

Corrosion and passivity of metals in methanol solutions of electrolytes

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Abstract Electrochemical and corrosion behaviour of metals in alcohols are the subject of numerous investigations because of the application of mentioned solvents in chemical engineering, production of oxide nanoparticles (sol-gel techniques) and application of alcohols as fuels. Despite relatively rich bibliography related to electro-catalytic oxidation of alcohols on metal surface in mixed aqueous–alcohol solutions, the knowledge of the mechanism of reactions on metal/anhydrous alcohol interface is still not sufficient. Anodic oxidation of metal surface in alcohol leads to several electro-catalytic reactions with formation of surface compounds being the product of metal and alcohol oxidation. Identification of these products is very difficult. Therefore, our knowledge of the composition and structure of passive films or corrosion products on metal surface in anhydrous alcohol solvents is poor. Our paper presents the investigations of anodic behaviour of metals (Cu, Zn, Fe, Ni, Al and Ti) and semiconductors (p-Si) in methanol solutions of electrolytes, performed in our laboratory within the last 10 years. On the base of

electrochemical measurements (linear sweep voltammetry, electrochemical impedance spectroscopy), spectroscopic investigations (X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and low-energy electron diffraction) and scanning electron microscopy techniques, the role of metal–alcohol intermediates in the formation of surface and soluble compounds is discussed. The practical application of electrochemical etching of metals as a method of production of micro- and nanoparticles of metals and oxides is also shown.

Keywords Corrosion · Passivation · Alcohols

Introduction

The knowledge of anodic properties of metals in alcoholic solutions of electrolytes has gotten significant meaning for many branches of science and technology. Such solutions find application in surface treatment, obtaining metallic and composite layers or nanoparticles of metals. Pure alcohols can be applied as fuels or components of liquid fuels. Despite wide bibliography dedicated to anodic properties of metals in alcoholic solutions [1–12], the mechanism of dissolution of metals in these solvents, especially the effect of alcohol molecules on mechanism of charge transfer and formation of surface products, is poorly recognised.

So far, the research shows that, in anhydrous alcoholic solutions of electrolytes, the surface of most metals undergoes unstable passivation. The forming intermediate plays the role of membrane inhibitor rather than the passive oxide layer. It is removed at higher overpotentials, which effects in uniform or pitting corrosion. [13–17]. Stability of surface layer seems to grow up with the size of alcohol particle.

Oxide passivation in anhydrous alcoholic solutions is possible in the presence of undissociated oxy-acid particles.

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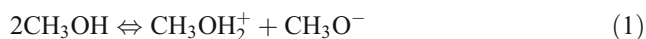
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Such molecules undergo decomposition on the metal surface and become the source of oxygen for passivation process [18–21]. Anhydrous alcoholic solutions of oxyacids (e.g. sulphuric, phosphoric, and formic acids) act as the oxidants similarly to concentrated acids.

This paper presents our research on corrosion and passivation mechanism of selected metals in anhydrous methanolic solutions of electrolytes. There will also be resented possibilities of application of metals and semiconductors etching in alcoholic and mixed water–alcohol solutions for production of nano- and micro-particles of metals and oxides.

Mechanism of anodic dissolution of metals in methanol

Methanol belongs to protogenic solvents and undergoes auto-dissociation according to the equilibrium:

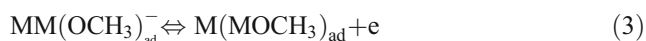


The solvent shows similar properties to water, and therefore, electrochemical behaviour of metals in this medium should be similar to the behaviour in aqueous environments. Analogous to water, polar methanol molecule undergoes adsorption on the metal surface and, after that, undergoes electro-catalytic or thermal decomposition [22]. Contrary to water, decomposition of methanol is a more complicated process and can provide different surface intermediates, depending on water content in the alcohol ($\text{CH}_3\text{O}_{\text{ad}}$, $\text{CH}_2\text{O}_{\text{ad}}$ and CO_{ad}) [22–27].

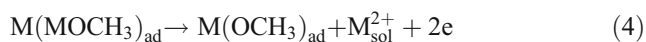
The $-\text{OCH}_3$ group plays very important role in the reactions of anodic dissolution and cathodic deposition (similarly to OH group). The presence of adsorbed oxygen or surface oxide film promotes the surface methoxylation according to the reaction [22, 23]:



It seems that the surface of active metals is very rapidly covered by $-\text{OCH}_3$ and the anodic oxidation in methanol proceeds according to the reaction:



The $(\text{MOCH}_3)_{\text{ad}}$ intermediate is more stable than analogous MOH_{ad} compound, and their oxidation needs higher over-voltage than oxidation of MOH_{ad} intermediate. Therefore, anodic polarisation curves of metal dissolution in methanol show characteristic inhibition effect at low over-voltage. Oxidation of $(\text{MOCH}_3)_{\text{ad}}$ and activation of metal surface in methanol solutions proceed according to the reaction:



Reaction 4 proceeds on energetically privileged places (kinks and steps) according to catalytic mechanism [28, 29], and crystallographic etching of metal surface can be observed.

Anodic dissolution of zinc and copper

Figure 1 shows stationary polarisation curves of zinc in $\text{CH}_3\text{OH}-\text{LiClO}_4-\text{LiCl}$ solutions [12]. The anodic curve forms an “S” shape. At low anodic over-voltage, polarisation curve is relatively flat, and at definite potential, rapid increase of anodic current connected with the crystallographic etching of metal surface can be observed [13, 30]. The transient polarisation curves of zinc show time-dependent desorption of $(\text{MOCH}_3)_{\text{ad}}$ and thus surface activation over the definite anodic potential. Increase of current in time leads to increase of IR-drop and to decrease of real anodic potential on zinc electrode, and therefore, stationary polarisation curve shows characteristic “S” shape in these conditions. The “ $\log i-E$ ” relation, obtained by extrapolation of potentiostatic transients to very short time (10 ms), is linear with the Tafel slope $dE/d\log i \sim 120$ mV, which proves that the first oxidation step is limited by transfer of one electron. Participation of surface compounds in oxidation process of zinc in methanol solutions of electrolytes can be confirmed with help of cyclic linear sweep voltammetry (LSV). The analysis of LSV data [13, 30] enables to obtain kinetic parameters of anodic dissolution of zinc and the surface concentration of reactants Γ^* . The presented results show that the process of anodic dissolution of zinc in methanol is a two-step mechanism. In the first reaction (Eq. 5a), which leads to the creation of the surface, intermediate product Zn_{ad}^+ is very fast and reversible (Tables 1). This reaction proceeds with a faster rate on the surface (0001) than on the $(11\bar{2}0)$. Shifting the standard potential $E_{\text{Zn}^+/\text{Zn}^{2+}}^0$ of the second reaction (Eq. 5b) to more positive potentials indicates that the better

