Oxygen electrocatalysis on the Pt-modified carbon
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It is well known that oxygen reduction reaction (ORR) can proceed via a 4-electron pathway to give water as the final product or 2-electron pathway to form peroxide ions, depending on the electrode material. Platinum and several metals of the platinum group promote the 4-electron pathway [1-5]. A study of ORR in alkaline solutions at various carbons (Vulcan, C(Mo2C)) supported Pt catalysts is reported. One of the aims of this work is to reduce the loading of expensive Pt. The carbon supported Pt (20wt% and 60wt% metal) nanoclusters activated electrodes have been tested in 0.1M KOH solutions. Experiments in KOH aqueous solutions show that in this medium there is an important contribution from the carbon on the electrode-reduction process of O2 [6,7].

The scanning electron microscopy (SEM), X-ray diffraction (XRD), high resolution transmission electron microscopy and low temperature N2 adsorption experiments were carried out to characterize the structure of prepared materials. A comparison of the XRD patterns of the carbon supported catalysts in Figure 1 shows that the intensities of Pt peaks are increasing with the increase of the Pt loading in materials, but calculated average crystallite diameter d is practically independent of the proportion of the Pt [8].

![Figure 1. X-ray diffraction data for various Pt-modified systems: 1 – 60%Pt-C(Mo2C); 2 – 20%Pt-C(Mo2C); 3 – 60%Pt-Vulcan; 4 – 20%Pt-Vulcan.](image)

![Figure 2. SEM images for 20%Pt-C(Mo2C) (a); 60%Pt-C(Mo2C) (b).](image)

Figure 2 illustrates the SEM images for studied materials. SEM images demonstrate that the structural integrity was still very well reserved even after increase of the catalyst loading. Small nanoparticles of the platinum were also uniformly observed in the supported Pt catalyst particles are almost identical, which implies that the metal loading does not have a significant effect on the Pt metal dispersion in these four catalysts. The particle sizes measured directly from SEM images at randomly selected regions for all samples were approximately ~50 Å, which confirms the value determined from the XRD results.

The electrochemical measurements were carried out in a three-electrode electrochemical cell. Electrochemical characteristics for various Pt-modified micro- and mesoporous carbons have been established by cyclic voltammetry and rotating disc electrode (RDE) methods. RDE data were measured at rotation rates from 0 to 3000 rpm (v=10 mV/s) and in the region of potentials from +0.31 to -0.55 V vs. Hg/HgO, 0.1M KOH. The potentials were measured against Hg/HgO, 0.1M KOH reference electrode. Cyclic voltammograms were measured at potential scan rates (v mV/s) 5, 10, 20, 30, 50, 70, 100, 150 and 200, in both Ar and O2 saturated solution. The solutions were saturated with Ar or O2, respectively, between measuring of each voltammogram. It was established that the ORR activity for 20%Pt-C(Mo2C) is comparable to 60%Pt-Vulcan. Pt-metal loadings play a dominant role in the kinetics of the ORR on Vulcan based electrodes. In contrast, the supportive carbon, C(Mo2C), play key role in 20 and 60% Pt-based C(Mo2C) electrodes in alkaline solution [6,7].

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References