

KINETICS OF THE HYDROGEN OXIDATION ON Pt MODIFIED MoO_x 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 (RuO_x, H₂) [6].

In the present work, the electrocatalytic of home made highly dispersed nano-sized MoO_x-Pt/C catalysts prepared by the polyole method combined with 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 V s⁻¹ and compared it with the sweep on the clean electrode, by measuring the decrease in the hydrogen desorption charge, ΔQ_H.

MoO_x(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 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 MoO_x 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 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 MoO_x post-deposition does not lead to a significant growth of the Pt nanoparticles. To gain further insight on the distribution of the MoO_x 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 MoO_x-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 MoO_x 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 MoO_x-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 14mΩ 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/mg_{cat}, 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 voltammetric 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 to 0.14 V. It is clear that MoO_x-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*_k / (*i*_k - *i*)] or *E* vs log [*i*_k / (*i*_k - *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 the Tafel-Volmer reaction route in that 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 MoO_x-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 MoO_x(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 MoO_x species at low overpotentials by a redox-mediated mechanism.

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

θ _{CO}	<i>b</i> / mV dec ⁻¹	<i>i</i> _k / mA (30 mV)	Mechanism
0.0	32	10.2	Tafel-Volmer
0.27	33	9.8	
0.44	36	8.7	
0.46	36	7.3	
0.48	58	5.8	

References:

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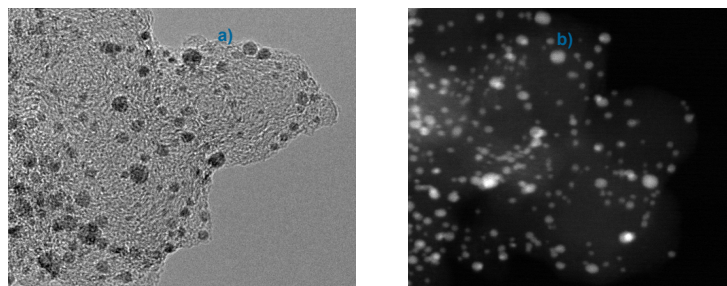


Fig.1 a) HRTEM micrographs of Mo_x-Pt nanoparticles on carbon support. b) high angle annular dark-field (HAADF) image

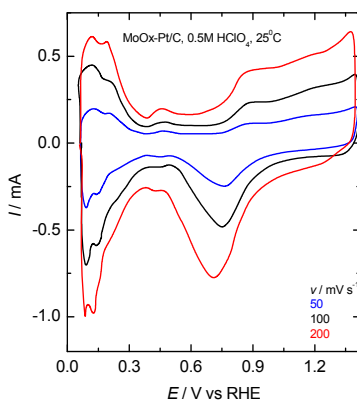


Fig.2. Cyclic voltammograms of MoO_x-Pt/C in 0.5 mol dm⁻³ HClO₄ free CO solution.

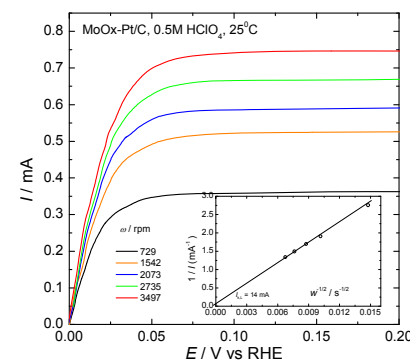


Fig.3. Linear-sweep voltammograms for the HOR at MoO_x-Pt/C RDE in 0.5 mol dm⁻³ HClO₄ solution saturated with pure H₂. Inset: Levich-Koutecky plot in the diffusion-limited potential region at 0.14 vs RHE.

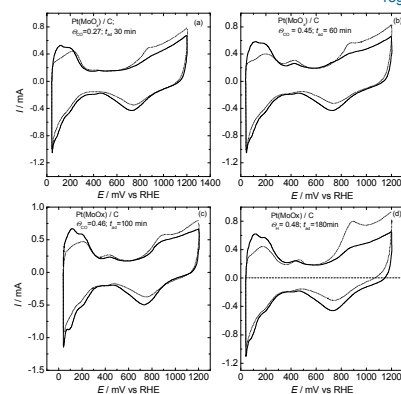


Fig.4. CO-stripping cyclic voltammograms at MoO_x-Pt/C electrode measured in N₂ saturated 0.5 mol dm⁻³ HClO₄ solution at *v* = 0.1 V s⁻¹. The full line shows CV at the CO-free surface.

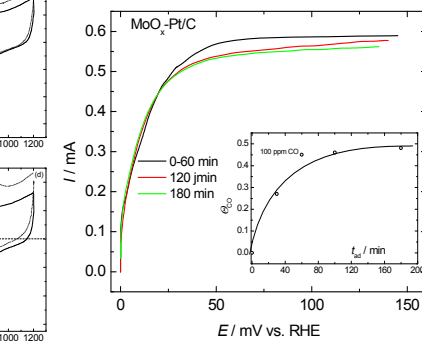


Fig.5. Changes in the linear-sweep voltammograms (0.01 V s⁻¹) for the HOR at MoO_x-Pt/C with various θ_{CO} at 2070 rpm. The HOR voltammograms were measured in H₂ (100 ppm CO) saturated 0.5 mol dm⁻³ HClO₄ solution at 25°C before recording CO-stripping voltammograms. Inset: Time course for CO adsorption at *E* = 50 mV vs RHE;

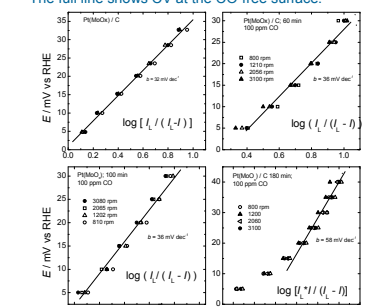


Fig.6. Plots of *E* = log [*i*_k / (*i*_k - *i*)] and *E* = log [*i*_k / (*i*_k - *i*)] for the HOR at MoO_x-Pt/C electrode with various θ_{CO} in 0.5 mol dm⁻³ HClO₄ solution saturated with H₂ containing 100 ppm CO.

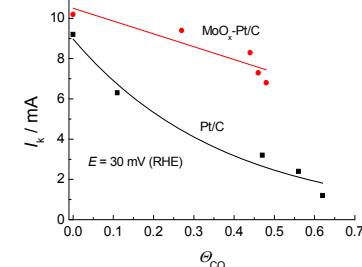


Fig.7. The dependence of kinetic current, *i*_k, for the HOR on θ_{CO} on MoO_x-Pt/C and Pt/C catalysts in 0.5 M HClO₄ solution at 25°C.