Fig. 1 Stationary polarisation curves of polycrystalline zinc in $\text{CH}_3\text{OH}-\text{LiClO}_4-\text{LiCl}$ solutions deaerated with Ar [12]

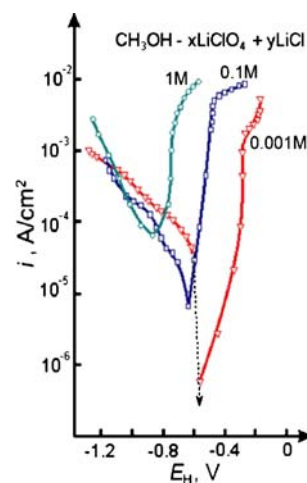


Table 1 Kinetic parameters of anodic dissolution of Zn in CH₃OH-LiClO₄ [13]

Zn	Γ_{Zn} (mol/cm ²)	$\Gamma_a^* Zn$ (mol/cm ²)	$\Gamma_c^* Zn$ (mol/cm ²)	E^f_{Zn/Zn^+} (V)	$E^0_{Zn^+/Zn^{2+}}$ V	αn_a	αn_c	k^0 1/s	k_a^0 1/s	k_c^0 1/s
Reaction Zn → Zn _{ad} ⁺ + e (Eq. 5a)										
(0001)	2.71 × 10 ⁻⁸	1.95 × 10 ⁻⁷	6.02 · 10 ⁻⁷	-1.275		0.56	0.43		0.74	0.079
(11 $\bar{2}0$)	1.02 × 10 ⁻⁹	7.68 × 10 ⁻⁸	7.68 × 10 ⁻⁸	-1.010		0.45	0.45		0.31	0.31
Reaction Zn _{ad} ⁺ → Zn ²⁺ + e (5b)										
(0001)					-0.866	0.45	0.35	4.62 × 10 ⁻³		
(11 $\bar{2}0$)					-0.517	0.42	0.26	0.12		

adsorption of Zn_{ad}⁺ product occurs on the low index plane (11 $\bar{2}0$). The difference between these two surfaces is significant and equals around 0.350 V.

Comparison of the surface concentration of electrochemical active places occupied by the anodic surface product Γ^* indicates that the value Γ^* with relation to Γ_{Zn} is bigger on the surface (11 $\bar{2}0$) than on the (0001) that may indicate better adsorption properties of the low index plane. It is assumed that the preferred adsorption on the (11 $\bar{2}0$) surface is a result of physical properties of these surface-like gaps, where the product can be easily anchored. Little is known about the structure of adsorbate. Presumably, it is a methoxy ion ZnOCH₃. We have estimated the adsorption energy for two planes. The adsorption free energy of surface product Zn_{ad}⁺ (β_{Zn^+}) for Zn(0001) is 2.603 J m⁻² and is much lower than the β_{Zn^+} value for the lower index plane Zn (11 $\bar{2}0$), which amounts to 13.456 J m⁻² [13, 30]. Activation of Zn surface according to reaction 4 leads to crystallographic etching of metal surface.

Copper shows similar anodic behaviour in anhydrous methanol solutions like zinc [31, 32]. Polarisation curves of copper (Fig. 2) show that anodic dissolution of this metal proceeds with surface intermediates containing Cu⁺ ions (first anodic peak i_{a1}) and Cu²⁺ ions (second anodic peak i_{a2}). Formation of the first anodic product in solutions of

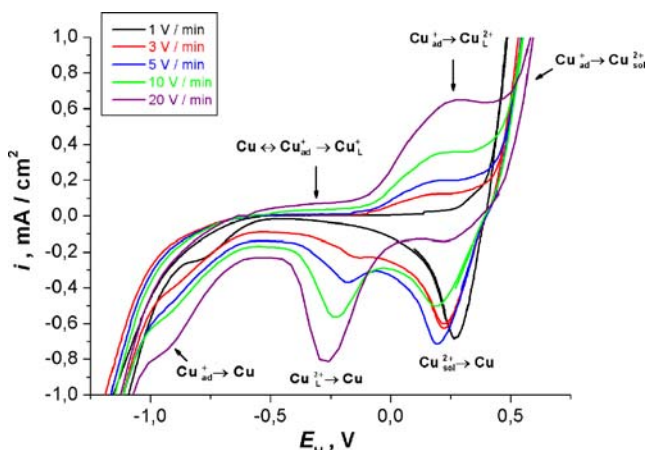
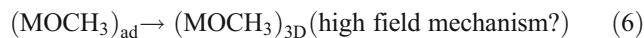
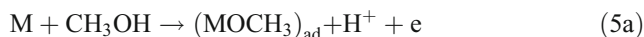


Fig. 2 LSV curves of Cu (111) in CH₃OH–0.1 M LiClO₄ deaerated with Ar

low chloride concentration is controlled by adsorption. It can be confirmed by the linear relationship of current density vs. potential scan rate at the range of first current plateau (Fig. 3a) At high concentrations of chlorides, there can be observed change of the type of process control from adsorption to diffusion (Fig. 3b). Formation of surface product Cu²⁺ in solutions of low chloride concentration is a diffusion-controlled reaction, which can be concluded from linear relationship i_{a2} ($v^{0.5}$; Fig. 4). The effect of Cl⁻ ions concentration on anodic current in the range of second anodic peak is more significant. Anodic peak disappears in concentrated solutions (0.1 M LiCl), and dissolution proceeds to formation of soluble product.

Formation of surface product Cu_{ad}⁺ in the range of first current plateau (<-0.220 V) is a very fast process. The high frequency part of impedance spectrum connected with formation of this product is a flattened half circle with time constant of order 10⁻⁵ s (Fig. 5). Adsorption of chloride ions makes proceeding of this reaction difficult, which can be concluded from the increase of charge transfer resistance R_{ct} in 0.1 M LiCl. The growth of Cu_L⁺ layer is much slower (time constant about 10⁻² s). This process is controlled by surface reaction rate, which can be concluded from capacitive nature of impedance spectrum at range of frequencies from 10⁻¹ up to 10² Hz (Fig. 6a). Impedance spectrum obtained at the range of potential corresponding to the formation of Cu²⁺ has gotten diffusion nature. It can be concluded from its shape the strongly activating influence of chloride ions concentration (Fig. 6b). Surface layer almost disappears in 0.1 M LiCl, and the copper surface undergoes uniform etching.

