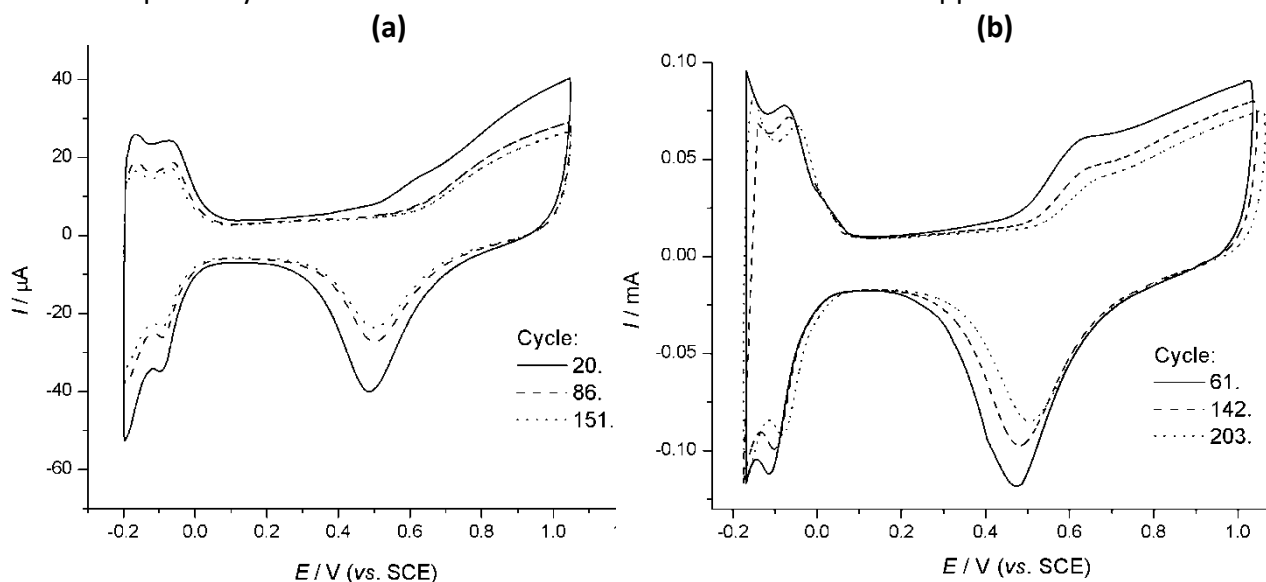


Figure 1. Characteristic cyclic voltammograms of Pt supported on TiO₂ at sweep rates of 50 (a) and 200 mV s⁻¹ (b), registered during continuous cycling in deaerated 0.1 M HClO₄.

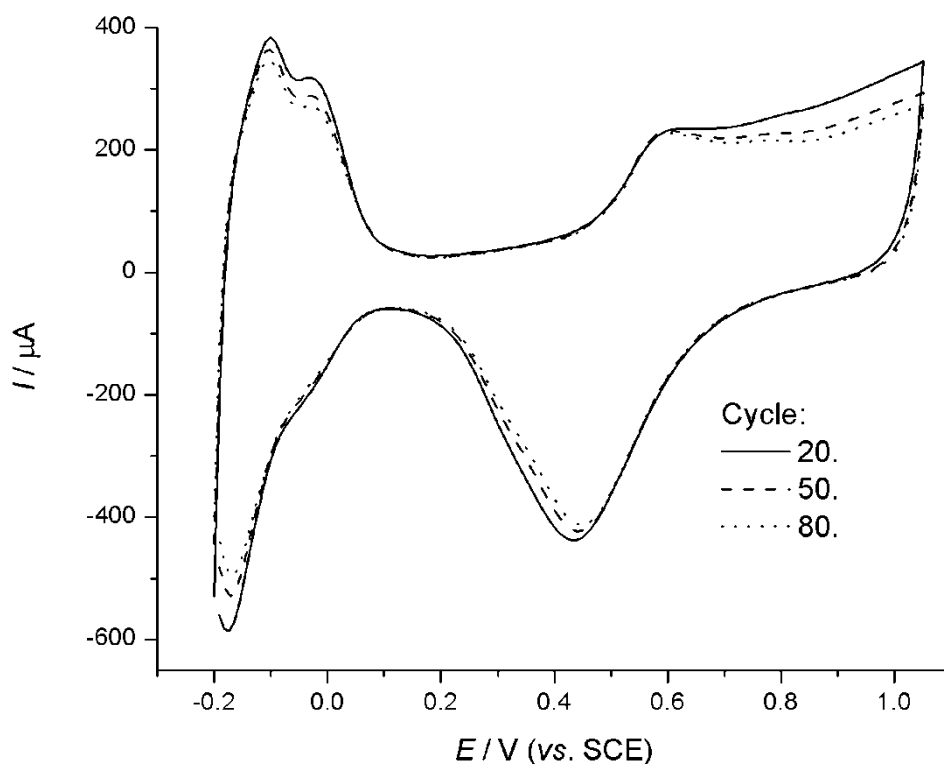


Figure 2. Characteristic cyclic voltammograms of Pt supported on C, registered during continuous cycling in deaerated 0.1 M HClO₄ at sweep rate of 100 mV s⁻¹.

