Cathodic Reactions on the Surface of Nickel in Methanol Solutions of Electrolytes

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Abstract

This paper concerns the cathodic reactions occurring on the surface of nickel in methanolic solutions of electrolytes. Methanol reduction process, in this potential range, is inhibited by formation of surface compound, product of reaction parallel to methanol reduction – oxidation of nickel with participation of CH_3OH molecules. Competitive processes, formation of surface product (reaction of metal surface with methanol) and its dissolution (reaction of surface product with complexing agent), decide about free surface area on which can occur reduction of methanol. Presence of complexing agents – CH_3O^- and Cl^- anions, causes "cleaning" the surface of surface anodic product and thereby facilitates cathodic reduction of methanol (reactions 3, 5, 6, 7). Removing of surface product is the process controlled by diffusion of anions to the electrode surface.

Keywords: methanol, nickel, cathodic reduction

1. Introduction

Electrochemical and corrosion behavior of metals in anhydrous alcoholic solution of electrolytes are very important as well for science as for applications reasons. This importance is connected with wide application of metal-alcohol reaction in chemical engineering, in production of oxide nanoparticles of metal and their oxides [1-5] and application of alcohols as liquid fuels in motor industry (bioethanol) and fuel cells (methanol). Scientific importance is connected with not sufficient knowledge about participation of methanol molecules in electrochemical reactions metal – alcohol, especially lack of information about structure of surface passive layer forming on the surface of metals in alcoholic solutions.

In our previous works, devoted to the electrochemical properties of the metal in an alcoholic media we focused on their characteristics in terms of anodic dissolution and passivation of metals[1,6-12] and on the use of these processes to the formation of metal and oxide nano-particles [1,2-4]. Little attention was paid to the cathodic reactions in anhydrous alcohols. These reactions can greatly affect the formation of the alkoxy product on the metal surface, a phenomena similar to alkalization of metal surface in an aqueous media during cathodic polarization.

The aim of the presented work was to explain the mechanism of cathodic reduction of anhydrous methanol, especially at low over voltages, when surface product can be formed on the on metal surface.

2. Experimental

Cyclic voltammetric measurements (CV) were performed with use of the electrochemical workstations AutoLab PGStad 30 in three-electrode system (working electrode – Ni, counter electrode – Pt, reference electrode – Ag/AgCl). Every potential value has been recalculated vs. standard hydrogen electrode. Investigations were performed in anhydrous solutions of LiCl and CH_3ONa dearated

by argon purging at the temperature 25 ºC. Dehydrated methanol was obtained by means of Lund and Bjerrum methods [13] (water content in alcohol was below 0.02 %).

3. Results

3.1. CH₃OH – CH₃ONa solution

Fig. 1 illustrates the polarization of nickel in CH_3OH-0.1M CH_3ONa at low (100 rpm) and high (1500 rpm) rotation rate of disk electrode. For low rotation speed the cathodic curve, from cathodic to anodic direction (forwards curve), contains of a well defined Tafel slope and limiting diffusion current at large overvoltages (Fig. 1a).

a)

b)
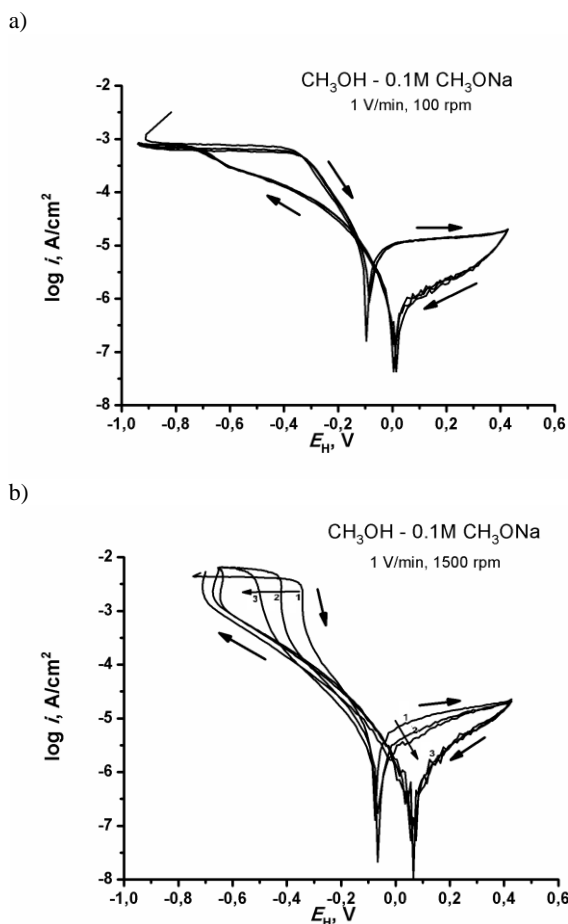
Fig. 1. Cyclic voltammetric polarization curves of nickel CH_3OH-0.1M CH_3ONa, 100 rpm (a) and 1500 rpm (b)

