

Inhibiting effect of acetonitrile on oxygen reduction on polycrystalline Pt electrode in sodium chloride solution

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Abstract

The oxygen reduction reaction (ORR) was studied on a polycrystalline Pt electrode in 0.1 M NaCl electrolyte containing various amounts of acetonitrile (AcN). The state of the electrode surface was characterized by cyclic voltammetry in oxygen free electrolytes, while ORR studies were performed on a polycrystalline Pt rotating disc electrode by linear sweep voltammetry in oxygen saturated electrolytes. The acetonitrile is chemisorbed on Pt over a wide potential range, inhibiting both hydrogen adsorption and oxide formation. The extent of AcN chemisorption depends on its concentration in the solution. The initial potential of oxygen reduction is shifted negatively, while the ORR current is increasingly reduced with the increase of AcN concentration. Complete inhibition of ORR in the potential range of AcN and Cl⁻ anion coadsorption is achieved for a 0.1 M NaCl + 1 M AcN solution.

Keywords: oxygen reduction, platinum, acetonitrile, chlorides, rotating disc electrode.

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Acetonitrile (AcN) plays a significant role either as an organic aprotic solvent for the studies of the electrical double layer of chosen electrodes [1] or as a solvent of various organics for the studies of their oxidation [2] or reduction behavior [3]. Platinum electrodes modified by chemisorbed acetonitrile can be used as sensors for the detection of some nitroaromatic compounds in natural media [4]. In the latter case, the oxygen reduction reaction (ORR) is often superimposed with the electro-reduction processes of interest, since natural media contains dissolved oxygen. Therefore, we have found that it is important to study ORR alone on polycrystalline platinum in neutral chloride electrolytes containing acetonitrile.

Following earlier reported studies of AcN chemisorption on polycrystalline and single crystal platinum in various solutions [5–7], the adsorption behavior and stability of acetonitrile was widely studied using different electrochemical and spectroscopic techniques [8–12]. In the most recent systematic study in acidic sulfate solutions [13], it was shown that there was no electrochemical conversion of AcN in the potential range of its adsorption 0.03–0.9 V (vs. SHE) on well-defined Pt single crystals, while at higher potentials the oxidation of AcN on Pt(poly) proceeded simultaneously with the product desorption.

Rotating disc electrode (RDE) studies of oxygen reduction on Pt(poly) in aprotic acetonitrile solutions [14,15] have shown that the first step is a reversible one and occurs with the exchange of one electron giving a superoxide anion as a product. The superoxide anion is stable in the absence of proton sources, but with the addition of water or proton to the aprotic AcN solution, the ORR occurs with a further charge transfer resembling the pathways observed for acid or alkaline solutions [16]. The same was found in our previous report on oxygen reduction on Pt(poly) in perchloric acid in the presence of acetonitrile [17].

In this work, ORR will be studied on Pt(poly) in neutral chloride solutions containing acetonitrile. Chlorides adsorb strongly on the Pt electrode surface, and the effect of their presence together with coadsorbed AcN molecules on the kinetics of ORR will be studied in detail. Neutral chloride solution containing a constant concentration of chlorides will be used, while acetonitrile will be added in a wide range of concentrations up to saturation, when the ORR becomes completely inhibited in the potential range of AcN and anion coadsorption.

EXPERIMENTAL

A polycrystalline Pt rotating disc electrode, 5 mm in diameter, mounted on a modulated speed rotator (Pine Instruments Co.) was used as a working electrode. The state of the electrode surface was checked by cyclic voltammetry (CV), while oxygen reduction measurements were performed by a linear sweep voltammetry

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(LSV). The carrying electrolyte was 0.1 M NaCl, while the concentration of acetonitrile in solutions varied from 0.04 mM to 1 M. All LSV curves were recorded while scanning the potential in the negative direction. Before each experiment, the preparation of the Pt electrode surface consisted of electrochemical polishing and of the potential cycling in deaerated solutions in the potential range within hydrogen and oxygen evolution reactions until clean and stable CV curves were obtained.