In order to check possible morphological relationships between Pt and TiO₂, particle size distribution (PSD) of the TiO₂ powder suspended in the medium for Pt deposition was analyzed by dynamic light scattering (DLS). Figure 3 shows the registered PSD averaged on ten successive runs expressed as distributions by intensity and volume. DLS registers the particles of ca. 400 nm and agglomerates of ca. 2.5-3 μm. The material appears mainly concentrated in agglomerates since the distribution by volume is considerably larger. On the other hand, the number of particles and

agglomerates are comparable since the distribution by intensity is similar (10 and 8 %, respectively).

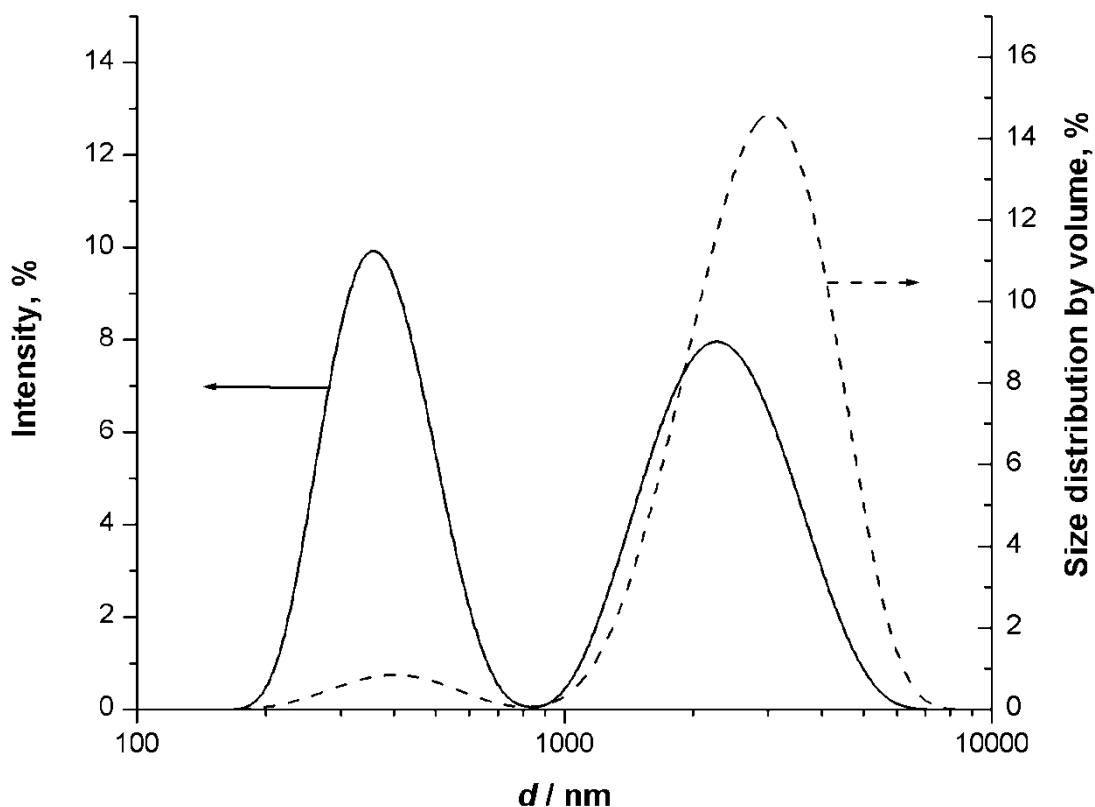


Fig. 3. Particle size distribution by dynamic light scattering of TiO_2 solid phase in the medium for Pt deposition.

If 400 nm-sized TiO_2 particles would be considered as a support to host 7 nm-sized Pt particles (both ideally spherical), the monolayer of Pt particles could produce around 30 mass % of Pt, fairly above projected value. This indicates that the size of TiO_2 and Pt particles are optimal for the production of composite catalyst with desired Pt content. On the other hand, 3 μm -sized TiO_2 agglomerates are able to accommodate 4.5 mas. % of Pt in full particle monolayer. It could be that pronounced agglomeration as seen in Fig. 3 causes the Pt hosted by 400 nm-sized TiO_2 to be trapped within agglomerates and hence not available for CV response. Consequently, those Pt particles on the surface of agglomerates are able in a high degree to create connection pathways toward GC substrate, and produce a CV response corresponding to few mass % as obtained from Fig. 1.

Loss of activity, quantified by the voltammetric charge related to hydrogen adsorption/desorption, can be additionally analyzed as a function of a cycling and applied sweep rate. The relative changes in charge, *i.e.*, catalyst activity, is presented in Fig. 4. Pt/ TiO_2 loses 10-13 % of initial activity in first 40 cycles, which appears only slightly dependent on sweep rate. The initial decrease of *ca.* 8 % is registered at 50 mV s^{-1} , whereas additional 20 cycles at 200 mV s^{-1} produces further loss of *ca.* 5 %. This slowing down of the loss by the increase in sweep rate indicate that related transformations of Pt particles are sweep rate-dependent. It could be that the transformations are of more pronounced reversibility at higher sweep rates (*e.g.*, reverse coarsening) [22] or that Pt particles from the inner part of a layer reach the final state of transformations much easier than the particles from the outer part of a layer. These effects could cause also the differences in CV responses from Fig. 1a and b, in which the hydrogen adsorption/desorption region is less pronounced at lower (Fig. 1a) than at higher sweep rate (Fig. 1b).

