

The Oxidation of Methanal on Platinum Coatings on Titanium in Acidic Media

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Abstract: A platinum coating was thermally obtained on an adequately prepared titanium substrate. As determined by x-ray investigations, the coating contained 10-60 nm microcrystals of pure metal platinum. The electrochemical oxidation of methanal on the platinum coating took place following the dual path mechanism. Methanal was directly oxidized to CO₂ and H₂O. Parallel reactions of formation of strongly adsorbed –CO_{ad} species blocking the platinum surface thus preventing direct methanal oxidation were performed. The mechanism of the –CO_{ad} poisoning species formation in the hydrogen region was different from the one in the double-layer region.

Key words: methanal, electrochemical oxidation, electrode, cyclic voltammograms, polarization curves

Introduction

Most of the energy used today in the world is derived from fossil fuels. Fossil fuel reserves are limited. Energy utilization efficiency during fossil fuel exploitation is low. Furthermore, the process of obtaining energy from fossil fuels considerably pollutes the environment.

Renewable sources of energy are considered to be the future of energetics. Biomass is one of major renewable energy sources to be amply used in the future due to its high potential, cost-effectiveness and environmental protection. Presumably, in

2050, 38 % of energetic fuels and about 17 % of electrical energy will be obtained from biomass. The potential of biomass as an energy source depends on the type of biomass and development of efficient technologies for biomass energy conversion. Technological procedures used today for the obtainment of energy from biomass are relatively undeveloped. Chemical biomass energy is firstly, as in fossil fuels, converted into thermal energy which is, then, transferred into electrical energy with relatively low utilization efficiency (maximumly 36 %).

Numerous analyses indicate that the future of energetics lies in direct conversion of chemical energy into electrical energy. Fuel cells directly turn chemical fuel energy into electrical energy. The advantages of the direct conversion are the following: high utilization efficiency, possibility of producing electrical energy where and when desired, without causing environmental pollution. Methanol, methanal and methanic acid are readily obtained by simple technological procedures (fermentation) from biomass. Methanol, methanal and methanic acid are fuels of high energetic capacity for fuel cells, suitable for transport and storage. The main problem in the creation of fuel cells is the development of a catalyst with good corrosion resistance and high catalytic activity for the electrochemical oxidation of the fuels concerned [1-7]. All devices installed to date used pure platinum catalysts. The cost of platinum is extremely high and, moreover, the high initial current of oxidation of small organic molecules rapidly decreases because strongly adsorbed intermediates are formed on the surface blocking surface Pt atoms and thus preventing further fuel oxidation [1-12].

The aim of this paper was to obtain a thin coating of platinum microcrystals on an adequately prepared titanium substrate and to examine its catalytic activity for the electrochemical oxidation of methanal in an acidic solution.

Experimental

Catalytically active coatings were thermally obtained on the titanium substrate [13]. The smooth titanium substrate surface was first roughened in order to increase the actual surface area and provide good coating adhesion. A solution of H_2PtCl_6 in 2-propanol was spread over the titanium substrate prepared. After the evaporation of the solvent, the electrodes were heated in an air atmosphere at $t = 450^\circ\text{C}$. The procedure was repeated until the desired thickness of the coating was achieved. After the final layer had been placed, the electrodes were baked at 500°C for 60 min. Adherent coatings with good mechanical properties were obtained. The coatings thus obtained were composed of metal platinum microcrystals.

The electrochemical measurements were performed in a standard electrochemical cell with a Luggin capillary and a special part for a reference electrode. A standard circuit containing a programmer with a potentiostat (RDE 3 POTENTIOSTAT Pine Instrument Co., Grove City, Pennsylvania), an X-Y recorder (Hewlett Packard 7035B) and a digital voltmeter (Pro's Kit 039303C) was used. The potential values were measured with respect to a saturated calomel electrode, and the counter electrode was a platinum wire placed in the main part of the cell, together with the working electrode.

The catalytic activity of the coatings for the reactions of the oxidation of simple organic molecules was established by recording of polarization and potentiodynamic curves.