The solutions were prepared from NaCl salt (Merck), acetonitrile (HPLC grade) and Milli-pure water. CV measurements were performed in solutions deaerated by N₂ (99.999%, Messer, Serbia), while LSV measurements were performed in O₂ (99.999%, Messer, Serbia) saturated solutions. The counter electrode was a Pt wire and the reference electrode was Ag/AgCl, 3M KCl. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Cyclic voltammetry characterization of Pt(poly) surface in 0.1 M NaCl containing acetonitrile

Cyclic voltammograms for a Pt(poly) electrode in oxygen free pure 0.1 M NaCl solution and in ones with the addition of 4 mM–1 M of acetonitrile are presented in Figure 1.

On the negative going sweep, the hydrogen evolution reaction begins at -0.62 V and proceeds further at more negative potentials, while on the reverse sweep hydrogen oxidation takes place. The effect of the presence of acetonitrile on these processes will not be further discussed since they are not of particular in-

terest for ORR. Two reversible peaks, which refer to the adsorbed hydrogen, are hindered in neutral chloride electrolyte due to the lack of H⁺ as well as due to the chloride adsorption [18]. Instead, two smaller peaks appear at -0.55 V and -0.45 V on the positive going scan. The peaks appear at slightly lower potentials on the reverse scan. Chloride adsorption extends further over a wide potential range, which is visible as the enlarged double layer. At higher potentials it competes with OH adsorption [18] causing a significant shift of the potential of PtOH formation to the more positive values. The behavior of Pt electrode in 0.1 M NaCl solutions containing acetonitrile can be seen in the changes of CV profiles. With the addition of acetonitrile both hydrogen and chloride adsorption peaks are being increasingly suppressed, while the double layer narrows with the increase of AcN concentration indicating that AcN adsorption occurs in the whole potential region investigated and competes with the adsorption of hydrogen and chlorides. The effect of chlorides and acetonitrile coadsorption on the initial potential and kinetics of oxygen reduction reaction will be further examined in oxygen saturated 0.1 M NaCl solution with the addition of increasing amounts of AcN using the RDE technique.

Rotating disc electrode measurements of ORR on Pt(poly) in 0.1 M NaCl containing acetonitrile

Linear sweep voltammetry curves for ORR on Pt(poly) in 0.1 M NaCl solution without and with the addition of the increasing amount of AcN are presented in Figure 2 for the same rotation rate of 1600 rpm. The initial potential for ORR in pure 0.1 M NaCl is 170 ± 10 mV and falls within the double layer potential region. Since the

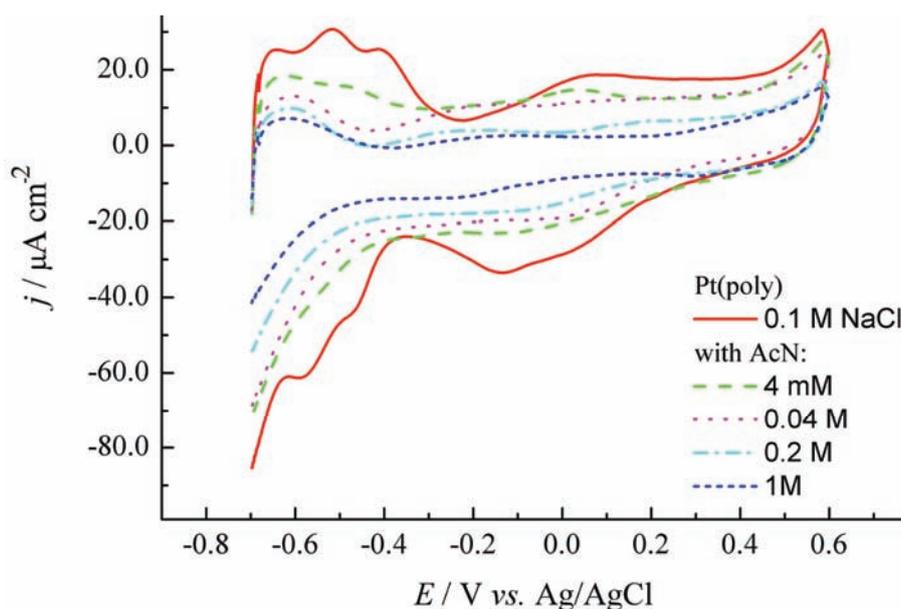


Figure 1. CVs for a Pt(poly) electrode recorded in oxygen free solution of 0.1 M NaCl without and with the addition of 4 mM–1 M of acetonitrile. Potential scan rate was 50 mV/s.

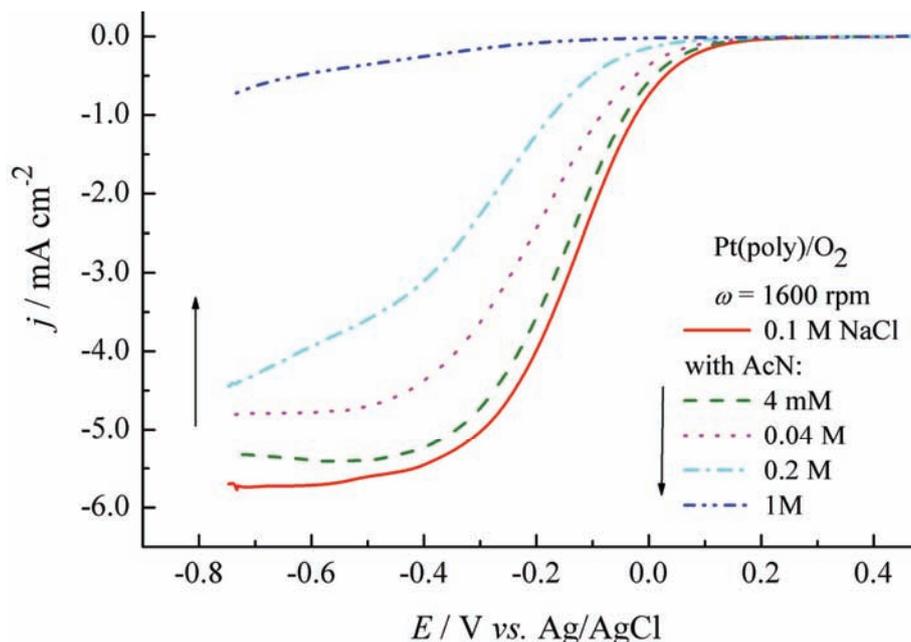


Figure 2. LVs for ORR on a rotating Pt(poly) electrode in oxygen saturated 0.1 M NaCl solution without and with the addition of 4 mM – 1 M of acetonitrile, obtained for the same rotation rate of 1600 rpm. Potential scan rate was 50 mV/s.

PtOH formation is shifted to potentials higher than 0.4 V due to the strong adsorption of chlorides, it is no more relevant for ORR. In the presence of acetonitrile in concentrations of 4 mM, 0.04, 0.2 and 1 M, the initial potential for oxygen reduction shifts to 150, 125, 100 and –100 mV, respectively.

LSV curves for ORR on Pt(poly) in 0.1 M NaCl without and with the addition of AcN in concentrations of 0.04 and 0.2 M, recorded for six rotation rates and corresponding kinetic analysis are presented in Figure 3.

According to the Koutecky–Levich theory, the measured current, j , is given by:

$$1/j = 1/j_k + 1/j_l \quad (1)$$

where j_k is the kinetic current and j_l is the diffusion limiting current, or:

$$1/j = 1/j_k + 1/B\omega^{1/2} \quad (2)$$

where the measured current density is expressed as a function of the rotation rate and B is a constant.

Koutecky–Levich plots are obtained when the inverse current density ($1/j$) is plotted as a function of the inverse of the square root of the rotation rate ($\omega^{-1/2}$). The linearity and parallelism of these plots for ORR in pure 0.1 M NaCl solution and in one containing AcN in the lowest concentration of 4 mM (not presented) indicate first-order kinetics with respect to molecular oxygen. On the other hand, for higher AcN concentrations both linearity and parallelism of these plots are being gradually lost with the increase of AcN concentration. This apparent change in reaction kinetics with potential and with the increase of AcN concentration

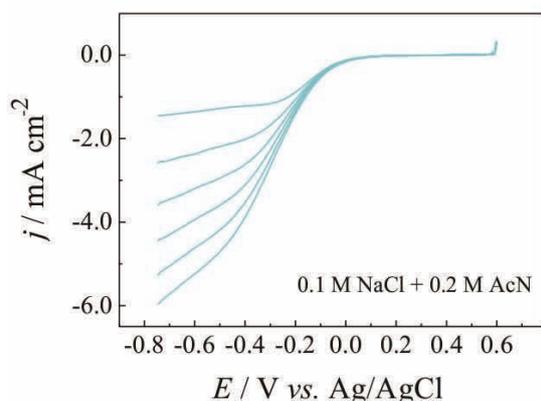
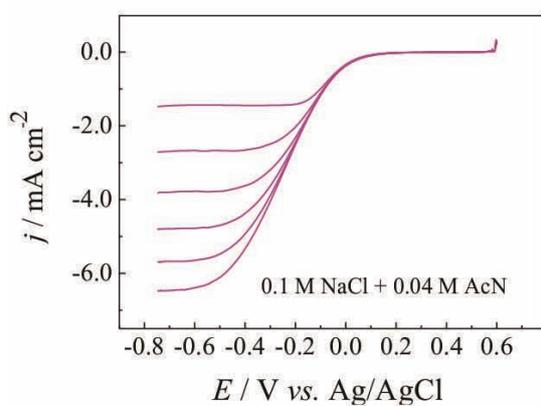
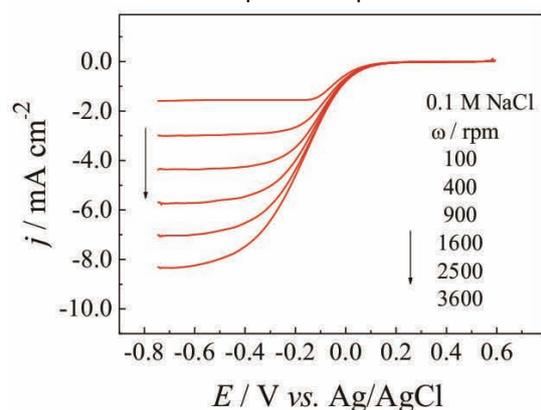
occurs most likely due to the increasing occupation of Pt sites by adsorbed AcN, which consequently leads to the decrease of the amount of adsorbed oxygen as a reactant.

From Eq. (1), the kinetic current can be expressed as:

$$j_k = j/(1-j/j_l) \quad (3)$$

A Tafel plot, defined as a function of the gradient of the potential versus kinetic current gradient ($\Delta E/\Delta \log j_k$), is obtained by plotting E vs. $\log j_k$, where j_k is taken as the average value for six rotation rates. In Figure 4, the slope of the Tafel plots of –120 mV per decade for ORR on Pt(poly) at lower potentials obtained in pure 0.1 M NaCl solution and in one containing a lower amount of AcN (0.04 M) indicates that the rate determining step is the exchange of the first electron. The change of the Tafel slope to higher values indicates the change in reaction kinetics at higher potentials, which occurs in neutral solutions due to the local pH changes [19]. However, different behavior is observed when one compares the change in Tafel slope in pure 0.1 M NaCl and in ones containing acetonitrile, as illustrated in Figure 4 for AcN concentration of 0.04 M. Since the beginning of ORR is shifted to the more negative potentials due to the acetonitrile adsorption, the increase of the local pH due to the production of OH^- in the course of ORR [19] is also shifted to the more negative potentials. That is why the change in the Tafel slope occurs at more negative potentials than in the case of pure 0.1 M NaCl. On the other hand, the rate of ORR decreases due to AcN adsorption, and consequently