For both copper and zinc, a similar two-step consecutive mechanism of anodic dissolution in methanolic solutions of LiClO₄–LiCl can be assumed:



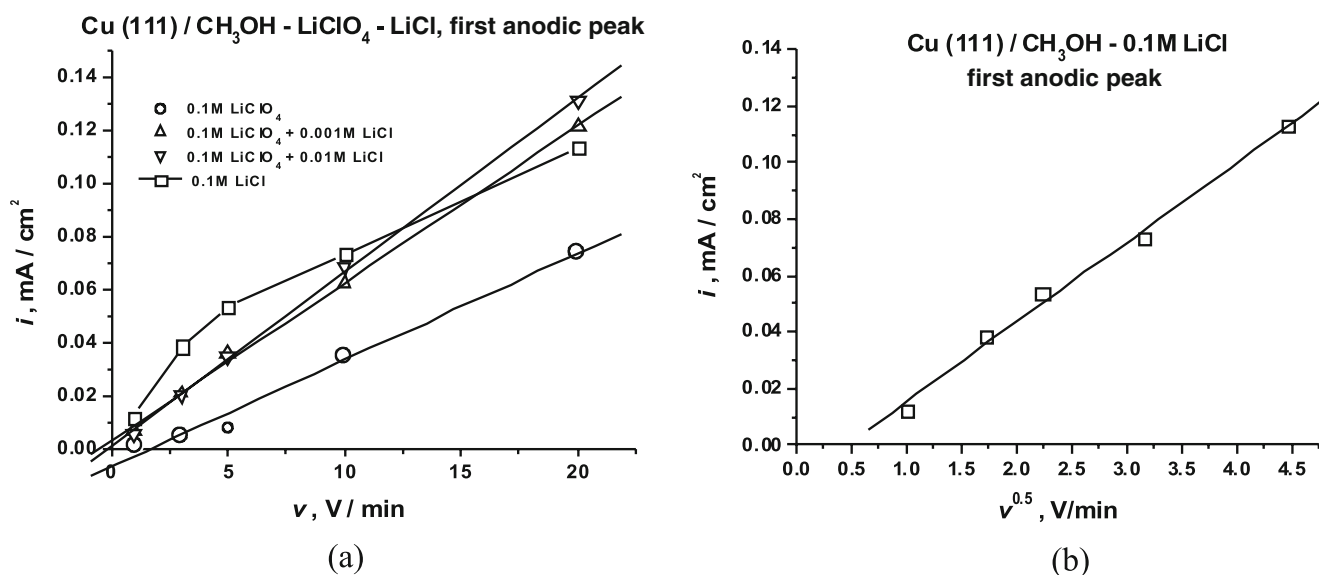
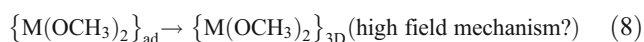


Fig. 3 Anodic peak i_{a1} as a function of scan rate: **a** low chloride concentration—linear function of v ; **b** high chloride concentration—linear function of $v^{0.5}$



The first step of reaction is fast surface product formation with participation of methoxy groups (Eq. 5a). Parallel competitive reaction can also be possible in the presence of chloride ions (Eq. 5b), although our research showed that the influence of Cl^- at low overpotentials (first anodic peak) is negligible. At the range of second anodic peak, oxidation of $(\text{MOCH}_3)_{\text{ad}}$ to $\{\text{M}(\text{OCH}_3)_2\}_{\text{ad}}$ can be

observed. Investigations showed that anodic layers are not monolayers but 3D films [13]. The mechanism of 3D layer growth (processes 6 and 8) is not yet completely explained. We assume that it proceeds in a way of migration in high electric field. Activating effect of chloride anions observed at potential range corresponding to divalent cations formation can be explained by reaction 9. It is possible that the soluble compound is the methoxy–chloride complex of the general formula, $\{\text{M}(\text{OCH}_3)_x\text{Cl}_y\}_{\text{sol}}^{2-}$ where $x + y = 4$.

Participation of methoxy groups in reaction 5a has been confirmed with X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements of copper surface anodically polarised at the range of

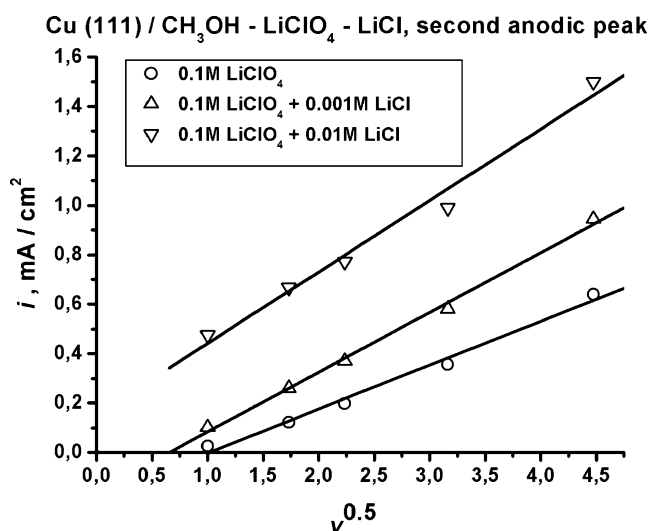


Fig. 4 Anodic peak i_{a2} as a function of scan rate

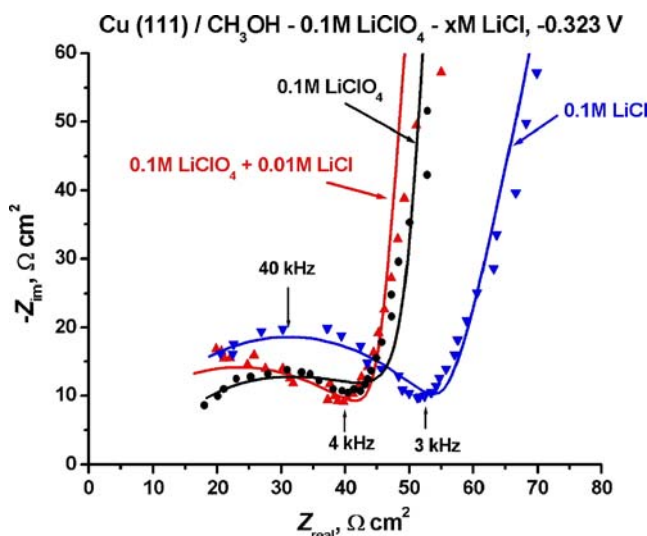


Fig. 5 High frequency part of impedance spectrum for Cu(111)/ $\text{CH}_3\text{OH-LiClO}_4\text{-LiCl}$ deaerated with Ar at -0.323 V

