KINETICS OF THE HYDROGEN OXIDATION ON Pt MODIFIED MoOx NANO-SIZED CATALYST IN THE PRESENCE OF CARBON MONOXIDE

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1. Introduction with Experimental Details

Due to the importance of the HOR in fuel-cells technology, various Pt-based catalysts have been examined from the viewpoint of immunity of the electrocatalysis of the HOR from CO-poisoning of the anode catalysts. An appreciable improvement of the CO tolerance has been found at Pt with adatoms such as Ru, Sn [1,2], Pt-Mn/Mn-Ru, Rh, Os, W Sn [3-5] based alloys, and Pt with oxides (RuOx) [6].

In the present work, the electrocatalytic of home-made highly dispersed nano-sized MoOx-Pt/C catalysts prepared by the polyol method combined by MoOx post-deposition was investigated in the presence of CO, in 0.5 mol dm-3 HClO4 solution. The partial pressure of CO in CO2/H2O gas mixture was 100 ppm.

Carbon monoxide was adsorbed on the RDE for various time interval with keeping the potential at 0.05 V (RHE). The coverage of CO was determined by applying the first potential sweep (from 0.04 to 1.20 V), in N2 saturated solution at potential scan rate of 1.0 V s-1 and compared it with the sweep on the clean electrode, by measuring the decrease in the hydrogen desorption charge, ∆QH2.

MoOx(20%)/Pt/C catalyst exhibits an excellent CO tolerance, as it was found that the reduction in kinetic current, I△, negligible at rad = 0.46. It was found for this catalyst too, that the CO adsorption rate was much slower than that of Pt and the Pt sites for HOR were not so rigidly blocked by adsorbed CO partially due to its enhanced mobility, resulting from their modified electronic structure of surface Pt sites. Voltammetric studies suggested that an excellent tolerance of this catalyst could also be result of the oxidation of adsorbed CO to CO2 by oxophilic MoOx species at low overpotentials by a redox-mediated mechanism.

2. Results and Discussion

Representative images of MoOx-modified Pt/C catalyst are presented in Fig.1. As evident from Fig.1 Pt/MoOx nanoparticles are homogeneously distributed over the carbon support, with no evidence for pronounces particle agglomeration. All catalyst samples show monodermal particle size distribution, which results in a mean particle sizes of 2.3 nm. These results, confirm that MoOx post-deposition does not lead to a significant growth of the Pt nanoparticles. To gain further insight on the distribution of the MoOx species on the Pt nanoparticle surface, we determined the active surface area of the catalysts under study by UPD region of corresponding, cyclic voltammograms. The results for MoOx-Pt/C are presented in Fig.2. A stable response was found after few cycles with no current of Mo oxidation or dissolution for potentials up to 1.30 V. This indicates that the MoOx particles are stabilized by the interactions with neighboring Pt atoms. Pt-O-Mo species at low overpotentials by a redox-mediated mechanism.

Table 1. Kinetic Parameters for the HOR at MoOx-Pt/C electrode in 0.5 M HClO4 at 25°C

<table>
<thead>
<tr>
<th>Potential (V vs RHE)</th>
<th>β/mlV dec⁻¹</th>
<th>I△/mA (30 mV)</th>
<th>Mechanism</th>
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<tr>
<td>0.0</td>
<td>32</td>
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<td>5.8</td>
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</table>

References:

Fig.1 a) HRTEM micrographs of MoOx-Pt nanoparticles on carbon support. b) high angle annular dark-field (HAADF) image.

Fig.2. Cyclic voltammograms of MoOx-Pt/C in 0.5 mol dm-3 HClO4 free CD solution.

Fig.3. Linear-sweep voltammograms for the HOR at MoOx-Pt/C RDE in 0.5 mol dm-3 HClO4 solution saturated with pure H2. Inset: Levich-Koutecky plot in the diffusion-limited potential region at 0.14 V vs RHE.

Fig.4. CO-stripping cyclic voltammograms at MoOx-Pt/C electrode measured in N2 saturated 0.5 mol dm-3 HClO4 solution at 0.01 V s⁻¹. The full line shows CV at the CD-free surface.

Fig.5. Changes in the linear-sweep voltammograms (0.01 V s⁻¹) for the HOR on MoOx-Pt/C with various rads, at 2073 mV. The HOR voltammograms were measured in H2 (100 ppm CO) saturated 0.5 mol dm-3 HClO4 solution at 29°C before recording CD-stripping voltammograms. Inset: Time-course for CO adsorption at E= 50 mV vs RHE.

Fig.6. Potentials of k/La = 0.46 and k/Lb = 0.46. Data taken from the corresponding linear-sweep voltammograms for the HOR at MoOx-Pt/C electrode with various rads in 0.5 mol dm-3 HClO4 solution saturated with H2 containing 100 ppm CO.

Fig.7 The dependence of kinetic current, k, for the HOR on rad, on MoOx-Pt/C and Pt/C catalysts in 0.5 M HClO4 solution at 25°C.