Results and Discussion

Figure 1 presents cyclic voltammograms of CH_2O oxidation on a thermally obtained coating of Pt/Ti in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{ CH}_2\text{O}$. The curve presented by a solid line shows that at the potential shift in the anodic direction, two current peaks were appeared in the potential range of 0.7 to 1.4 V. As the potential shifted in the cathodic direction, following the oxide reduction, there occurred CH_2O oxidation peak with a shoulder at 0.7 V. Both curves are presented in Figure 1 showing that with the potential shift in the anodic direction CH_2O oxidation in the potential range of 0.45 to 0.76 V was obtained relatively slowly.

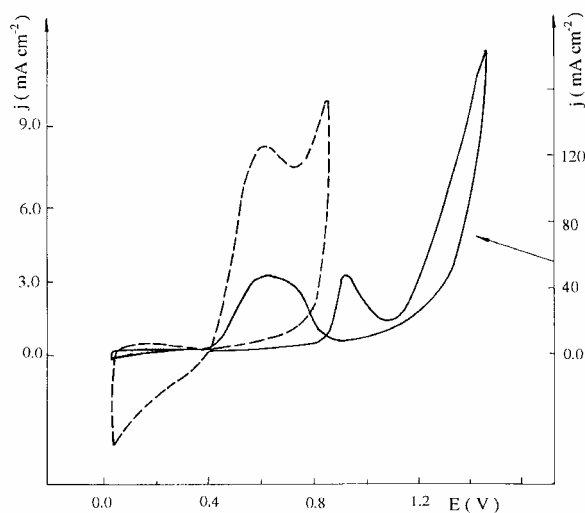


Figure 1. Cyclic voltammograms of the Pt/Ti electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{ CH}_2\text{O}$ with different anodic potential limits. The potential sweep rate 100 mVs^{-1} ; $t=25^\circ\text{C}$.

A rapid CH_2O oxidation occurred only at potentials more positive than 0.7 V. There are no hydrogen desorption peaks in the curves, indicating that adsorbed species produced by the interaction of CH_2O and surface Pt atoms could also be found on the thermally created platinum. Characteristics of the adsorbed species were identified based upon cyclic voltammograms recorded after the "washing procedure" (Fig. 2). The curves were recorded after the electrodes had been kept for twenty minutes at a 0.26 V in the solution $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{ CH}_2\text{O}$ and the solution replaced by a basic electrolyte ($0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$). The curves obtained were identical to the ones recorded after the electrodes had been kept in the CH_3OH solution. The existence of the

current peak of the oxidation of the species created by CH_2O adsorption identical to the current peak of the oxidation of strongly bound intermediates generated by CH_3OH oxidation indicated that the CH_3OH and CH_2O oxidations resulted in the formation of identical adsorbed species ($-\text{CO}_{\text{ad}}$) [5, 7-12].

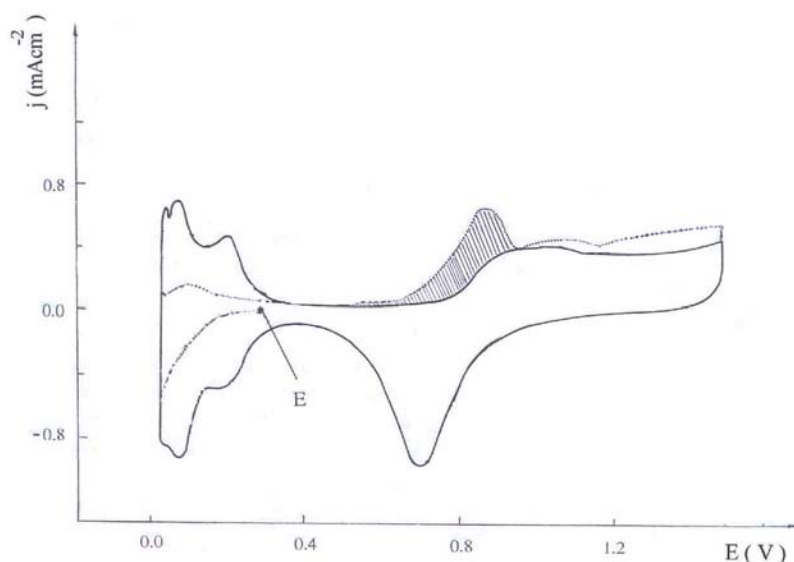


Fig. 2. Cyclic voltammograms of the Pt/Ti electrode in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 0.05 \text{ mol dm}^{-3} \text{CH}_2\text{O}$: (—) the basic curve (in the absence of CH_2O); (---) the curve recorded after the Pt/Ti electrode had been kept for 20 minutes at a 0.26 V and the solution replaced by the basic electrolyte. Sweep rate 166 mVs^{-1} ; $t = 25^\circ\text{C}$.