The anodic part of polarization curve (in forwards direction) shows limiting current related to the formation of surface product. The product inhibits the anodic and cathodic reaction what was confirmed by shape of reverse polarization curve (hysteresis). At low rotation rate polarization curves are very well reproducible in

subsequent cycles of polarization (Fig. 1a). At high rotation speeds the anodic and cathodic current decreases in subsequent cycles, which proves the gradual overlap of the anode electrode process (Fig. 1b).
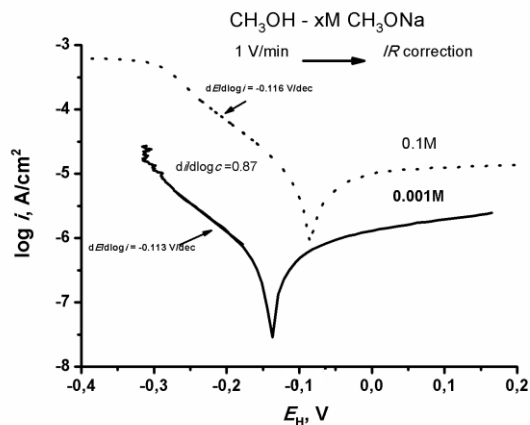

Fig. 2. Effect of methylate concentration on polarization of nickel in anhydrous methanol, (a) plot in anodic direction, (b) plot in cathodic direction (reverse curve)

Fig. 2 presents the effect of concentration of sodium methylate on the polarization of nickel in solutions of CH_3OH-CH_3ONa. For transparency, the scanning in the anodic direction (for words plot) and cathodic direction (reverse plot) are shown separately (Fig. 2a and 2b, respectively). Significant influence of methylate concentration on the course of polarization is visible. The Tafel slope of cathodic plot equal to about -0.120 V/dec and the reaction order of methylate close to unity (di/dlog c=0.87) may indicate that cathodic polarization, conducted from the potential of approximately -1 V in anodic direction (for bare, free from surface compounds nickel electrode), is the reduction of methanol according to reaction (1).

$$CH_3OH + e = CH_3O^- + \frac{1}{2}H_2 \tag{1}$$

Polarization in the reverse direction (Fig. 2b) shows that the electrode is covered with anodic product that inhibits the cathodic and anodic reactions.

The voltammetric diagram in methanol with very low content of methoxy ions indicates the formation and reduction of surface compound on nickel electrode (Fig. 3a). The diagram is limited to low overvoltages because of low conductivity of the solution. The process is diffusion controlled (Fig. 5) and is related to one electron oxidation – reduction process (Fig. 4).

At high concentration of sodium methylate (Fig. 3b) formation of surface product is not dependent on the diffusion (Fig. 3b and Fig. 7). Diffusion control can be observed only at high cathodic overvoltages (Fig. 3b and 6).

The increasing influence of diffusion on anodic and cathodic reactions on nickel surface in anhydrous methanol, as a result of a decrease of concentration of methoxy ions, was confirmed in polarization experiments on disc electrode (Fig. 8).

Presented research show influence of methanolate anions on the course of electrode reactions on the nickel surface in anhydrous methanol. In such environment nickel surface undergoes rapid

coverage with surface product [NiOCH$_3$]$_{ad}$ type (reaction 1) as an effect of methanol electrosorption.
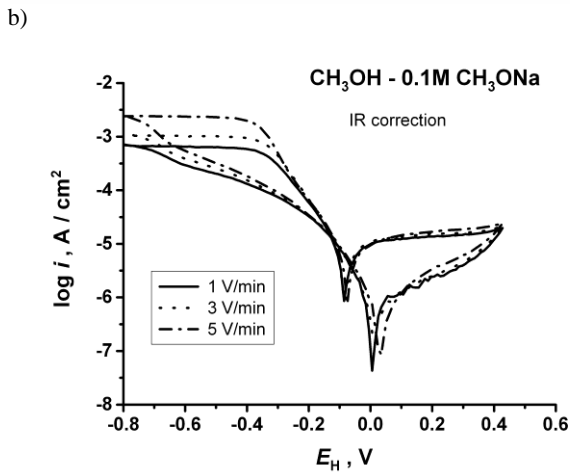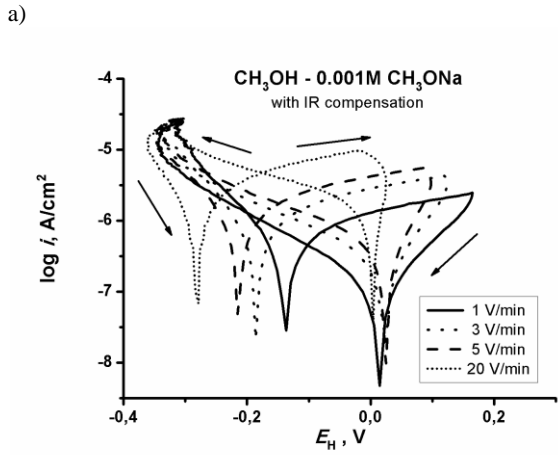
a)