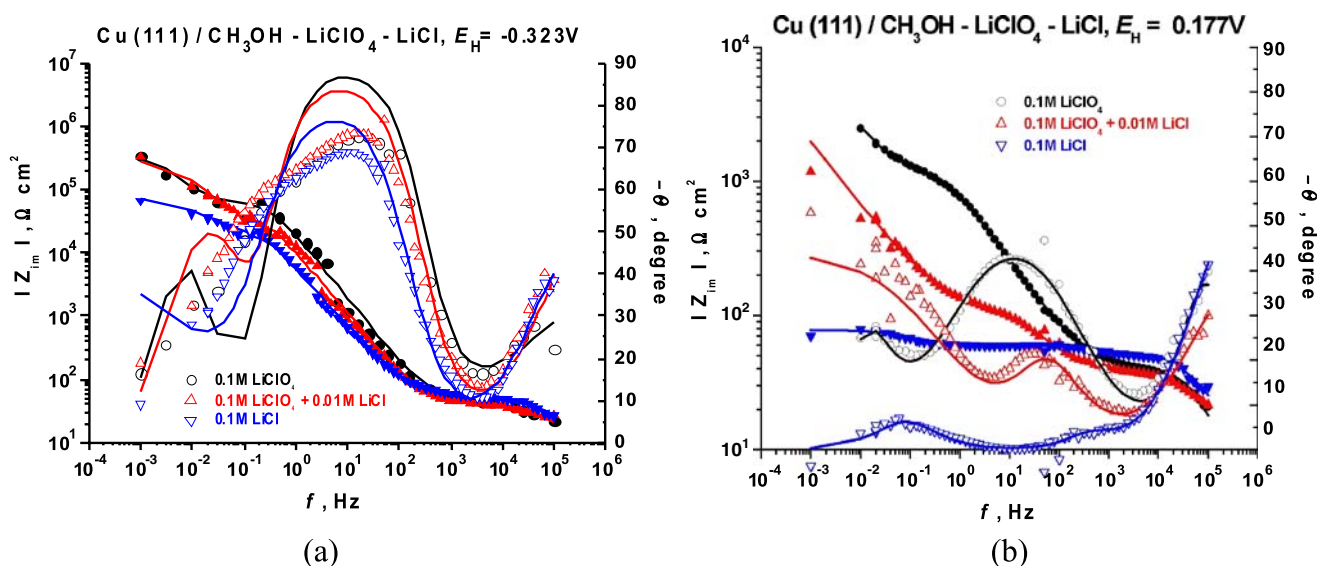


Fig. 6 Bode diagrams for Cu (111) in CH₃OH–LiClO₄–LiCl deaerated with Ar: **a** $E_H = -0.323$ V, **b** $E_H = 0.177$ V

first peak/plateau (range of Cu_{ad}⁺ stability). Figure 7 presents XPS spectrum of bare surface covered with adsorbate. There appears, beside peaks corresponding to OCH₃ and CH₃OH bounds, very clear peak at binding energy of 285 eV, which can be attributed to formaldehyde HCHO as the methanol and methoxy groups' oxidation product [33]. Two broad features below the Fermi level on UPS spectrum (Fig. 8), observed at 6–7 and 9–10 eV, confirm the presence of major component as methoxy group.

Anodic dissolution of iron and nickel

Our research on anodic properties of iron in anhydrous methanolic solutions of LiClO₄ has showed that anodic dissolution of this metal is inhibited at a wide range of potential [34]. Polarisation curve presented in Fig. 9 shows two characteristic anodic and cathodic peaks corresponding to the formation of Fe²⁺ and Fe³⁺ compounds. Over the potential of ~1.0 V_{SHE}, activation of electrode surface and fast etching of iron surface starting locally can be observed.

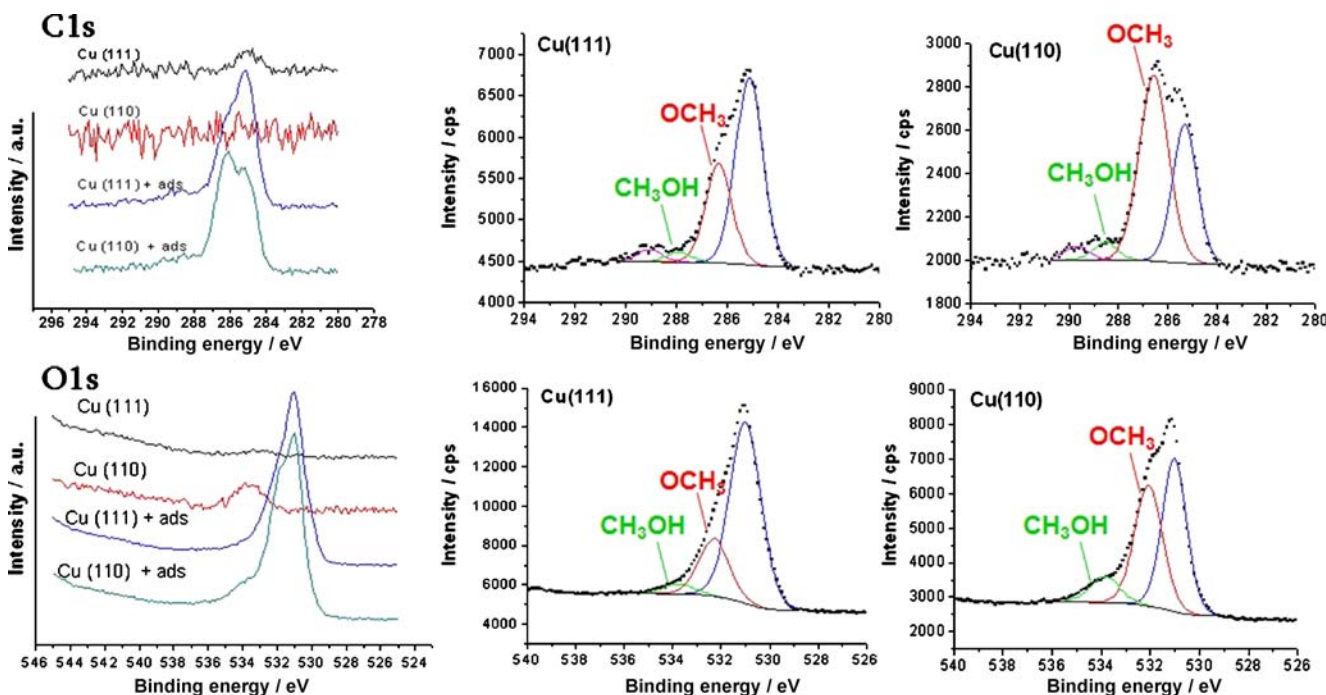


Fig. 7 XPS spectrum of Cu(111) and Cu(100) surface before and after polarisation in CH₃OH–0.1 M LiClO₄ deaerated with Ar ($E_H = -0.323$ V)

