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 immortality of the electrolysis 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-Mu-Ru, Rh, Os, W Sn [3-5] based alloys, and Pt with oxides (RuOxHx) [6].

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

Carbon monooxide was adsorbed on the RDE for various time intervals 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 0.1 Vs-1.

Fig. 4 shows typical stripping voltammograms (0.1 V s-1) obtained in N2 saturated 0.5 M HClO4 solution. The hydrogen desorption current from 0.04 to 0.4 V are reduced by the occupation of Pt sites with adsorbed CO and inset of Fig. 4 shows the dependence of CO coverage on adsorption time. Icorr in an electrolyte saturated with H2 containing 100 ppm of CO at 0.05 V and 2500 rpm.

Fig. 5 shows typical cyclic voltammetric polarizations (10 mV s-1) at 2070 rpm for the HOR in H2/0.05 ppm CO saturated solution with various H2O/CO ratio. It was found that MoO3-Pt/C electrode has lost the HOR activity slightly high at H2O/CO. It was found that MoO3-Pt/C electrode has lost the HOR activity slightly high at H2O/CO ratio.

2. Results and Discussion

Representative images of MoO3/Pt/C catalyst are presented in Fig.1. As evident from Fig.1 Pt-MoO3 nanoparticles are homogeneously distributed over the carbon support, with no evidence for pronounced particle agglomeration. All catalyst samples show monomodal particle size distribution, which results in a mean particle sizes of 2.3 nm. These results confirm that MoO3 post-deposition does not lead to a significant growth of the Pt nanoparticles. To gain further insight on the distribution of the MoO3 species on the Pt nanoparticles surface, we determined the active surface area of the catalysts under study by UPD H region of corresponding, cyclic voltammetry.

The full line shows CV at the CO-free surface. The CO-stripping cyclic voltammograms for the HOR at MoO3-Pt/C with various H2O/CO ratio. The HOR reaction rate is 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 suggest that an excellent CO tolerance of this catalyst could also result from the oxidation of adsorbed CO to CO2 by oxophilic MoO3 species at low overpotentials by a redox-mediated mechanism.

Table 1. Kinetic Parameters for the HOR at MoO3-Pt/C electrode in 0.5 M HClO4 at 25°C

<table>
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<th>HClO4</th>
<th>k / mV dec-1</th>
<th>Icorr / mA (30 mV)</th>
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<tr>
<td>0.0</td>
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<td>0.06</td>
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</table>

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References: