

## **The effect of the composition of the dispersing medium of oxide sols on the electrocatalytic activity of sol-gel obtained RuO<sub>2</sub>-TiO<sub>2</sub>/Ti anodes\***

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The influence of the addition of methanol, ethanol, 1-propanol and 2-propanol to the dispersing medium of a mixture of RuO<sub>2</sub> and TiO<sub>2</sub> sols on the electrochemically active surface area for proton exchange, as well as on the electrocatalytic activity for the chlorine evolution reaction (CER) of RuO<sub>2</sub>-TiO<sub>2</sub>/Ti electrode obtained by sol-gel procedure was investigated. The electrochemically active surface area was examined by cyclic voltammetry, while the analysis of the activity for the CER was performed by polarization measurements. The stability of the obtained anode coatings was also checked by an accelerated stability test. The anode properties depend on the number of C atoms in the alcohol molecule, as well as on the elapsed time between the preparation of the sols/alcohol mixture and its application onto the titanium support. The addition of alcohol increased the activity of the anodes for the CER, compared to those prepared without the addition, but their stability was smaller.

*Keywords:* activated titanium anodes, RuO<sub>2</sub> sol, TiO<sub>2</sub> sol, sol-gel procedure, dispersing media, chlorine evolution reaction.

### INTRODUCTION

Noble metal oxide electrodes, especially those based on RuO<sub>2</sub>, are important materials in practical electrochemistry. Coated anodes such as RuO<sub>2</sub>-TiO<sub>2</sub>/Ti are widely used in chlor-alkali technologies,<sup>1–3</sup> but they are also good electrocatalysts for the hy-

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\* Dedicated to our teacher, Professor Dragutin M. Dražić, in recognition of his contribution to the electrochemistry.

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drogen evolution reaction<sup>4–6</sup> and electroorganic synthesis,<sup>7–9</sup> as well as being useful in cathodic corrosion protection. Recently, RuO<sub>2</sub> based materials were developed for supercapacitive purposes.<sup>10,11</sup> The basic properties of RuO<sub>2</sub>-TiO<sub>2</sub>/Ti anodes, especially their coating stability, could be considerably improved by the application of sol-gel procedure in the preparation of the coating,<sup>12–14</sup> as compared to the standard thermal decomposition of appropriate chlorides.<sup>15,16</sup> It has been established that the morphology and, consequently, the electrochemical properties of sol-gel obtained electrodes depend on the duration of the forced hydrolysis used for the preparation of RuO<sub>2</sub> and TiO<sub>2</sub> sols.<sup>13,14</sup> Also, it was noticed that the addition of alcohols into the sol mixture had an influence.<sup>17</sup>

The aim of this work was to investigate in more details the influence of alcohol addition on the electrochemical properties of sol-gel obtained anodes, especially on their electrocatalytic activity for the chlorine evolution reaction. The anode properties were investigated as functions of a number of C atoms in the alcohol molecule.

#### EXPERIMENTAL

The RuO<sub>2</sub> and TiO<sub>2</sub> sols were prepared by forced hydrolysis of RuCl<sub>3</sub> and TiCl<sub>3</sub>, dissolved in aqueous 5 M HCl solution at the boiling temperature, as described previously.<sup>12</sup> The aging time for the RuO<sub>2</sub> sol was 46 hours, while for the TiO<sub>2</sub> sol it was 30 hours. The coatings obtained from sols after these aging times had the best electrochemical properties.<sup>13,14</sup> The obtained oxide sols were concentrated by evaporation to provide the optimal amount of the dispersed (solid) phase, and mixed to obtain 40 % Ru : 60 % Ti in the coating. The mixture was divided into four parts; to each of them methanol, ethanol, 1-propanol or 2-propanol was added up to an alcohol : sol mixture ratio of 50 : 50. In order to investigate the influence of an alcohol on the anode properties through the coagulation rate of the dispersed phase, the sol/alcohol mixtures (S/A) were kept before application onto the substrate for 0, 24 and 48 h (*t<sub>k</sub>* – keeping time). The obtained S/A mixture showed no visible signs of destabilization, precipitation or coagulation.

Titanium plates, 2 cm × 2 cm × 1 mm in size, were used as the substrate, previously prepared for the deposition as described elsewhere.<sup>16</sup> The application of the S/A mixtures was done by multilayer painting. Each layer was calcined at 380 °C for 10 min and the final annealing was done at 450 °C for 30 min. The coating amount was 2 ± 0.4 mg cm<sup>-2</sup> (RuO<sub>2</sub>+TiO<sub>2</sub>) on each anode. The denotations for prepared anodes *mtl*, *etl*, *ppl*, *ipl* and *wtr* mean that the anodes were prepared by the application of a sol mixture containing methanol, ethanol, 1-propanol, 2-propanol and no alcohol, respectively.

The working electrode (surface area: 0.785 cm<sup>2</sup>) was mounted in a poly(methyl methacrylate) holder. A Pt plate served as the counter electrode and a saturated calomel electrode (SCE) as the reference. All potentials are referred to the SCE.

The anode properties were investigated by cyclic voltammetry (CV), polarization measurements (PM) and by an accelerated stability test (AST). The CV measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub>, while the PM were done in 5 M NaCl, pH 2, at room temperature. The AST was performed galvanostatically (*j* = 2 A cm<sup>-2</sup>) in 0.5 M NaCl, pH 2 at *t* = 33 °C.

#### RESULTS AND DISCUSSION

The cyclic voltammograms of electrodes obtained by the sol-gel procedure with the addition of methanol (*mtl*), ethanol (*etl*), 1-propanol (*ppl*) and 2-propanol (*ipl*) into the dispersing medium are shown in Fig. 1. The keeping times of the S/A mixtures are indicated in the graphs. The voltammograms are of the usual shape for this type of electrodes with a

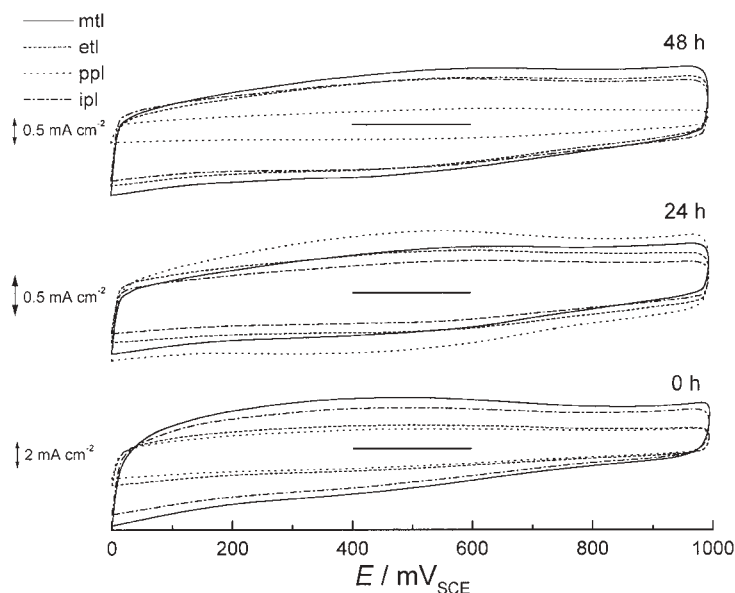


Fig. 1. Cyclic voltammograms of sol-gel obtained  $\text{RuO}_2\text{-TiO}_2/\text{Ti}$  electrodes prepared from mixtures of sols with methanol (*mtl*), ethanol (*etl*), 1-propanol (*ppl*) and 2-propanol (*ipl*). The keeping times of the S/A mixtures are indicated in the graph. Electrolyte: 0.5 M  $\text{H}_2\text{SO}_4$ , room temperature. Scan rate:  $50 \text{ mV s}^{-1}$ .

broad anodic/cathodic peak and relatively large capacitance attributed to a redox reaction coupled with proton exchange between the active sites and the electrolyte:<sup>2,3,18,19</sup>



The added alcohols had a different influence on the voltammetric currents, which also depended on the keeping time of the applied mixtures. In the case of electrodes obtained from freshly prepared mixtures ( $t_k = 0 \text{ h}$ ), the anodic currents at potentials of  $\approx 500 \text{ mV}$  were close to  $2 \text{ mA cm}^{-2}$  for the *etl* and *ppl* electrodes and about  $4 \text{ mA cm}^{-2}$  for the *mtl* and *ipl* electrodes. These currents, especially the last two, exceed the currents registered for a *wtr* electrode in earlier studies,<sup>12-14</sup> which were not higher than  $1.5 \text{ mA cm}^{-2}$ , and those for electrodes obtained by thermal decomposition ( $\approx 1 \text{ mA cm}^{-2}$ ).<sup>15,17</sup> This increase of the anodic currents suggests that alcohol addition causes considerable enlargement of the electrochemically active surface area (EASA). The increase could, however, also imply that added alcohols change the electronic state of the active sites which become more active for reaction (1) than they are in the case of *wtr* electrodes and electrodes obtained by thermal decomposition.

According to Fig. 1, an increase of  $t_k$  leads to a considerable decrease of the voltammetric currents as compared to the voltammograms of the electrodes obtained from freshly prepared mixtures, which suggests a decrease of the EASA.<sup>3,13,18</sup> The changes in EASA occur mainly during the first 24 h of keeping, except in the case of *ppl* electrode, for which the current continued to decrease during the 24–48 h keeping pe-

riod. This means that the *ppl* electrode suffered the most pronounced decrease of the EASA. The different decrease of the EASA could be the consequence of an enlargement of the oxide particles, caused by the addition of different alcohols into oxide sols, which provokes a time-dependent coagulation of the solid phase of the dispersion.

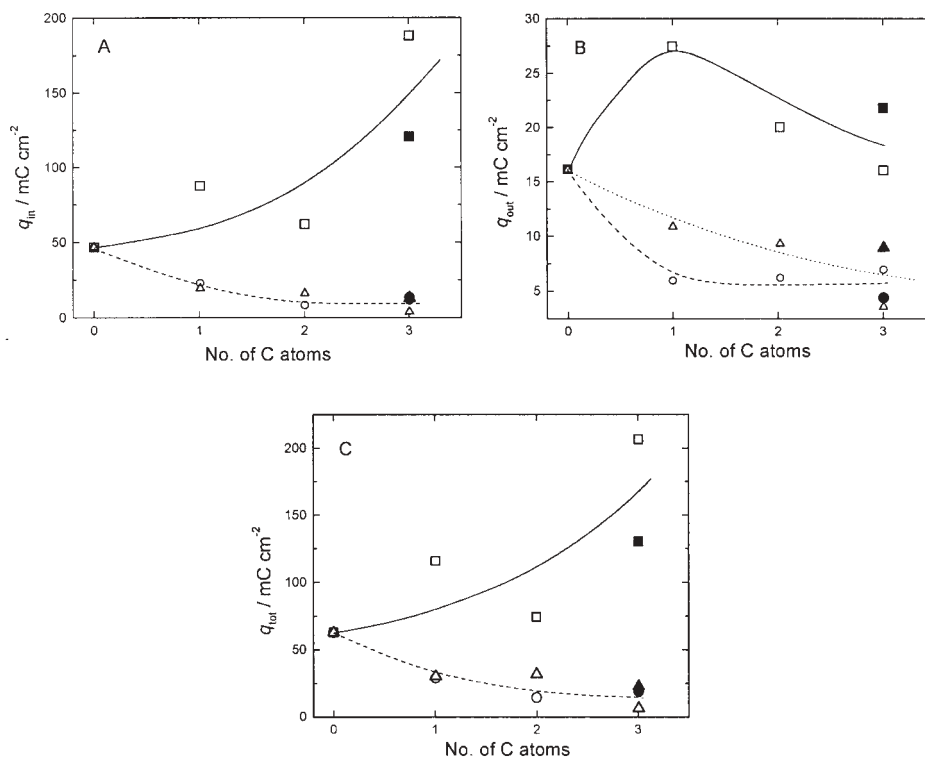


Fig. 2. The characteristic charge densities,  $q_{in}$  (A),  $q_{out}$  (B) and  $q_{tot}$  (C), as a function of the type of added alcohol for the electrodes obtained from S/A mixtures with keeping times: (□) 0 h, (○) 24 h and (△) 48 h. The solid symbols indicate the data for 2-propanol.

The sequences for the decrease of the voltammetric currents for the electrodes obtained from fresh and kept S/A mixtures are shown in Table I. These are the sequences of decreasing activity for proton exchange, reaction (1). They coincide, in general, with the sequence of the number of C atoms in the alcohol molecule. Actually, the voltammetric currents decrease with increasing number of C atoms, except in the cases of *ipl* for  $t_k = 0$  h and *ppl* for  $t_k = 24$  h. The deviation of the *ppl* and *ipl* electrodes from the sequences could be connected with the different influence of these alcohols on the coagulation rate of the solid phase of the oxide sols mixture, which depends on the position of the OH-group in the alcohol molecule. The sequences of the electrodes indicate that methanol and 2-propanol cause the highest coagulation rate in the 0–24 h keeping period, but thereafter the coagulation becomes “frozen” in the next 24 h for all S/A mixtures, except in the case of *ppl*.

TABLE I. The sequences of decreasing voltammetric current densities for sol-gel obtained RuO<sub>2</sub>-TiO<sub>2</sub>/Ti electrodes prepared from sol/alcohol mixtures, with different keeping times,  $t_k$ , obtained by the addition of methanol (*mtl*), ethanol (*etl*), 1-propanol (*ppl*) and 2-propanol (*ipl*) into the dispersing media of the oxide sols

$t_k/h$	Sequence
0	$mtl > ipl \gg etl \approx ppl > wtr$
24	$wtr > ppl > mtl \approx etl > ipl$
48	$wtr \approx mtl > etl \approx ipl \gg ppl$

Analysis of the dependence of the voltammetric charge on sweep rate can give a detailed characterization of the changes of the EASA. According to Ardizzone and coworkers,<sup>18</sup> the dependence is connected with the porous structure of the coating. The charge exchanged between the active sites of the coating and the electrolyte is a measure of the number of active sites in the coating. The active sites situated in the inner part of the coating (pores and cracks) are progressively excluded from the exchange process as the sweep rate increases, as a consequence of the limited diffusion of hydrogen ions towards the inner active sites. This approach enables an evaluation of the total charge,  $q_{tot}$ , related to the whole EASA, and its components: the inner charge,  $q_{in}$ , related to the inner EASA, and the outer charge,  $q_{out}$ , related to the outer EASA, which is directly exposed to the electrolyte.<sup>13,14,17,18</sup>

The changes of the characteristic charges,  $q_{in}$ ,  $q_{out}$  and  $q_{tot}$ , with the number of C atoms in the alcohol molecule and with keeping time of the S/A mixtures are shown in Fig. 2. The voltammetric charge for all the electrodes considerably decreases during 24 h of keeping, as it is also indirectly seen in Fig. 1. For  $t_k = 0$  h,  $q_{in}$  and  $q_{tot}$  increase with the number of C atoms, while  $q_{out}$  decreases. The electrode obtained with methanol addition has the greatest value for  $q_{out}$  as compared to the other electrodes, including the electrode obtained without alcohol addition. These values for the *etl*, *ppl* and *ipl* electrodes are close to that of the *wtr* electrode. The changes in  $q_{in}$  and  $q_{out}$  with the type of added alcohol for electrodes obtained with  $t_k = 0$  h suggest that the enlargement of the EASA can be attributed to its inner part, as a consequence of the different state of the inner active sites, while the state of outer ones resembles that of a *wtr* electrode.

Taking into account the results obtained with  $t_k = 0$  h, the influence of alcohol on the state of the active sites could be commented on in two ways. One possibility is that the contact between alcohol molecules and sol oxide particles results in the formation of hydrogen-inserted oxide H<sub>γ</sub>RuO<sub>2</sub>, with different degrees of insertion ( $\gamma = 0-1.4$ ), which depends on the type of the added alcohol.<sup>11</sup> In this case, the state of both the outer and inner coating active sites should be changed. The second assumption is that the alcohol molecules are "trapped" within the pores and cracks and undergo thermal decomposition during the thermal treatment of the coating. This causes the presence of residual hydrocarbon groups (RHCG) on the surface of the inner active sites. Such an assumption is based on the FTIR spectroscopic results of Guglielmi *et al.*, who reported the presence of RHCG in oxide coatings obtained by the sol-gel procedure when the oxide sols were prepared from metalorganic compounds.<sup>20</sup> In this way, only the surface of the

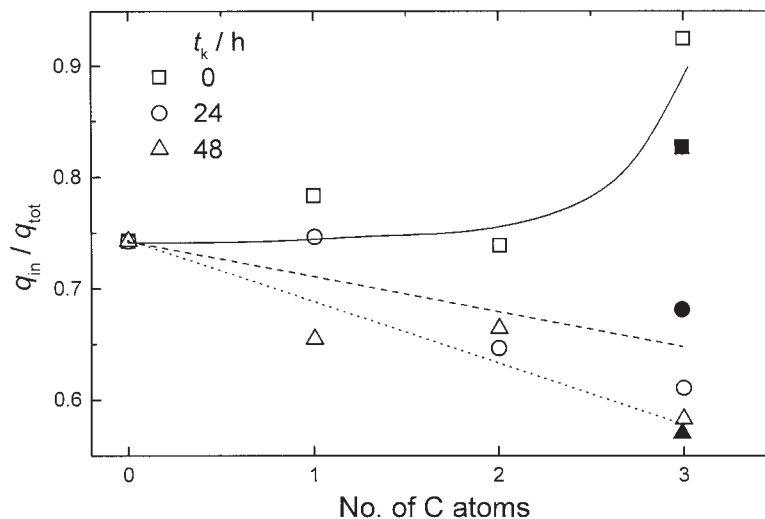


Fig. 3. The dependence of the ratio of the inner and total charge density on the type of added alcohol for electrodes obtained from S/A mixtures for keeping time ( $\square$ ) 0 h, ( $\circ$ ) 24 h and ( $\triangle$ ) 48 h. The solid symbols indicate the data for 2-propanol.

inner active sites is modified. If this is so then the changes in  $q_{out}$  shown in Fig. 2B are connected only with changes in the state of the outer active sites influenced by hydrogen insertion, while the changes in  $q_{in}$  from Fig. 2A should be interpreted as a mutual effect of hydrogen insertion and the presence of RHCG. The similar values of  $q_{out}$  for the *etl*, *ppl*, *ipl* and *wtr* electrodes indicate that hydrogen insertion could be neglected, which is not the case for the *mtl* electrode. The content of RHCG in the inner part of the coating increases with the number of C atoms in the alcohol molecule, which results in the *ppl* and *ipl* electrodes exhibiting the greatest activities (Fig. 2A and 2C).

Considering the influence of  $t_k$ , the activity decreases in the first 24 h as compared to the activity of electrodes obtained with  $t_k = 0$  h (Fig. 2), indicating the effect of coagulation. The decrease of the activity is caused by the reduction of the real surface area of the coating, since the oxide particles are larger than in the case of coatings obtained with  $t_k = 0$  h. Also, the pores in the coating became wider, enabling the trapped organic molecules to be more readily cracked. As a consequence, the RHCG content decreases, which additionally decreases the inner activity. In the 24–48 h keeping period, there are no significant changes in all three kinds of charges for the *mtl*, *etl* and *ipl* electrodes. This means that the coagulation is completed for these electrodes during the first 24 h, while this is not the case for the *ppl* electrode.

The effect of alcohol addition and keeping time on the dimensions of pores and cracks of the coatings is also seen through the changes of  $q_{in}/q_{tot}$  ratio, given in Fig. 3. For electrodes obtained with  $t_k = 0$  h, the  $q_{in}/q_{tot}$  ratio does not change significantly with increasing number of C atoms, except for the *ppl* and *ipl* electrodes. The larger  $q_{in}/q_{tot}$  values for the *ppl* and *ipl* electrodes mean that the RHCG content has the dominant influence on the activity, while the influence of hydrogen insertion is negligible. The

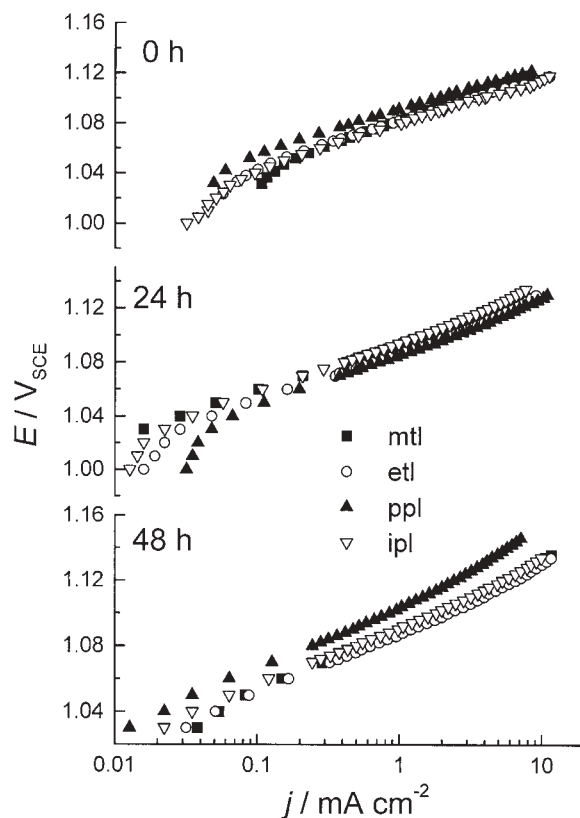


Fig. 4. The Tafel plots of sol-gel obtained  $\text{RuO}_2\text{-TiO}_2/\text{Ti}$  electrodes prepared from mixtures of sols with methanol (*mtl*), ethanol (*etl*), 1-propanol (*ppl*) and 2-propanol (*ipl*) for keeping time: 0 h, 24 h and 48 h. Electrolyte: 5 M NaCl, pH 2, room temperature.

$q_{\text{in}}/q_{\text{tot}}$  ratio decreases with increasing  $t_k$ , meaning that the inner parts of the coating are more accessible for the electrolyte due to pore widening by the coagulation of the solid phase in the dispersion. The effect of pore broadening becomes more pronounced as the number of C atoms increases. Thus, the greatest decrease of the  $q_{\text{in}}/q_{\text{tot}}$  ratio is registered for the *ppl* and *ipl* electrodes with  $t_k = 48$  h.

The Tafel plots for the obtained electrodes are shown in Fig. 4. The Tafel slopes for all the prepared electrodes are close to 40 mV, the value usually reported in the literature<sup>12,21</sup> for the chlorine evolution reaction (CER) on this type of oxide electrode. An influence of the type of added alcohol and  $t_k$  on the apparent current densities is seen. However, the real current density is influenced by two effects: the magnitude of real surface area and the electronic state of the active sites. In order to see the electronic effects on the electrocatalytic activity for the CER, the apparent current density should be normalized by dividing the currents with the apparent charge density obtained from CV measurements.<sup>2,22</sup> The normalized current density at a potential of 1.10 V (typical for potentials within the Tafel region) as a function of the type of added alcohol is shown in Fig. 5. For  $t_k = 0$  h, a slight decreasing trend of the electrocatalytic activity for the CER with the number of C atoms in the alcohol molecule can be seen, but the activity is close to that for the *wtr* anode. When S/A mixtures with increasing  $t_k$  are used for the prepara-

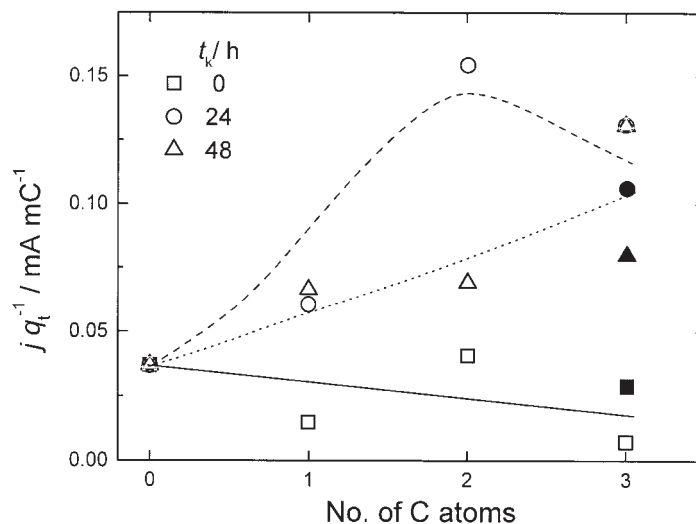


Fig. 5. The influence of the type of added alcohol on the electrocatalytic activity for the chlorine evolution reaction of anodes obtained from S/A mixtures with different keeping times. The solid symbols indicate the data for 2-propanol.

tion of the anode, the anode activities are 2–3 times higher compared to anodes prepared with  $t_k = 0$  h. The highest activity is seen when ethanol is the additive to the sol mixture with  $t_k = 24$  h. Also, a considerable increase in the activity for all the anodes was observed when the  $t_k$  was 24 h. After additional 24 h, all the anodes maintained the achieved activity, except the *etl* anode, the activity of which decreased after 48 h to almost the level of activity of the *etl* anode obtained with  $t_k = 0$  h.

The changes in activity can be discussed from the standpoint of the three mentioned effects of alcohol addition on the structural changes of the coating: hydrogen insertion, the RHCG content and the coagulation of the dispersed phase during the pre-application period.

There is no coagulation effect for the anodes obtained with  $t_k = 0$  h, and the activity is influenced only by modification of the surface of active sites by hydrogen insertion and by the presence of RHCG. The amount of inserted hydrogen decreases in the sequence methanol/ethanol/2-propanol,<sup>11</sup> while the RHCG content in the inner part of the coating should increase with increasing number of C atoms because of the increasing size of the alcohol molecule. The activity data in Fig. 5 for  $t_k = 0$  h indicate that these effects, which decrease the activity, are rather small.

Considering the coagulation effect, the following comment can be made. As  $t_k$  increases, the coatings consist of more larger particles and wider pores. As it was observed in an earlier study, the growth of oxide particles, especially those of  $\text{TiO}_2$ , cause a considerable increase of the anode activity for the CER, which is connected with the facilitated formation of a more active solid oxide solution.<sup>13</sup> This is the cause for the increase of the anode activity during the initial 24 h keeping period, together with the decreasing RHCG content. Also, an additional effect connected with hydrogen insertion has to be mentioned. For  $t_k = 0$  h, the hydrogen insertion process is located on the very



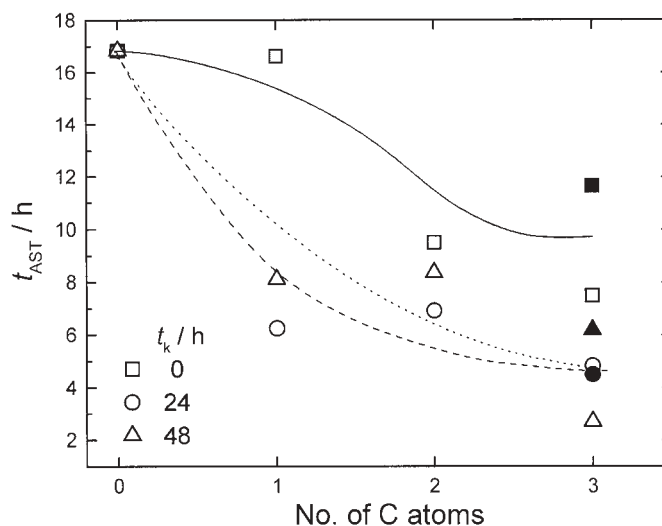


Fig. 6. The dependence of the lifetime ( $t_{AST}$ ) of anodes prepared from S/A mixtures with different keeping time on the type of added alcohol as obtained by accelerated stability test (0.5 M NaCl, pH 2,  $t = 33$  °C,  $j = 2$  A cm<sup>-2</sup>). The solid symbols indicate the 2-propanol data.

surface of the oxide particles, but as  $t_k$  increases, the particles grow by condensation of smaller, surface-hydrogenated particles. As the result, the hydrogen insertion process “penetrates” the bulk of the oxide particles, and this “in-depth” hydrogen insertion during the coagulation decreases the activity of coatings formed from such particles.

The smallest increase of activity (0–24 h keeping period) was registered in the case of methanol addition because of the slowest coagulation rate (Fig. 2) and highest amount of “in-depth” inserted hydrogen. Similarly, the low amount of inserted hydrogen and low RHCG content make the *etl* anode the most active after  $t_k = 24$  h.

A subsequent decrease of activity during the 24–48 h keeping period was registered for the *etl* and, to some extent, for the *ipl* anode. In the case of the *ipl* anode, the continuing coagulation results in a more pronounced “in-depth” insertion, which reduces the active surface area. On the other hand, since there is no evidence of intensive coagulation during the 24–48 h keeping period for the *etl* anode (Figs. 2 and 3), the cause for the decrease of activity in this case is not clear. A tentative explanation could be based on the dense packing of the hydrogen inserted active particles, which reduces the active surface area.

The AST data confirmed the earlier observed decrease of the anode stability caused by added alcohol.<sup>17</sup> The stability decreases with the number of C atoms in the alcohol molecule (Fig. 6), the effect being more pronounced with increasing  $t_k$ . Thus, the most stable anode is the *mtl* one obtained with  $t_k = 0$  h, while the shortest lifetime was shown by the *ppl* anode obtained with  $t_k = 48$  h. The changes of stability with the number of C atoms for  $t_k = 0$  h could be attributed to the considerable presence of RHCG, while the stability decreases with  $t_k$  due to the increase of the real current density of dissolution of the electrochemically active Ru species, which is caused by a decrease of the real surface area resulting from the coagulation process.

## CONCLUSIONS

The electrochemically active surface area of the electrodes obtained immediately after the preparation of the sol/alcohol mixtures is higher than the area of the electrodes obtained without alcohol addition and increases with the number of C atoms in the alcohol molecule. The enlargement is the consequence of hydrogen insertion into the oxide particles and of the presence of residual CH groups in the inner parts of the coating. The application of sol/alcohol mixtures with keeping periods leads to a considerable decrease of the electrochemically active surface area, with the decrease being more pronounced as the number of C atoms increases. The decrease is caused by coagulation of the solid phase of the dispersion which leads to the growth of the oxide particles. The electrocatalytic activity of the obtained anodes for the chlorine evolution reaction considerably increases if the coatings are obtained from sol/alcohol mixtures with a 24 h keeping time. These changes in activity are caused by the different influence of hydrogen insertion, the content of CH residuals in the coating pores and the rate of solid phase coagulation. The addition of alcohol causes a decrease of the anode lifetime. The effect is more pronounced if the keeping time of sol/alcohol mixtures is longer.

## ИЗВОД

УТИЦАЈ САСТАВА ДИСПЕРЗНЕ СРЕДИНЕ ОКСИДНИХ СОЛОВА НА  
ЕЛЕКТРОКАТАЛИТИЧКУ АКТИВНОСТ  $\text{RuO}_2\text{-TiO}_2/\text{Ti}$  АНОДА ДОБИЈЕНИХ СОЛ-ГЕЛ  
ПОСТУПКОМ

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У раду је испитиван утицај метанола, етанола, 1-пропанола и 2-пропанола, додатих у дисперзну средину  $\text{RuO}_2\text{-TiO}_2$  смеше солова, на електрохемијски активну површину и електрокаталитичку активност за реакцију издвајања хлора (РИХ)  $\text{RuO}_2\text{-TiO}_2/\text{Ti}$  електрода добијених сол-гел поступком. Електрохемијски активна површина испитивана је методом цикличне волтаметрије, док је активност за РИХ испитивана поларизационим мерењима. Такође је и убрзаним тестом стабилности испитивана постојаност добијених оксидних превлака. Утврђено је да особине добијених анода зависе од броја угљеникових атома у молекулу додатог алкохола и времена протеклог од припреме смеше алкохола и солова до nanoшења смеше на титански носач. Уочено је да додаток алкохола проузрокује повећање активности анода за РИХ у односу на аноде добијене без додавања алкохола. Истовремено, аноде добијене додавањем алкохола су мање стабилне од анода добијених без додавања алкохола.

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