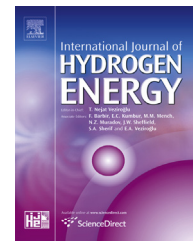


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Short Communication

A simple method for estimating the electrochemical stability of the carbon materials

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ABSTRACT

The corrosion stability of a series of carbon supports of various porous structure and morphology: commercial carbon blacks, carbon–carbon composite, and multiwall carbon nanotubes was studied using start-stop protocol cycling (1–1.5 V vs reversible hydrogen electrode (RHE) potential range with 0.5 V/s of scan rate) in an electrochemical cell at 25 °C using 0.1 M HClO₄ as electrolyte. Two stability regions were revealed for the first time depending on the cycle number. The first one is characterized by a constant value of quinone/hydroquinone (QH) transition potential. In the second part anode and cathode QH peaks gradually shift toward higher and lower potentials respectively, which is due most likely to a complete degradation of the supports. We proposed an effective resistance (R_{eff}) as the corrosion stability parameter that can be easily obtained from the cyclic voltammetry (CV) data. Based on these results, a model of corrosion of porous carbon materials supported on glassy carbon rod was proposed. It was shown that the decrease in the R_{eff} of the samples in the initial stages of degradation is due to the increase in the number of QH groups on the surface, while a sharp increase in the R_{eff} upon further cycling can be explained by a decrease in the number of contacts between the carbon grains.

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Introduction

Currently polymer electrolyte fuel cells (PEFC) are regarded as promising energy sources for cars. One of the main problems hindering their commercialization is low corrosion stability of their components, in particular, Pt/C catalysts [1–6]. This problem occurs due to a jump of cathode potential up to 1.4 V vs. reversible hydrogen electrode (RHE) upon starting and/or stopping the engine [7].

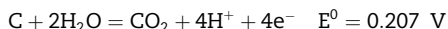
Degradation of the platinum catalysts in the oxidation tests is due to the loss of platinum electrochemically active surface (EAS), which leads to a decrease in their activity and Pt utilization in the oxygen electroreduction reaction. Several mechanisms of the Pt/C degradation were evaluated in the literature, including: 1) dissolution of platinum nanoparticles upon cycling above 0.85 V RHE [8,9], followed by redeposition onto the large Pt nanoparticles (electrochemical analog of Ostwald precipitation) [9,10] or inside proton-conducting

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polymer membrane [11,12]; 2) migration of Pt nanoparticles at the surface of carbon support, followed by coalescence [10,13,14], which leads to enlargement of Pt particles and reduce their mass activity; 3) the corrosion of carbon support by the following reaction [15–18], which was shown to be catalyzed by platinum nanoparticles [16,19].



Carbon corrosion can lead to detachment of large lumps of the material with supported Pt nanoparticles. All these degradation mechanisms has been confirmed for Pt/C catalysts by transmission electron microscopy [20,21]. It was shown in the literature and confirmed in our group that the carbon support stability is the main issue in the stability of Pt/C catalysts [4,5,22–24]. In fact, the jump of cathode potential up to 1.4 V RHE upon starting and/or stopping the engine is much higher than the carbon oxidation potential (0.207 V RHE [25]), so the development of new stable carbon materials and the study of the mechanisms of their electrochemical corrosion became an urgent issues [6,26,27]. In order to investigate the stability of various carbon materials in a short time an accelerated testing protocol (“start-stop cycling”) in a standard three-electrode electrochemical cell was developed comprising cycling in the 1–1.5 V RHE of potentials with a 0.5 V/s of scan rate [2,28].

The decrease in the EAS of Pt is the criterion for corrosion resistance of the catalysts [29,30], however yet no simple parameter to compare the corrosion resistance of the different supports upon the “start-stop” cycling was suggested. Obviously, the best indicator of the stability of the support is a rate of its mass change [31] or the rate of CO/CO₂ evolution [32] in the course of cycling, but such experiments are very difficult to perform in the electrochemical cell. The ratio of the intensity of the D1 to the G-band determined from Raman spectra (or the relative band area ratio) is classically used as descriptor of the robustness and of the extent of degradation of high surface area carbon supports [25,33,34]. However, these experiments cannot be performed *in situ* during the accelerated cycling process. The charge of the quinone/hydroquinone (QH) peaks obtained from the cyclic voltammograms (CV), which can be used as a criterion [15,35,36], in our view, does not reflect the whole picture of the material degradation, since it characterizes the surface properties only, which may not be related to the corrosion stability.