the increase of the Tafel slope is less pronounced. Po-



tential range where the Tafel slope has the value of

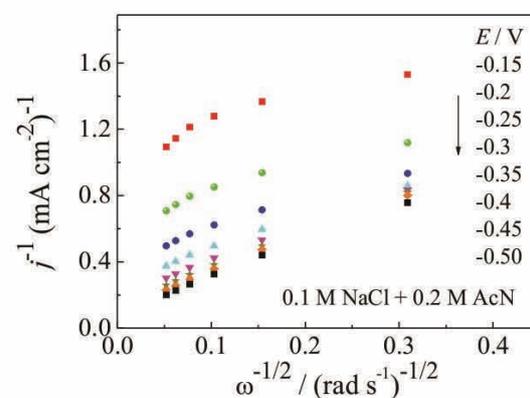
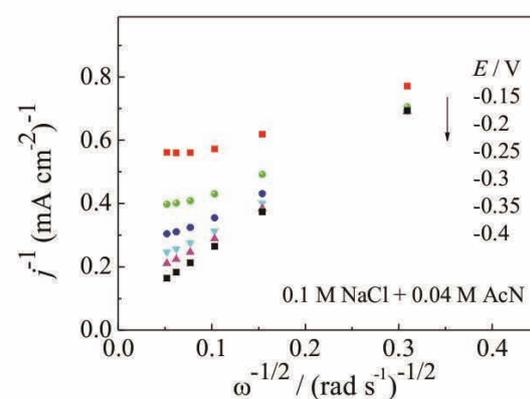
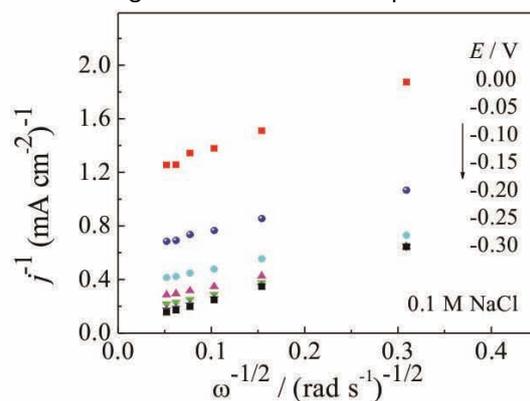


Figure 3. LVs for ORR on a rotating Pt electrode in oxygen saturated 0.1 M NaCl solution without and with the addition of acetonitrile (0.04 and 0.2 M), obtained for various rotation rates with the potential scan rate of 50 mV/s (left column); the corresponding Koutecky–Levich plots (right column).

–120 mV per decade narrows with the increase of acetonitrile concentration, and for AcN concentrations higher than 0.04 M it disappears.

It can be seen from LSV curves that starting from this AcN concentration, a proper diffusion control is not established. For AcN concentration as high as 1 M there is almost no dependence of ORR on the rotation rate (Figure 5). This means that under these particular conditions, the ORR is completely blocked in the whole potential region of AcN and Cl^- coadsorption. On the

other hand, this means that the saturation coverage of adsorbed acetonitrile molecules is achieved and that relatively small Cl^- which adsorb easily in between adsorbed larger AcN molecules occupy the remaining space on the Pt surface achieving thus saturation coverage for both acetonitrile molecules and chloride anions. In the absence of chloride or any other strongly adsorbing anions a higher concentration of AcN is needed for a complete inhibition of ORR. It is completely blocked in perchloric acid solution containing 3 M AcN,

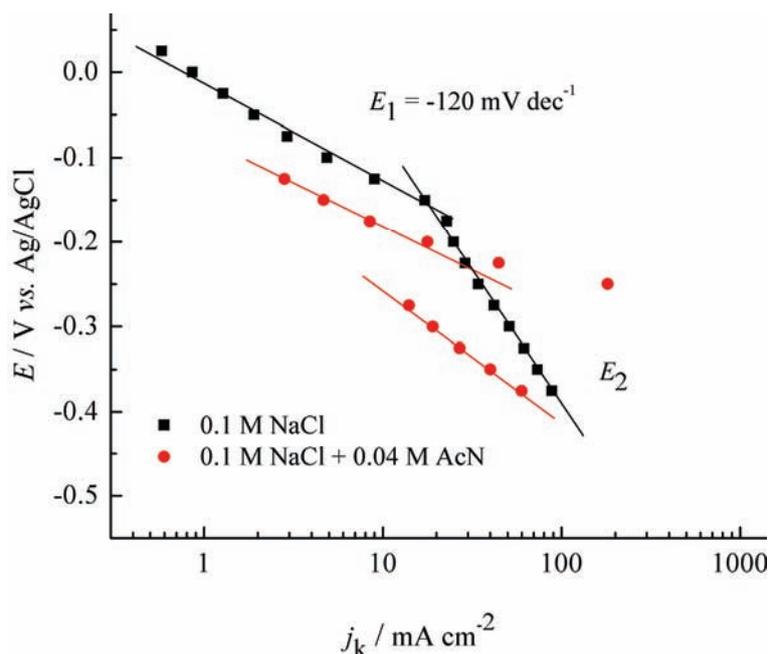


Figure 4. Tafel plots for ORR on Pt(poly) in 0.1 M NaCl and 0.1 M NaCl + 0.04 M AcN solutions. Plots are obtained from the data from Figure 3, taking the average value of j_k for six rotation rates.

