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-M(M=Ru, Rh, Os, W Sn) [3-5] based alloys, and Pt with oxides (RuOₓHᵧ) [6].

In the present work, the electrocatalytic of home made highly dispersed nano-sized MoOₓ-Pt/C catalysts prepared by the polyole 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 CO/H₂ 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 0.1 Vs⁻¹ and compared it with the sweep on the clean electrode, by measuring the decrease in the hydrogen desorption charge, ΔQ_H.

MoOₓ(20%)Pt/C catalyst exhibits an excellent CO tolerance, as it was found that the reduction in kinetic current, I_k, is negligible even at $\Theta_{CO} = 0.46$. 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 suggest that an excellent CO tolerance of this catalyst could be also result of the oxidation of adsorbed CO to CO₂ by oxophilic MoOₓ species at low overpotentials by a redox-mediated mechanism.

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

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 homogenously distributed over the carbon support, with no evidence for pronounces 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 MoOₓ post-deposition does not lead to a significant growth of the Pt nanoparticles. To gain further insight into the distribution of the MoOₓ species on the Pt nanoparticle surface, we determined the active surface area of the catalysts under study by UPD H 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. The redox pair observed at ca. 0.45 V could be attributed to the intermediate oxidation states of molybdenum, being between III and IV.

Fig. 3 shows potentiodynamic curves for the oxidation of pure H₂ on a MoOₓ-Pt / Vulcan electrode at different rotation rates.The HOR currents commence at 0.0 V vs RHE and reach diffusion-limited current at approximately 0.05V. A Levich-Koutecky-like plot based on experimental data at 0.14 V is shown in Inset of Fig.3 and the resistance through the Nafion film yielding a value of about 14mA or the current density of 50 mA cm⁻² (the current density is referenced to the geometric area). However, this value corresponds to maximum mass-specific current density of j = 3 A/mgPt, which is comparable with real PEMFC anode.

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 0.4V are reduced by the occupation of Pt sites with adsorbed CO and inset of Fig.5 shows the dependence of CO coverage on adsorption time, t_{ad} in an electrolyte saturated with H₂ containing 100 ppm of CO at 0.05 V and 2500 rpm. Fig. 5 shows typical voltametric polarization curves (10 mV s⁻¹) at 2070 rpm for the HOR in H₂(100 ppm CO) saturated solution with various Θ_{CO} in the potential range from 0.0 to0.14 V. It is clear that MoOₓ-Pt/C electrode has lost the HOR activity slightly at high Θ_{CO}. RDE polarization data were analyzed in terms of mass transport corrected Tafel diagrams. The kinetic equations used for such analysis were derived considering a reversible or an irreversible nature for the kinetics of the electrochemical reaction. Mass-transfer corrected Tafel plots, E vs log [I_L / (I_L − I)] or E vs log [$I_L \cdot I$ / (I_L − I)] are shown in Fig.6. The Tafel slope is 32 mV dec⁻¹ for the HOR in CO free condition (Fig. 6a) which is in accordance with theTafel-Volmer reaction route in which dissociative adsorption of H₂ is generally accepted as the rate-determining step (rds) for the HOR. The further increase of Θ_{CO} does not lead to the increase of Tafel slope (Figs.6b and 6c) for the HOR. However, only for Θ_{CO}=0.48, the corresponding value of Tafel slope is 0.058 V dec⁻¹ indicating that Volmer step is now rate determining step for the HOR. The corresponding values of Tafel slopes, together with the calculated values for the kinetic current, I_k, at E = 30 mV are presented in Table 1.
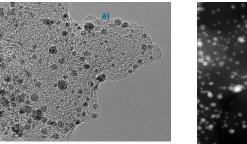
Finally, the dependence of the kinetic current for the HOR at E = 30 mV on Θ_{CO} are shown in Fig.7 for MoOₓ-Pt/C and Pt/C catalysts for comparison. The kinetically controlled current density (I_k) for the HOR at nano-sized Pt/C catalyst decreased seriously with the increase of CO coverage. In contrast, the MoOₓ(20%)Pt/C catalyst exhibits an excellent CO tolerance, as it was found that the reduction in I_k is negligible even at Θ_{CO} = 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 suggest that an excellent CO tolerance of this catalyst could be also result of the oxidation of adsorbed CO to CO₂ by oxophilic MoOₓ species at low overpotentials by a redox-mediated mechanism.
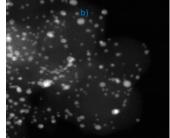
Table.1. Kinetic Parameters for the HOR at MoOₓ-Pt/C electrode in 0.5 M HClO₄ at 25⁰C

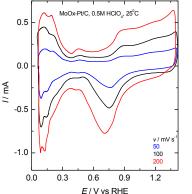| Θ_{CO}	b / mV dec⁻¹	I_k / mA (30 mV)	Mechanism
0.0	32	10.2	
0.27	33	9.8	Tafel-Volmer
0.44	36	8.7	
0.46	36	7.3	
0.48	58	5.8	

References:
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[2] H.Gasteiger, N.Marković, P.Ross, J.Phys.Chem., 99 (1995) 8945.
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[5] V.Clement, E.Herrero, J.M.Feliu, Electrochim.Acta 44 (1998) 1403.
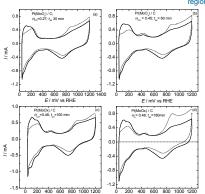[6] W.Sugimoto, T.Saida, Y.Takasu, Electrochem.Commun.,

Fig.2. Cyclic voltammograms of MoOx-Pt/C in 0.5 mol dm⁻³ HClO₄ free CO 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 vs RHE.
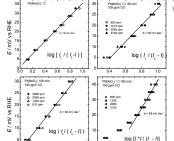

Fig.4. CO-stripping cyclic voltammograms at MoOx-Pt/C electrode measured in N₂ saturated 0.5 mol dm⁻³ HClO₄ solution at v = 0.1 V s⁻¹. The full line shows CV at the CO-free surface.

Fig.5. Changes in the linear- sweep voltammograms (0.01 V s⁻¹) for the HOR at MoOx-Pt/C with various Θ_{CO} at 2070 rpm.. The HOR voltammograms were measured in H₂ (100 ppm CO) saturated 0.5 mol dm⁻³ HClO₄ solution at 25⁰C before recording CO-stripping voltammograms. Inset:Time course for CO adsorption at E= 50 mV vs RHE;

Fig.6. Plots of E − log [I_L / (I_L − I)] and E − log [$I_L \cdot I$ / (I_L − I)]. Data taken from the corresponding linear-sweep voltammograms for the HOR at MoOₓ-Pt/C electrode with various Θ_{CO} in 0.5 mol dm⁻³ HClO₄ solution saturated with H₂ containing 100 ppm CO.
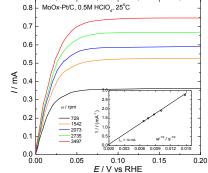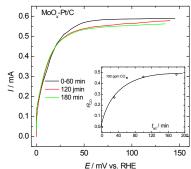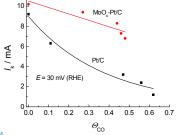

Fig.7 The dependence of kinetic current, I_k, for the HOR on Θ_{CO} on MoOₓ-Pt/C and Pt/C catalysts in 0.5 M HClO₄ solution at 25⁰C.