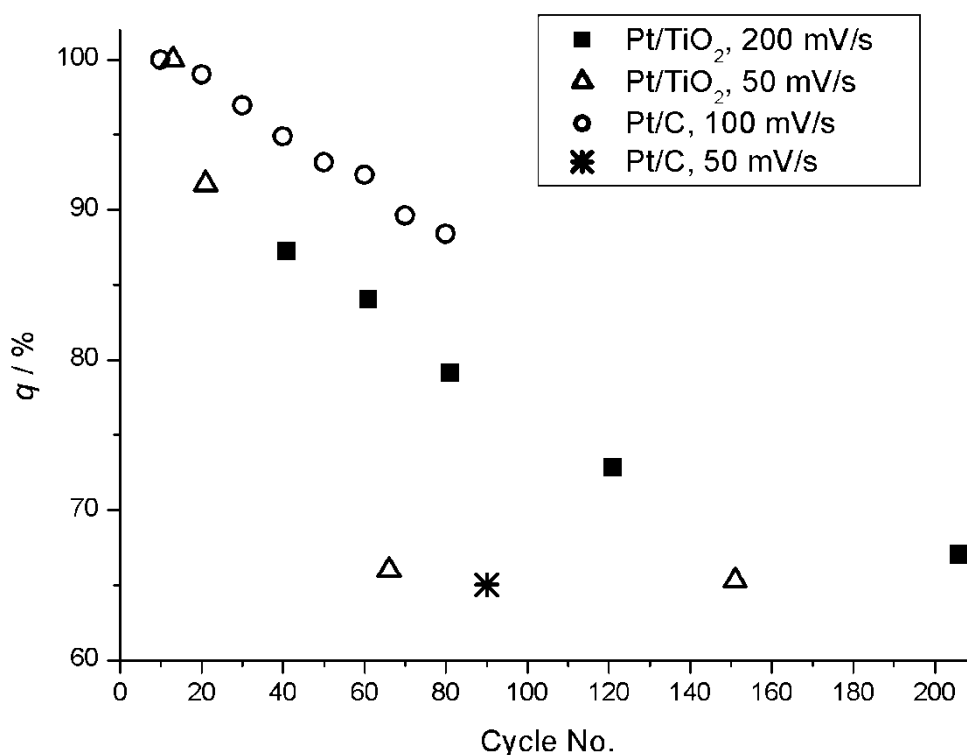


Figure 4. The relative changes in voltammetric charge of hydrogen adsorption/desorption for Pt/TiO₂ and Pt/C during the cycling.

In order to check the validity of the differences in charge at different sweep rate, the CV responses at 50 and 200 mV s⁻¹ are compared after 60th and 150th cycle. Indeed, the loss of the activity at 50 mV s⁻¹ is more than twice of that registered at 200 mV s⁻¹ after 60 cycles. As the Pt reaches the stable transformation state during next 60-90 cycles at 200 mV s⁻¹, this difference becomes considerably less pronounced (the losses of activity at 50 and 200 mV s⁻¹ are *c.a.* 35 and 28 %, respectively). In addition, this feature is checked also for Pt/C after 80 cycles; the result is similar and even more pronounced than for Pt/TiO₂: around 12 % loss at 100 mV s⁻¹ and 35 % at 50 mV s⁻¹. These findings are in fair accordance to the suppositions of sweep rate-sensitive reversed transformations and their rate distribution throughout composite layer.

The reported results indicate that Pt component in both Pt/TiO₂ and Pt/C behaves similarly with respect to stability and activity during the cycling. The loss of activity is linear upon cycling and appears strongly dependent on sweep rate. The steady state transformations of Pt is reached at the level of 65 % of activity with respect to initial state and require more than 100 voltammetric cycles. This behavior appears related to sweep rate-dependent reverse transformations, probably coarsening, and distribution of such transformations through the composite layer in a way that Pt particles from inner part of a layer are transformed much easier and faster.

Conclusion

Electrocatalytic activity and stability of Pt supported on TiO₂ and C were examined and compared on the basis of routine cyclic voltammetry measurements at various sweep rates. Platinum was synthesized by polyol process and deposited on sol-gel synthesized TiO₂ and commercial carbon. The loss of activity of Pt particles was quantified by the voltammetric charge related to hydrogen adsorption/desorption. The results showed that the Pt particles behave in similar manner for two different supporting materials. Steady state activities were reached after 100 cycles, when activity decreased by 35 % with the respect to the initial activity. The loss of

activity is strongly dependent on sweep rate and tends to be higher at lower sweep rates. This is probably due to less reversible Pt particles transformations at lower sweep rates, including agglomeration and coarsening.

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