b)

Fig. 3. Effect of scan rate on polarization of nickel in anhydrous methanol containing: 0.001M CH$_3$ONa (a) and 0.1M CH$_3$ONa (b)
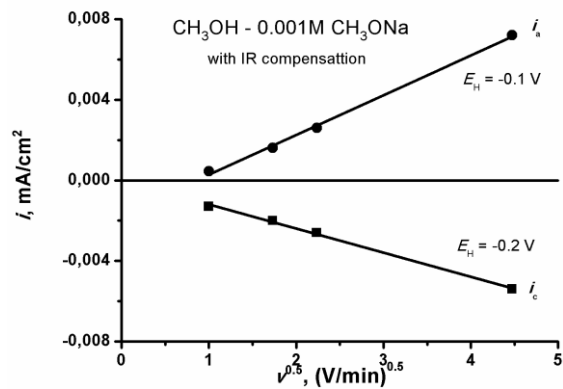

Fig. 4. Effect of scan rate on anodic and cathodic current for nickel in anhydrous methanol containing: 0.001M CH$_3$ONa.
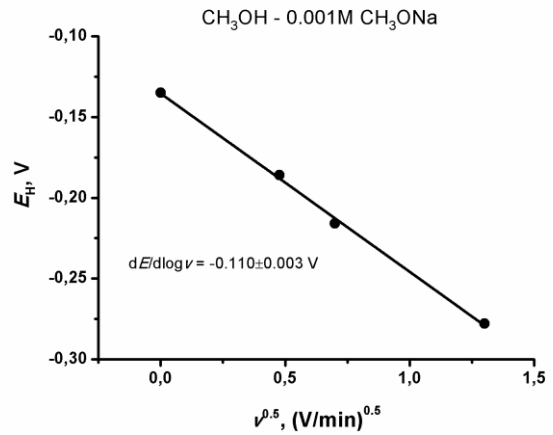

Fig. 5. Effect of scan rate on stationary potential for nickel in anhydrous methanol containing: 0.001M CH$_3$ONa
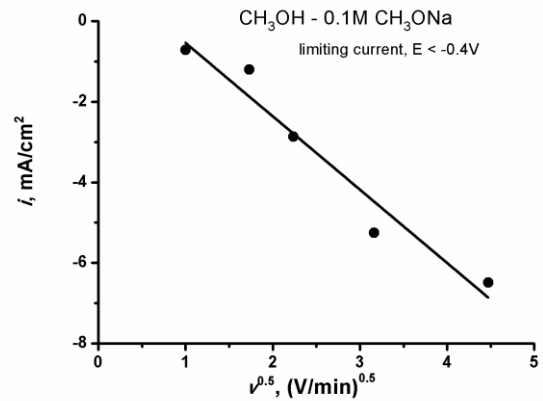

Fig. 6. Effect of scan rate on stationary potential for nickel in anhydrous methanol containing: 0.1M CH$_3$ONa
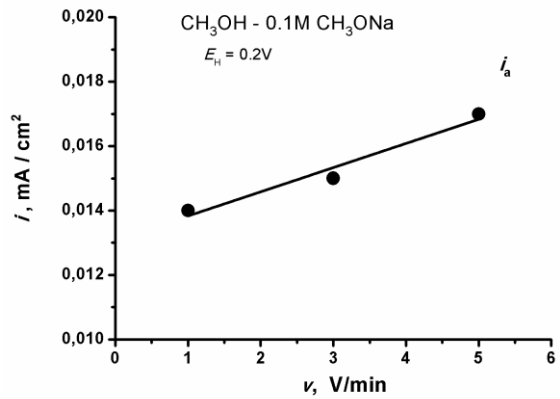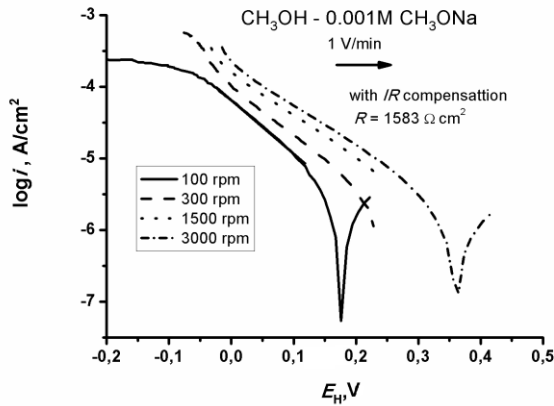