The potential range of the first anodic peak (Fig. 1) was identical to that of the strongly adsorbed species ($-\text{CO}_{\text{ad}}$) oxidation after the “washing procedure” [12]. This indicated that the first anodic peak current had occurred by the oxidation of the strongly adsorbed species and of the CH_2O molecules on the free surface site. By comparison of the dashed curve presented in Figure 1 and the curve of the strongly adsorbed species oxidation obtained after the “washing procedure” (Fig. 2) it could be concluded that the CH_2O oxidation on Pt/Ti was also performed at potentials more negative than the $-\text{CO}_{\text{ad}}$ oxidation potential. The polarization curve of the CH_2O oxidation reaction on Pt/Ti from $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{CH}_2\text{O}$ confirmed this conclusion (Fig. 3). This indicated that CH_2O on the thermally created Pt coating was oxidized following the dual path mechanism. The steady-state CH_2O oxidation rate on Pt/Ti in the potential range of $0.44 < E < 0.55 \text{ V}$ was relatively low, because the major part of the electrode surface was blocked by the $-\text{CO}_{\text{ad}}$ poisoning species.

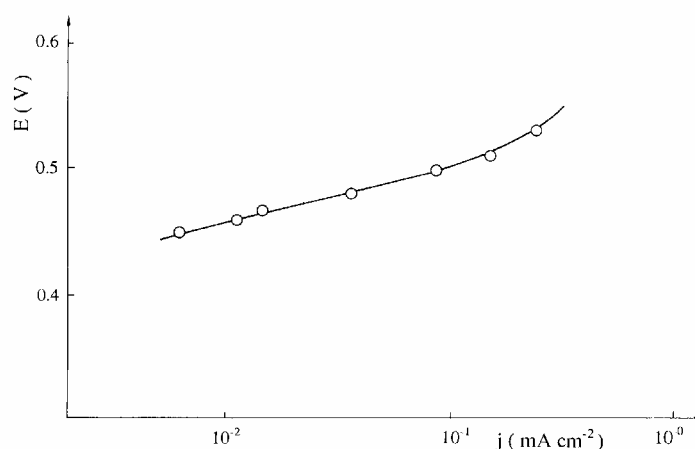


Fig. 3. A steady-state polarization curve for the of CH_2O oxidation on Pt/Ti ($0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{CH}_2\text{O}$; $t = 25^\circ\text{C}$). The current values measured after the electrodes had been kept for 20 minutes at the potential specified.

The surface blocking by the $-\text{CO}_{\text{ad}}$ poisoning species at potentials more negative than 0.7 V was established by the following experiment, as well. The potential of the Pt/Ti electrode kept in the solution $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{CH}_2\text{O}$ was cycled between 0.0 V and 1.0 V. Following the second cycle, at the potential sweep in the cathodic direction, the potential was kept for 10 s at $E = 0.84 \text{ V}$. All species were completely oxidized on the electrode surface during the time concerned. After the 10 s had elapsed, the potential was temporarily shifted to another value desired and the change of current over time at a given potential was recorded (Fig. 4).

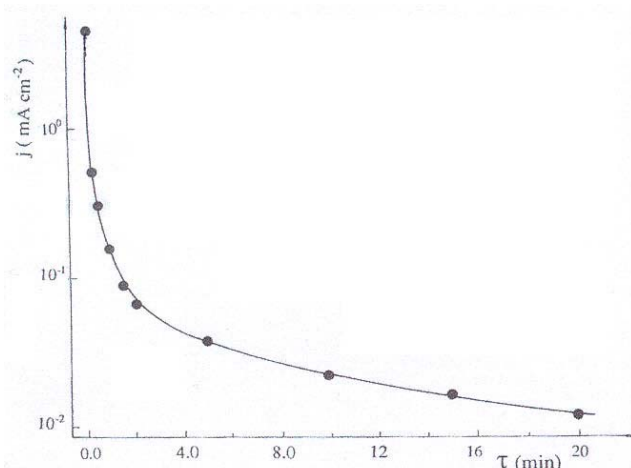


Fig. 4. Temporal dependence of the CH_2O oxidation current density on the Pt/Ti electrode in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{CH}_2\text{O}$ at $E = 0.46 \text{ V}$ and $t = 25^\circ\text{C}$.

For the first three minutes, the current decreased rapidly and then gradually asymptotically tending to a steady-state value. The current decrease was caused by a reduction of the direct CH_2O oxidation rate due to the blocking of the Pt surface by the emerged $-\text{CO}_{\text{ad}}$ poisoning species. The steady-state current values presented in the polarization curve (Fig. 3) are those recorded after 20 minutes. The current decline rate depended on the potential. The current decline rate in the hydrogen region was incomparably higher than in the double-layer one, indicating that the $-\text{CO}_{\text{ad}}$ poisoning species formation rate depended on the potential. In the hydrogen region, the poisoning species were created considerably more rapidly than in the double-layer region. Cyclic voltammograms with different cathodic limit potentials confirmed this conclusion (Fig. 5).

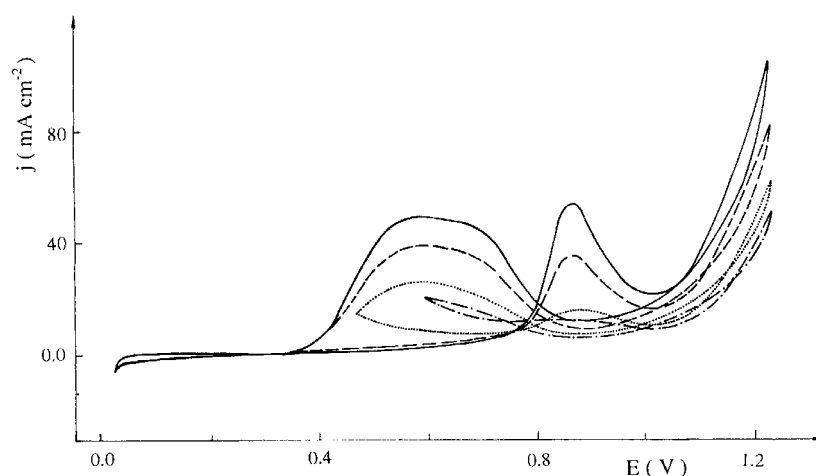


Fig. 5. Cyclic voltammograms for the Pt/Ti electrode in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{CH}_2\text{O}$ with progressive decrease of cathodic potential limit. Sweep rate 100 mVs^{-1} ; $t = 25^\circ\text{C}$.

The progressively more positive cathodic limit potential brought about an increase in the CH_2O oxidation current at the potential sweep in the anodic direction. The current increase was most pronounced with the cathodic limit potential in the double-layer region ($E > 0.35 \text{ V}$). There are no significant differences between the cyclic voltammograms with cathodic limit potentials in the hydrogen region ($E < 0.35 \text{ V}$) and the first voltammogram recorded after the potential had been kept for 60 s at the potential of 0.025 V (Fig. 6).

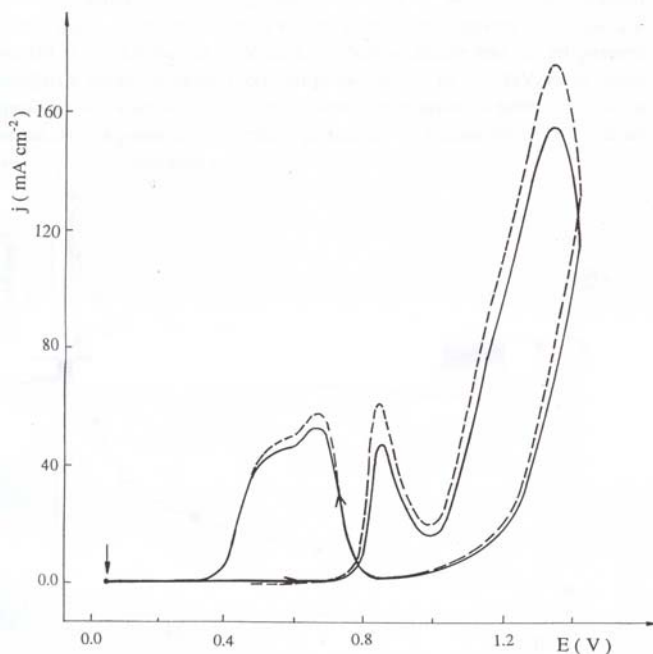
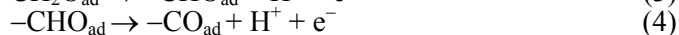
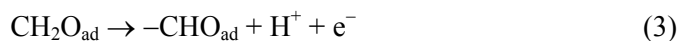


Fig. 6. Cyclic voltammograms for the Pt/Ti electrode in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4 + 0.25 \text{ mol dm}^{-3} \text{ CH}_2\text{O}$: (—) the basic curve; (-----) the curve recorded after the electrode had been kept for 60 s at the cathodic potential limit of 0.025 V. The potential sweep rate is 50 mVs^{-1} ; $t = 25^\circ\text{C}$.

Hydrated and non-hydrated methanal forms were probably simultaneously adsorbed on platinum. The hydrated form predominated in the solution, and so its adsorption was far more rapid than the adsorption of the non-hydrated form:



Following the adsorption, dehydrogenation took place. Dehydrogenation of the aldehyde form directly resulted in the formation of $-\text{CO}_{\text{ad}}$ poisoning species [5].:



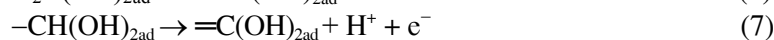
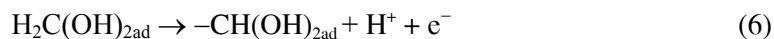
The surface concentration of the $-\text{CHO}_{\text{ad}}$ species was negligible compared to the $-\text{CO}_{\text{ad}}$ concentration since reaction (4) was more rapid than reaction (3) [3]. Some authors showed that by way of CH_2O oxidation on platinum the species $\equiv\text{COH}_{\text{ad}}$ and $-\text{COOH}_{\text{ad}}$ were also occurred. $\equiv\text{COH}_{\text{ad}}$ species were presumably formed

by the reaction of $-\text{CO}_{\text{ad}}$ with adsorbed hydrogen only at low degrees of the electrode coverage with the strongly bound intermediates [3]:

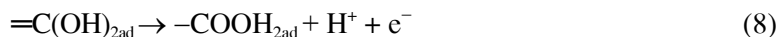


The $\equiv\text{COH}_{\text{ad}}$ species required three adjacent free Pt atoms for adsorption. At high degrees of Pt coverage, due to a deficiency of these adsorption sites (three adjacent free atoms), these intermediates could not be created. If the $-\text{CO}_{\text{ad}}$ species were formed only by reactions (3) and (4), the poison would block the platinum surface in the double-layer region more rapidly than in the hydrogen region. The more rapid species creation in the hydrogen region compared to that in the double-layer region indicated an active involvement of H_{ad} in their formation.

The adsorbed gem-diol species on the platinum surface formed $\equiv\text{C}(\text{OH})_{2\text{ad}}$ species by dehydrogenation:

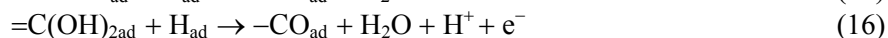
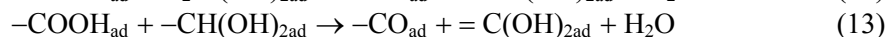
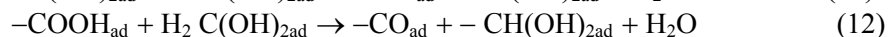
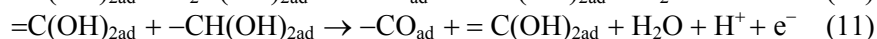
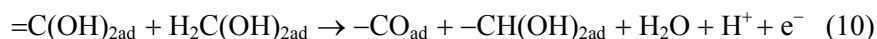


Further dehydrogenation of the $\equiv\text{C}(\text{OH})_{2\text{ad}}$ species produced CO_2 , the final product of methanal oxidation:



The reactions (6-9) refer to direct methanal oxidation path.