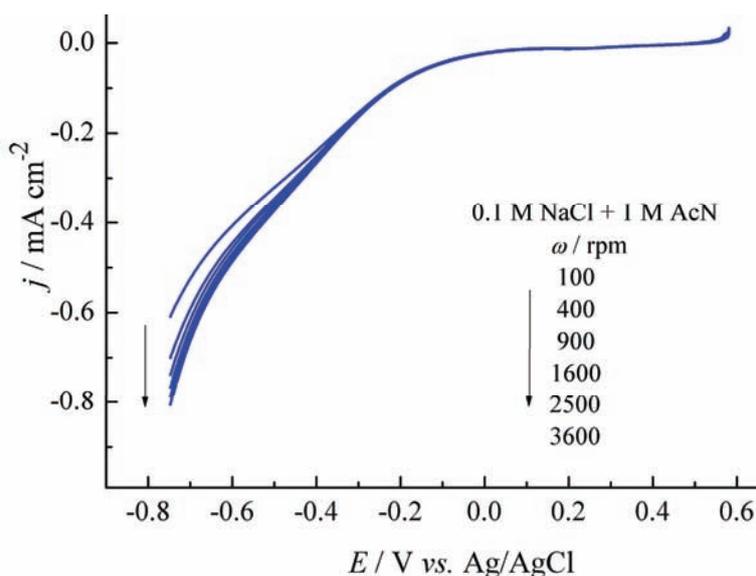


Figure 5. LVs for ORR on a rotating Pt electrode in oxygen saturated 0.1 M NaCl solution with the addition 1.0 M of acetonitrile, obtained for various rotation rates with the potential scan rate of 50 mV/s.

as shown in our previous report [17]. In the negative going sweep, the negative potential limit where ORR current begins is indicative of the beginning of AcN desorption for this particular solution. This can be determined for any other solution, by increasing the AcN concentration up to the complete ORR inhibition.

CONCLUSIONS

Acetonitrile adsorbs on the Pt(poly) surface in a wide potential range and competes with the adsorption of

hydrogen and chloride anions. Both hydrogen and chloride adsorption peaks are increasingly suppressed, while the double layer narrows with the increase of AcN concentration.

The pronounced inhibiting effect of AcN on the kinetics of ORR in neutral chloride solutions is reflected in the occupation of Pt surface sites by coadsorbed chlorides and AcN molecules. The number of Pt surface sites available for the adsorption of oxygen and its subsequent reduction thus significantly decreases with the increase of AcN concentration. In 0.1 M NaCl so-

lution, ORR is totally inhibited when the concentration of acetonitrile reaches 1 M.

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IZVOD**INHIBIRAJUĆI EFEKAT ACETONITRILA NA REDUKCIJU KISEONIKA NA POLIKRISTALNOJ Pt ELEKTRODI U RASTVORU NATRIJUM-HLORIDA**

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(Naučni rad)

Reakcija redukcije kiseonika je proučavana na polikristalnoj Pt elektrodi u 0,1 M NaCl elektrolitu koji je sadržavao različite količine acetonitrila (AcN). Stanje elektrodne površine je karakterisano cikličnom voltametrijom u deaerisanim rastvorima, dok je redukcija kiseonika ispitivana tehnikom rotirajuće disk elektrode u rastvorima zasićenim kiseonikom. Acetonitril je hemisorbovan na Pt u širokoj oblasti potencijala inhibirajući adsorpciju vodonika kao i formiranje oksida. Obim hemisorpcije zavisi od koncentracije acetonitrila u rastvoru. Početni potencijal redukcije kiseonika se pomera ka negativnijim vrednostima, dok se struja redukcije kiseonika sve više smanjuje sa povećanjem koncentracije acetonitrila. Potpuna inhibicija reakcije redukcije kiseonika u oblasti potencijala adsorpcije AcN molekula i Cl⁻ je postignuta u 0,1 M NaCl + 1 M AcN rastvoru.

Ključne reči: Redukcija kiseonika • Platina
• Acetonitril • Hloridi • Rotirajuća disk elektroda