Much attention is paid in the literature to comparison the CV curves of the supports with many different parameters like specific surface areas, pore volumes, surface chemical composition, etc. [37–39]. However, the identification of the factors determining the stability of such different supports is still not proposed [15,35,36]. As for the mechanism of electrochemical corrosion, the attempts to model the dependence of the mass loss on the oxidation time were suggested [17,40,41]. However, these models describe the real systems roughly.

In this paper the corrosion stability of a series of carbon supports of various porous structure and morphology was studied. Two stage of porous material degradation were revealed depending on the cycle number, with the second step being not described in the literature before. Based on a theoretical justification of the experimental data we suggested a

simple method for estimating the corrosion stability of porous materials from the CV curves obtained. A model of the degradation of the carbon materials deposited on glassy carbon was proposed.

Experimental part

The following materials with highly variable specific surface areas were studied: KetjenBlack DJ-600 (KB) (Cabot Corp.) ($S_{\text{BET}} = 1420 \text{ m}^2/\text{g}$), Sibunit 1562 (Sib) (Institute of Hydrocarbon Processing, Russian Academy of Sciences, Omsk, Russia) ($S_{\text{BET}} = 450 \text{ m}^2/\text{g}$), Vulcan XC-72 (Vu) (Cabot Corp.) ($S_{\text{BET}} = 210 \text{ m}^2/\text{g}$), multiwall carbon nanotubes (CNT) synthesized according to Ref. [42] ($S_{\text{BET}} = 270 \text{ m}^2/\text{g}$), Black Pearls 2000 (BP) (Cabot Corp.) ($S_{\text{BET}} = 1510 \text{ m}^2/\text{g}$).

The following reagents were used: isopropanol, perchloric acid, deionized water with a quality of purissimum speciale and higher. A glassy carbon rod (GC) (5 mm diameter) was supplied by Alfa Aesar. Pt foil was used as counter electrode, while homemade reversible hydrogen electrode (RHE) Pt/H₂/H⁺ (supporting electrolyte 0.1 M HClO₄) connected to the working electrode compartment via a Luggin capillary was used as reference one. Polished GC was coated with a thin layer of carbon sample suspended in a water-isopropanol solution (60 vol. %) added with Nafion ionomer dispersion (Nafion/C = 50 mass. %). The samples were dried at room temperature in a stream of Ar. The carbon load was 100 μg/cm². Potentiostat Autolab PGSTAT 100 was used to control the electrode potential using software from Metrohm Autolab BV (Nova). All measurements were carried out in an automatic mode. The working electrode was polarized at 25 °C by triangular potential signal in the range 1.0–1.5 V RHE with a 0.5 V/s of scanning rate in 0.1 M HClO₄ solution as a background electrolyte. CV curves were recorded in the 0–1.2 V RHE potential range using 0.05 V/s of scan rate before cycling, after 10, 20, 50, 100, 200, 500 and then after every 1000 cycles.

Results and discussions

Fig. 1 shows the evolution of CV curves of carbon samples during degradation.

The change of the CV curves upon cycling can be divided into two stages. In the initial phase (Fig. 1 part A) the peaks emerge at about 0.6 V in the anode and 0.55 V in the cathode branches of CV. Their intensities grow upon cycling, with the potentials being constant. The peaks were associated with the electron transfer in the surface QH transitions [43,44]. In a second stage (Fig. 1 part B) the anodic and cathodic potentials of QH peaks are shifted to higher and lower values, respectively, and then the peaks disappear. Finally, the experimental CV curve becomes similar to GC one (especially for BP and KB600 samples in Figs. 1,2B and 5B), indicating the complete degradation of the samples. The first stage of degradation is well known and described in the literature [15], while the complete disappearance of the carbon support signal in CV curves was not observed yet. Monotonous character of the dependence of capacitive current on the potential in CV curves (Fig. 1 part B) allows us to assume that the

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