Fig. 7. Effect of scan rate on anodic current for nickel in anhydrous methanol containing: 0.1M CH$_3$ONa
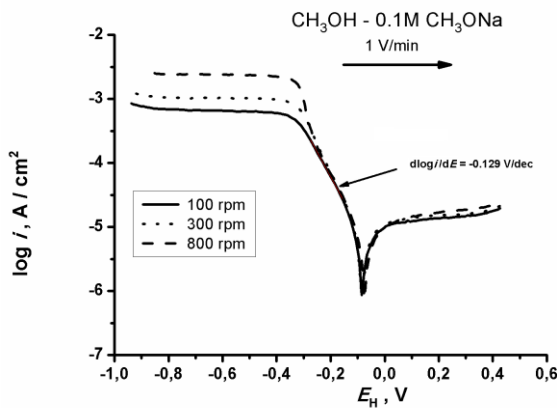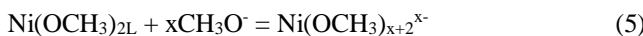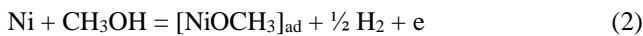
a)

b)

Fig. 8. Effect of rotation rate of disc electrode on polarization of nickel in anhydrous methanol containing: 0.001M CH_3ONa (a) and 0.1M CH_3ONa (b)

In cathodic area neutral molecules of methanol adsorb preferentially relative to the negative methanolate ions. Methanol molecules take also part in further oxidation of nickel leading to the formation of $Ni(OCH_3)_{2L}$ (reaction 4), while methanolate ions take part in complexing reactions of Ni(I) and Ni(II) and thereby activate metal surface by removing of anodic product (reactions 3 and 5). This activation allows methanol reduction according to reaction 1 parallel to reactions 2-5.

$$Ni + CH_3OH = [NiOCH_3]_{ad} + ½ H_2 + e \qquad (2)$$

$$[NiOCH_3]_{ad} + xCH_3O^- = Ni(OCH_3)_{2L} + e \qquad (3)$$

$$[NiOCH_3]_{ad} + CH_3OH = Ni(OCH_3)_{2L} + H^+ + e \qquad (4)$$

$$Ni(OCH_3)_{2L} + xCH_3O^- = Ni(OCH_3)_{x+2}^{x-} \qquad (5)$$

3.2. CH₃OH – LiCl solution

Fig. 9 illustrates effect of chloride anions on nickel polarization in absolute alcohol. Influence of Cl^- anions is similar to the effect of methanolate ions. Increase of concentration of chlorides causes increase of current density as well in cathodic as anodic potential range. In both cases reaction of formation and reduction of anodic product is diffusion controlled (Fig. 10 and 11).
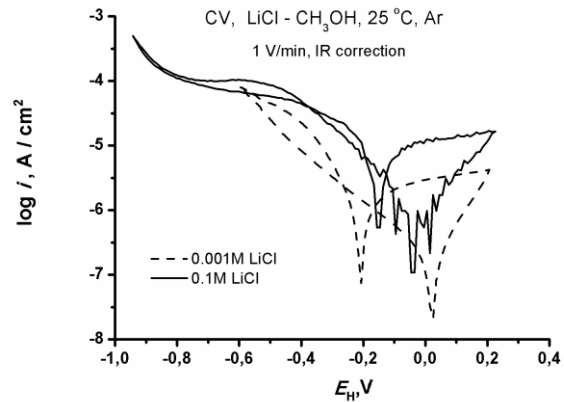