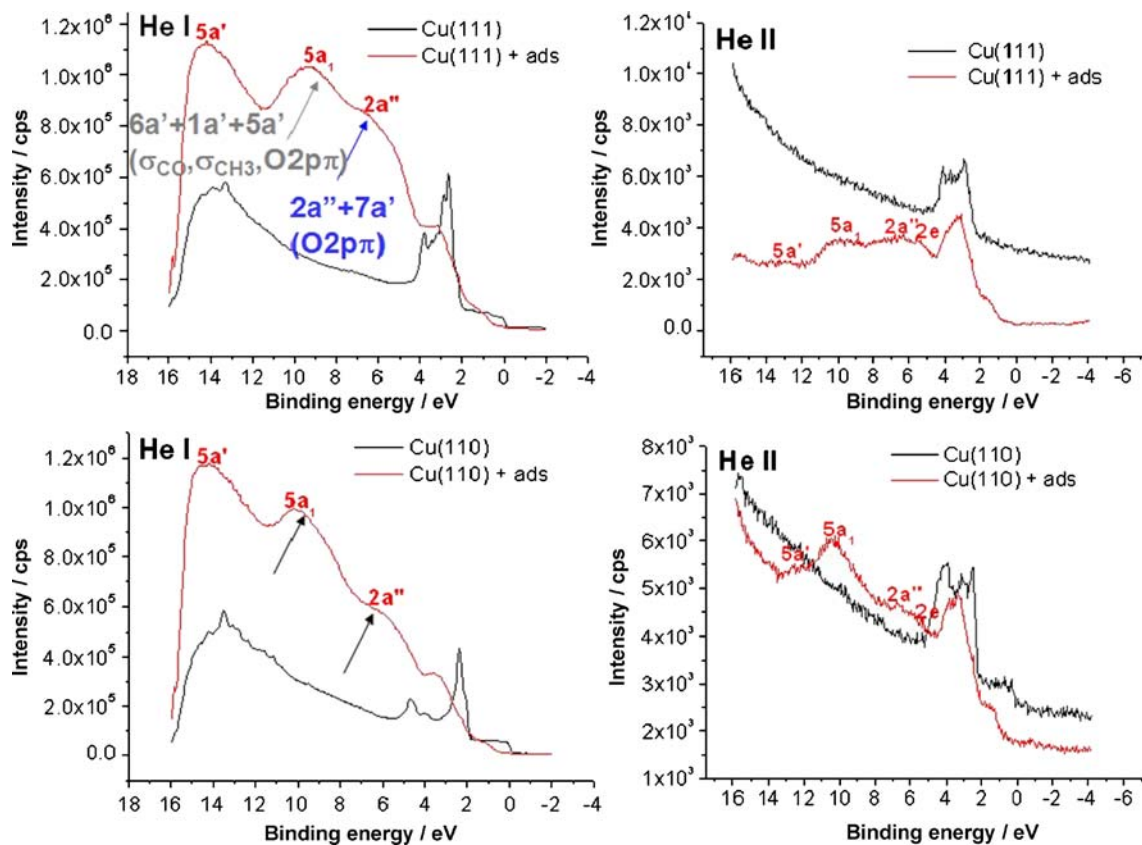
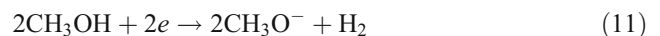


Fig. 8 UPS spectrum of Cu(111) and Cu(100) surface before and after polarisation in CH_3OH -0.1 M LiClO_4 deaerated with Ar ($E_{\text{H}}=-0.323$ V)

Blocking of iron surface in anhydrous methanol is not connected with oxide layer but rather with formation of methoxy species. Pseudo-passive layer of Fe-OCH_3 type products is formed by way of direct surface-controlled reaction, which can be concluded from the linear relationship of current density of anodic and cathodic peaks vs. potential scan rate. The range of stability of the layer

blocking anodic dissolution in the presence of high concentration of chloride anions in methanol is limited to the range of Fe^{2+} ions stability.

The presence of passivating $\text{Fe}(\text{OCH}_3)_2$ layer on iron surface formed during anodic polarisation of this metal in methanol- LiClO_4 solutions has been confirmed by Japanese researchers. Investigations of Arakami et al. [35–37] have shown that iron passivated in the air retains its passive properties in anhydrous solution of LiClO_4 , while the iron without oxide layer (prepared in dry Ar) corrodes under the same conditions. The rate of corrosion is decreasing in time because of the formation of methoxy-iron layer. They have proposed the following mechanism of corrosion and passivation of iron in $\text{Fe}/\text{CH}_3\text{OH-LiClO}_4$ [35]:



There precipitates sparingly soluble methoxy-iron which converts to iron oxide:

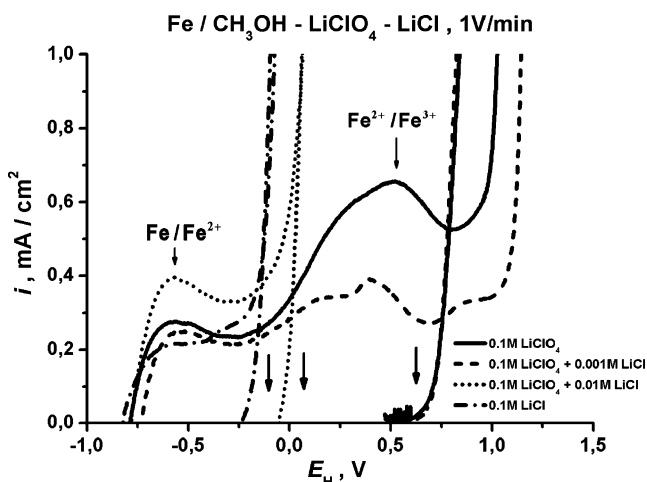
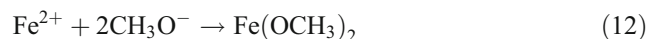
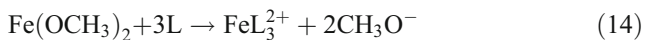


Fig. 9 Effect of chloride concentration on polarisation of iron in anhydrous methanol deaerated with Ar (1 V/min)

In our opinion, the FeO-type layer is not stable and does not protect against corrosion.

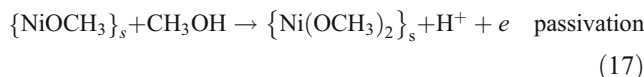
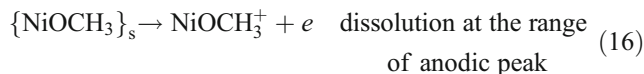
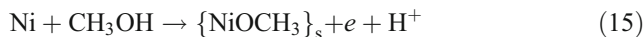
The investigations of Japanese researchers [38] have confirmed that complexing iron compounds such as 2,2' bipyridine (bpy), 1,10-phenantroline (phen) and others removes Fe(OCH₃)₂ layer and facilitates the iron corrosion according to the reaction:



Authors have found that the cathodic process is independent on H⁺ ions concentration and has assumed that the main cathodic reaction during the corrosion of iron in anhydrous methanol is the reduction of alcohol molecules with hydrogen evolution and formation of methoxy group according to reaction 11.

Investigations of anodic properties of nickel in anhydrous solutions of CH₃OH–LiCl have shown that, at low anodic overpotentials, the surface of Ni undergoes passivation with formation of alcoxy layer Ni-(OCH₃)₂ type. Activation of nickel surface in anhydrous CH₃OH–LiCl–CH₃ONa takes place at potential higher then 0.3 V_{SHE} and is accompanied with uniform etching of metal surface. The increase of methoxy group's concentration stabilises the passive layer. Active–passive transition is controlled by surface one-electron charge transfer reaction, which can be concluded from the linear relationship of anodic peak current density to potential scan rate (Fig. 10) and half peak width from 83 up to 90 mV ($E^p - E^{p/2} = 48/\alpha n$) [39].

Passivation of nickel in anhydrous methanol–chloride solutions can be described with the following reactions:



The presence of hydrogen ions stimulates the activation of nickel surface trough removing methoxy groups:



The increase of chloride anions concentration also causes the activation of metal surface:



The effect of Cl⁻ ions is particularly important in the range of high anodic potential, over the potential of oxidation of methanol (> about 0.3 V). Under these conditions, chloride ion plays the role of agent-complexing anodic product.

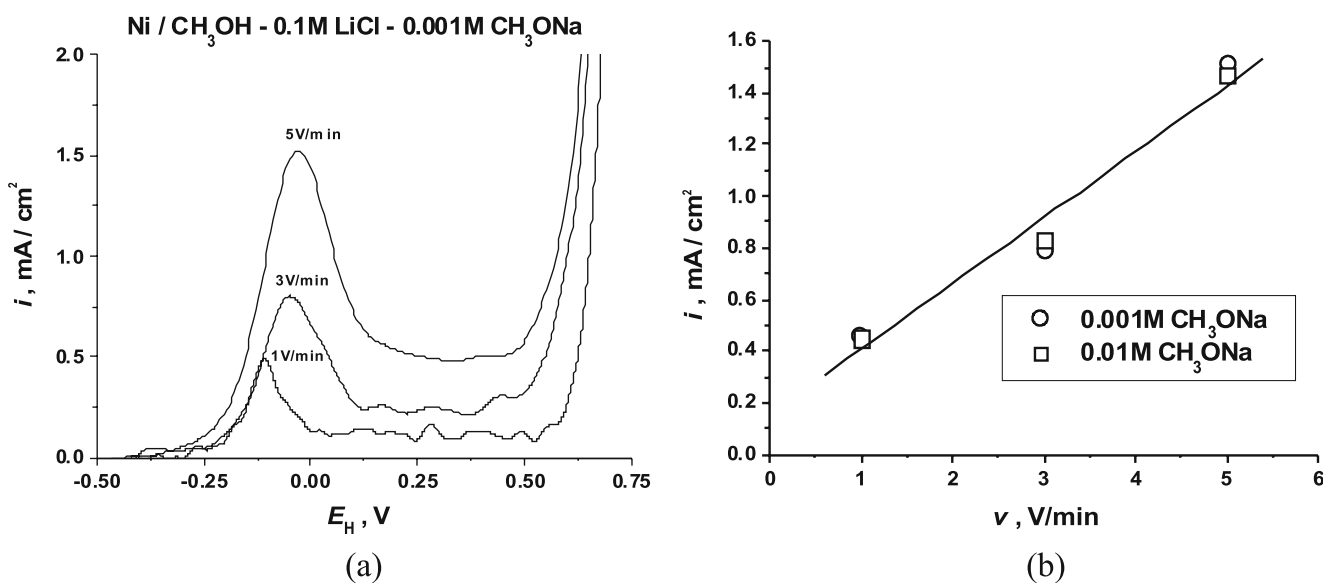


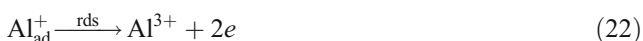
Fig. 10 Effect of scan rate on polarisation of nickel in CH₃OH–0.1 M LiCl deaerated with Ar (a) and on anodic peak value (b)

Anodic dissolution of wavel metals and silicon

Our research on anodic properties of wavel metals (Al and Ti) and single crystals of silicon semiconductor (p-Si) has shown that these materials are not resistant against anhydrous methanolic solutions of electrolytes.

Electrochemical measurements on the anodically activated surface allow to investigate processes taking place on bare oxide free surface. We have proceeded such research for titanium [43], aluminium [14, 40, 42], intermetallic phase TiAl [41] and silicon [16, 50].

Anodic dissolution of aluminium in anhydrous methanol proceeds in two consecutive steps with the participation of Al^+ intermediate [42]:



Adsorbed intermediate product is probably composed of Al^+ cations and organic compounds $-OCH_3$. The second step—oxidation of Al^+ intermediate—determines overall reaction rate. The oxidation of Al^+ intermediate proceeds with the participation of chloride ions. The reaction order $d \log i / d \log [Cl^-] = 1$ confirms participation of chloride anions in the second step of oxidation.

At low over-potentials, dissolution of aluminium is strongly inhibited by surface product (Fig. 11). At the definite anodic potentials, desorption of the surface product occurs and metal undergoes structural etching.

Passive oxide film on titanium surface is not resistant in methanol environments [43–45]. The layer loses its stability

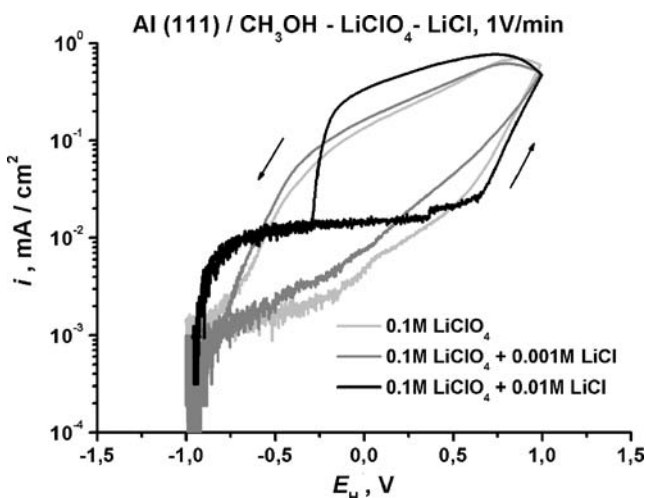
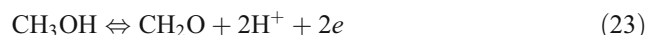


Fig. 11 Anodic polarisation curves of Al(111) in $CH_3OH-LiClO_4-LiCl$ deaerated with Ar (1 V/min)

at anodic potential over 0.3 V. The value of activation and repassivation potential is independent on chloride ions concentration. Loss of stability is, in our opinion, connected with the removal of methoxy groups from the oxide layer. In anhydrous methanol, the surface oxide is covered with products of electro-catalytic decomposition of methanol proceeding according to reaction 2. Methoxy groups “stabilise” surface of passive oxide and plays a role similar to OH groups stabilising passive layers in water solutions. There probably forms $TiOH_x(OCH)_y$ layer on the surface of titanium. Over the potential of methanol oxidation starts removing products of its electrosorption (CH_3O). The potential of methanol oxidation according to the following summary reaction equals 0.3 V:



This value corresponds nearly to the potential of titanium repassivation observed from 0.347 V_{SHE} to 0.447 V_{SHE} . It should be pointed that the value of equilibrium potential of reaction 23 is only thermodynamic value. In reality electrooxidation of methanol on the metallic and oxide surface is a very complicated multi-step process dependent on type of metal, number of surface defects or oxide defects [38, 46–49]. Thus removing methoxy groups from the oxide surface via the oxidation process can correspond to the range of potential differing from equilibrium potential.

Initiation of dissolution in the range of potential higher than potential of methanol oxidation has a local nature (breakdown of oxide layer) and proceeds on energetically preferred positions – surface cations of low coordination.

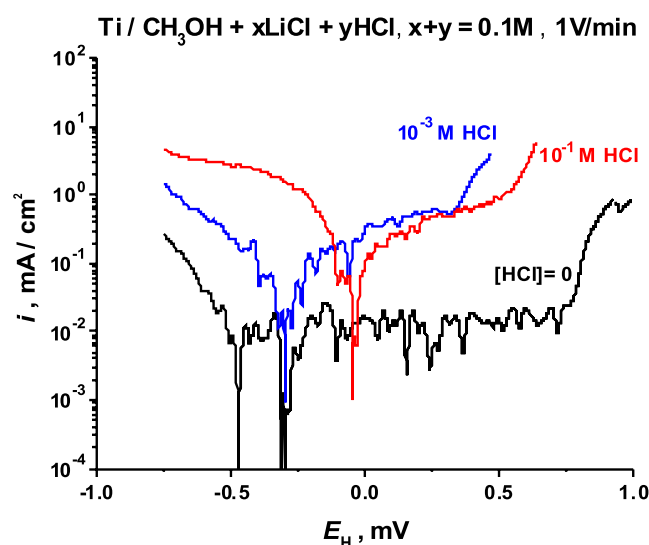


Fig. 12 Effect of acidity on anodic polarisation of titanium in $CH_3OH-0.1 M LiCl-HCl$ deaerated with Ar

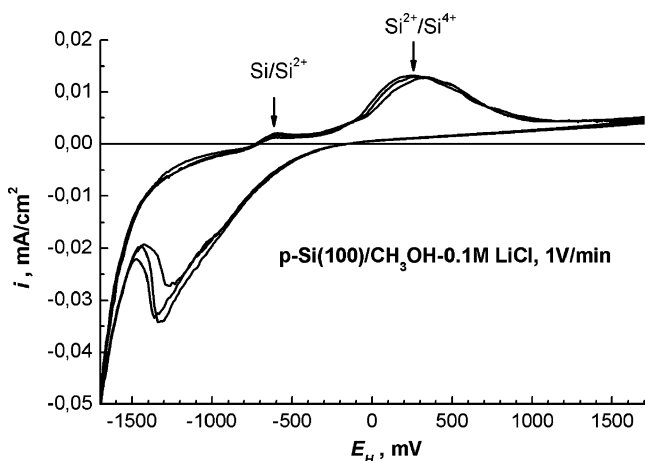
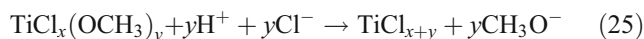
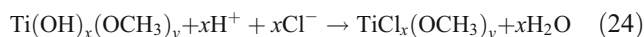


Fig. 13 Polarisation curves of p-Si(100) in CH₃OH–0.1 M LiCl deaerated with Ar

This is the origin of hysteretic on anodic polarisation curve connected with gradual increase of active surface.

Presence of hydrogen ions in methanolic solutions of chlorides facilitates the activation of titanium surface

(Fig. 12). This effect can be explained by following reactions:



Silicon behaves in methanolic solutions of chlorides dependent on the type of doping. According to the expectations, n-Si without exposing to high illumination does not undergo etching. The saturation current ($0.1 < A/cm^2$) can be only observed [16].

Figure 13 present polarisation curves of p-Si in CH₃OH–0.1 M LiCl. It can be concluded from the course of the curve that silicon dissolves in this environment according to a two-step reaction (two anodic peaks) with intermediate Si(II)_{surf}. The two-step mechanism with formation of Si(II)_{surf} and Si(IV)_{surf} compounds has been confirmed by transient technique—there appears second peak on $I=f(t)$ curve, over the potential 0.4 V (the potential impulse of 0.6 V imposed on constant potential of –0.2 V). Linear relationship of

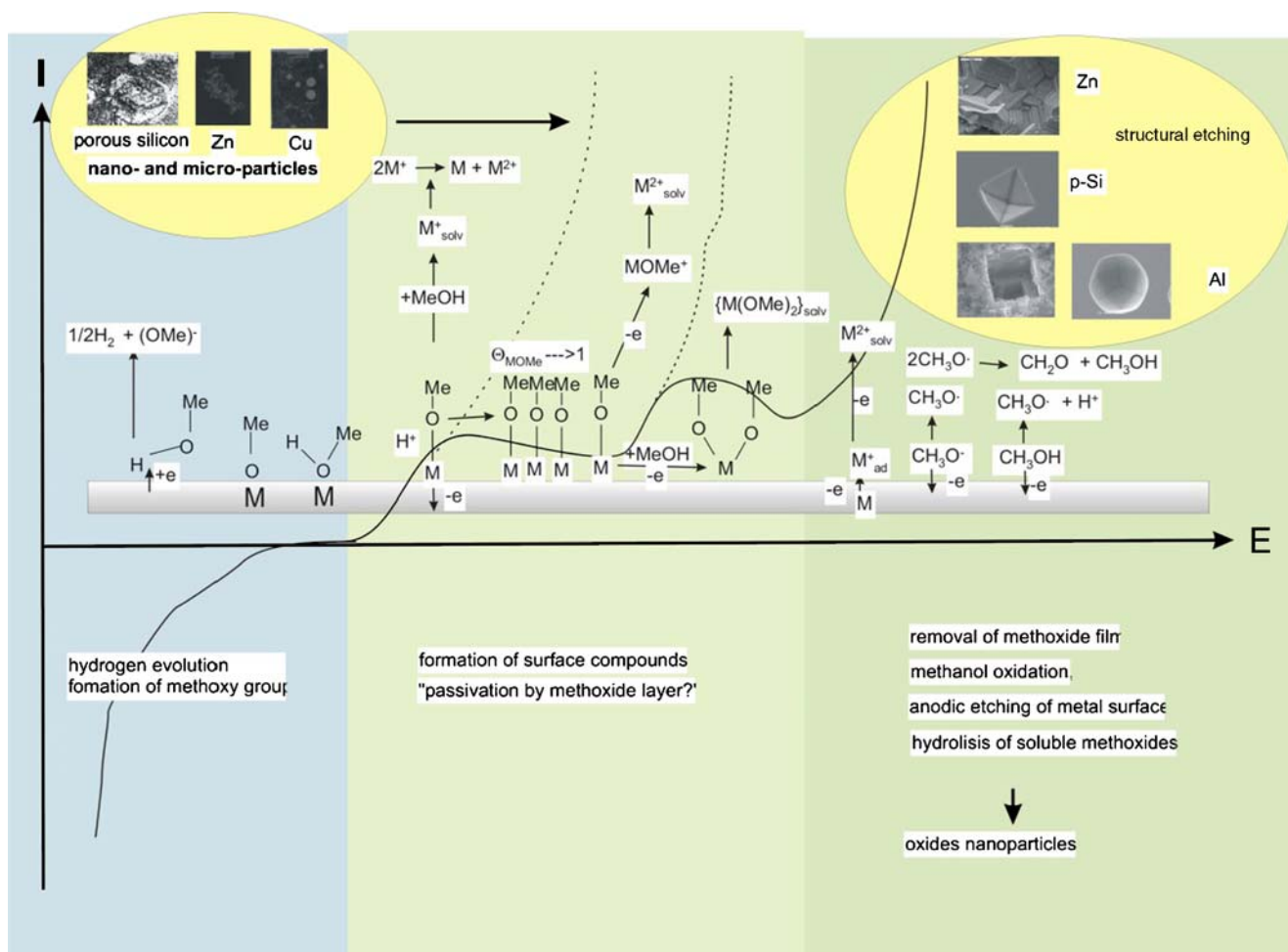
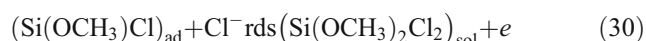
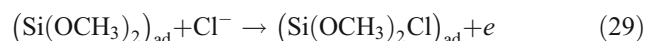
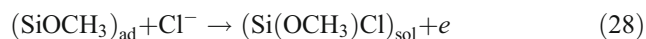
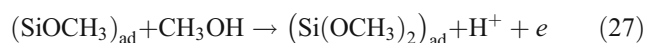
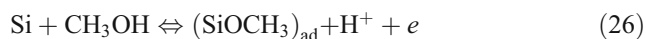