Parallel to the reactions (8) and (9) the reactions by which strongly bound species of $-\text{CO}_{\text{ad}}$ were formed were being performed:



The reactions (10-14) were performed in both hydrogen and double-layer regions, whereas the reactions (15) and (16) took place only in hydrogen region. The reactions (15) and (16) were much more rapid than the reactions (10-14) so that by these reactions in the hydrogen region a majority of $-\text{CO}_{\text{ad}}$ species was created. In the double-layer region, $-\text{CO}_{\text{ad}}$ species were formed much slower by the reactions (4, 10-14).

Based upon the hydrogen desorption peak decrease in the cyclic voltammogram obtained "after the washing procedure" (Fig. 2), it was established

that in the $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol dm}^{-3} \text{ CH}_2\text{O}$ solution, about 85 % of Pt surface was covered by $-\text{CO}_{\text{ad}}$ species. As a result of stern effects, the decrease of about 6.5 times in the number of free surface Pt atoms for direct methanal oxidation caused a 500 times decline in the methanal oxidation current. The direct electrochemical methanal oxidation (6-9) required clusters of at least two adjacent free Pt atoms. The cluster number rapidly decreased with an increase in the degree of platinum surface coverage with the poisoning species.

Conclusion

A catalytic activity of thermally obtained platinum coatings was examined for the electrochemical oxidation of methanal. It was determined that the electrochemical methanal oxidation on the platinum coating was performed following the dual path mechanism. Methanal was directly oxidized to CO_2 and H_2O , and a parallel reaction of formation of strongly adsorbed $-\text{CO}_{\text{ad}}$ species took place. The mechanism of $-\text{CO}_{\text{ad}}$ poisoning species creation in hydrogen region differed from the one in the double-layer region.

References

- [1] M. W. Breiter, *Electrochemical Processes in Fuel Cells*, Springer-Verlag Berlin-Heidelberg-New York, 1969.
- [2] P. Sidheswaran, H. Lal, *J. Electroanal. Chem.*, 1982, 34, 173.
- [3] V. E. Kazarinov, G. Ya. Tisyachnaya, *Elektrokhim.*, 1972, 8, 592.
- [4] V.S. Bagotzky, Yu.B. Vasiliev, O.A. Khazova, *J. Electroanal. Chem.*, 1977, 81, 229.
- [5] M. D. Spasojević, R. R. Adžić, A. P. Despić, *J. Electroanal. Chem.*, 1980, 109, 261.
- [6] R. R. Adžić, M. D. Spasojević, A. P. Despić, *J. Electroanal. Chem.*, 1978, 92, 31.
- [7] S. Wilhelm, T. Iwasita, W. Vielstich, *J. Electroanal. Chem.*, 1987, 238, 383.
- [8] S. Pons, *J. Electroanal. Chem.*, 1983, 150, 495.
- [9] P. A. Christensen, A. Hamnet, S. A. Weeks, *J. Electroanal. Chem.*, 1988, 250, 127.
- [10] K. Kunitatsu, *J. Phys. Chem.*, 1990, 94, 1025.
- [11] J. M. Leger, C. Lamy, *Phys. Chem.*, 1990, 94, 1021.
- [12] L. Ribić-Zelenović, A. Tripković, M. Spasojević, *J. Electroanal. Chem.*, in press.
- [13] M. Spasojević, N. Krstajić, M. Jakšić, *J. Res. Inst. Cat. Hokkaido Univ.*, 1983, 31, 77.

OKSIDACIJA METANALA NA PLATINSKIM PREVLAKAMA NA TITANU U KISELOJ SREDINI

- originalni naučni rad -

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Rezime

Na podesno pripremljenoj titanskoj osnovi termičkim postupkom formirana je prevlaka od platine. Rendgenografskim ispitivanjima ustanovljeno je da se prevlaka sastoji od mikrokristala čiste metalne platine veličine od 10 nm do 60 nm. Elektrohemijska oksidacija metanala na prevlaci od platine odvija se po "dual path mechanism"-u. Metanal se direktno oksiduje do CO_2 i H_2O . Paralelno sa ovom reakcijom odvijaju se i reakcije formiranja čvrsto adsorbovanih čestica $-\text{CO}_{\text{ad}}$ koje blokiraju površinu platine i time onemogućavaju direktnu oksidaciju metanala. Mehanizam formiranja čestica otrova $-\text{CO}_{\text{ad}}$ je različit u vodoničnoj i dvoslojnoj oblasti.