Fig. 14 Scheme of anodic behavior of divalent metal in methanol solvent

second peak current density to the potential scan rate indicates that dissolution process is controlled with adsorption of intermediate on electrode surface [16].

XPS measurements showed the presence of Si–OCH₃ bound on silicon surface, which indicates that molecules of methanol take part in the process. The anodic reaction order $d\log i/d\log[Cl^-]$ amounting 0.5/0.65 (dependent on crystallographic orientation of Si single crystal) suggest that chloride ions take part in further steps of electrode reaction [50].

Anodic reaction of silicon dissolution in methanolic solutions most probably proceeds according to the following reactions:



Formation of metal and oxide nanoparticles in alcohol solutions

Processes of anodic etching of metals in alcohol solutions of electrolytes at high anodic potential can find application for the synthesis of metal and oxide nanoparticles [31, 33, 51, 52] and for structural etching of metals and semiconductors [30, 50]. Figure 14 presents the scheme of anodic properties of divalent metal in methanol, possible electrochemical processes and formation of corrosion products.

Anodic etching of metal surface at high anodic potentials leads to the formation of soluble alkoxides. Nucleation of oxide micro- or nanoparticles occurs in mixed alcohol–water systems, depending on solvent and solute composition, as a result of the hydrolysis of soluble alkoxides. We obtained nanoparticles of ZnO and Cu₂O by means of anodic dissolution of zinc and copper in ethanol electrolytes [31, 53]. Figure 15 presents the transmission electron microscopy (TEM) of nanopowder of ZnO obtained during anodic etching of Zn in C₂H₅OH–3%H₂O–0.1 M LiCl solution [52].

Voltammetric studies of silver in saturated NaNO₃–C₂H₅OH revealed that anodic silver dissolution occurs above 0.6 V. For potentials higher than 0.8 V, oxidation of ethanol takes place [33]. In a course of chronoamperometric polarization, a precipitate was obtained for potential higher

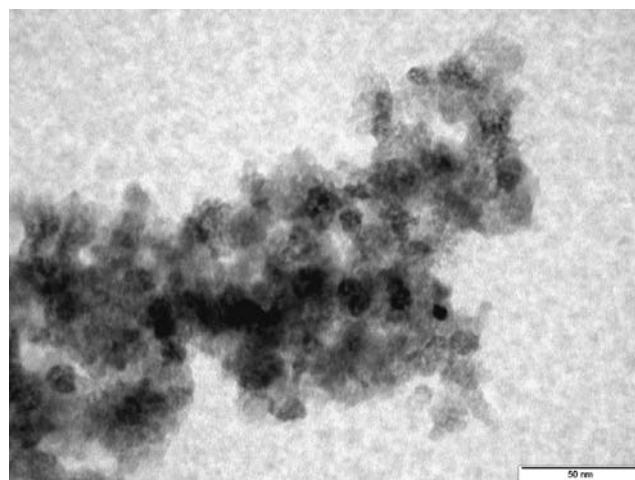
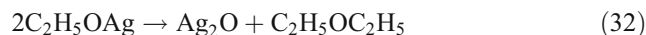
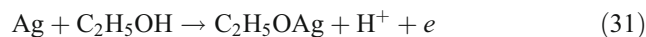


Fig. 15 TEM nanopowders obtained during chronoamperometric polarisation of Zn at potential –400 mV in 0.1 M LiCl–C₂H₅OH+3%H₂O

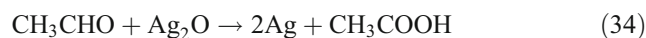
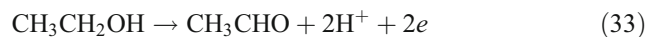
than 0.8 V, which suggests that ethanol oxidation plays an important role in the process.

The proposed mechanism assumes that both Ag dissolution and oxidation of ethanol to aldehyde takes place on anodic surface. The reaction of aldehyde with Ag₂O leads to the formation of silver nanoparticles.

$$E > 0.6 \text{ V}$$



$$E > 0.8 \text{ V}$$



The size of obtained metallic silver nanoparticles is of the order of approximately 20 nm [52].

Summary

- Anodic oxidation of metals in anhydrous alcohols proceeds with the formation of relatively stable surface alkoxy compounds. At low over-voltage, the surface anodic product acts as inhibitor membrane and plays a similar role to hydroxide layer in pre-passive range in aqueous solutions.

- At high anodic over-voltage, especially in the potentials range of alcohol oxidation, protective film loses its properties and metal corrosion occurs.
- The soluble product of alcoxides can be used for the production of nano-oxide particles and nano-metal particles in the course of chemical reaction in bulk solutions (hydrolysis, reduction and oxidation) coupled with electrochemical etching of metal surface.

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