Fig. 9. Effect of chloride concentration on polarization of nickel in anhydrous methanol
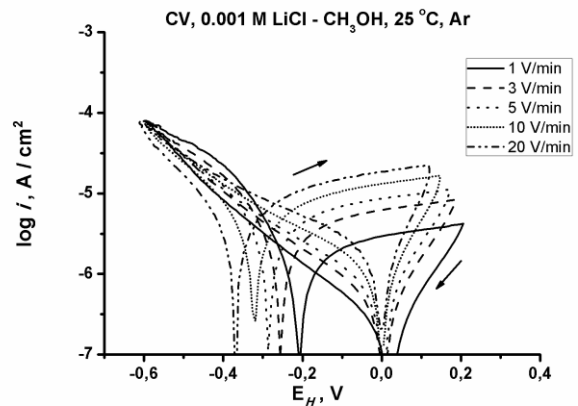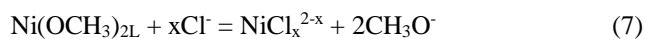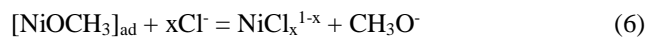

Fig. 10. Effect of scan rate on polarization of nickel in anhydrous methanol containing: 0.001M LiCl (a) and 0.1M LiCl (b)

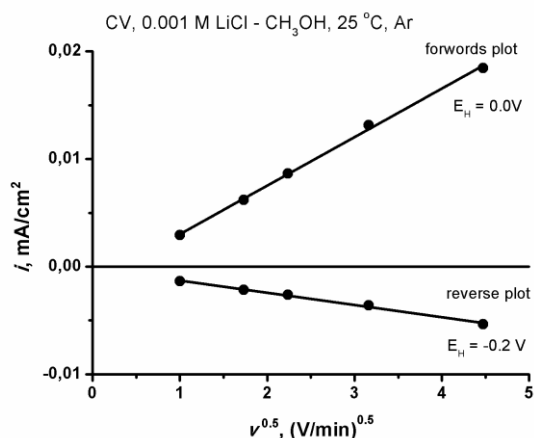Activating influence of chloride anions can be described with reactions 6 and 7, parallel to the reactions 2 and 4.

$$[NiOCH_3]_{ad} + xCl^- = NiCl_x^{1-x} + CH_3O^- \qquad (6)$$

$$Ni(OCH_3)_{2L} + xCl^- = NiCl_x^{2-x} + 2CH_3O^- \qquad (7)$$

Fig. 11. Effect of scan rate on stationary anodic and cathodic current for nickel in anhydrous methanol containing 0.001M LiCl
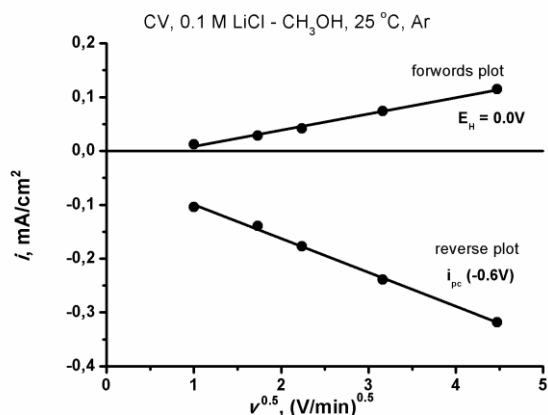

Fig. 12. Effect of scan rate on stationary anodic and cathodic current for nickel in anhydrous methanol containing 0.1M LiCl

4. Conclusions

Research conducted on Ni electrode in low anodic and cathodic overpotentials (without participation of soluble nickel compounds) allowed to determine participation of methanol and complexing agents – methanolate and chloride anions in methanol reduction process.

Undoubtedly, in investigated solutions the cathodic process is reduction of methanol proceeding according reaction (1). This process is efficiently inhibited in low over potentials range by parallel processes (2) and (4) leading to the coverage of electrode surface with $[NiOCH_3]_{ad}$ and $Ni(OCH_3)_{2L}$ products. Presence of complexing agents – CH_3O^- and Cl^- anions causes "cleaning" the

surface of anodic product and thereby facilitates cathodic reduction of methanol (reactions 3, 5, 6, 7). The surface product removing process is controlled by the diffusion of anions to the electrode surface.

Presented study is the first stage of wider research project. The next stage will embrace spectro-electrochemical "in situ" measurements (FTIR-ATR) which will allow to determine the surface products composition. There will be also developed the computer simulation of the electrode processes concerning parallel elementary cathodic and anodic reactions with participation of surface products.

Acknowledgements

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Reakcje katodowe na powierzchni niklu
w metanolowych roztworach elektrolitów

Streszczenie

Praca poświęcona jest reakcjom katodowym zachodzącym na powierzchni niklu w metanolowych roztworach elektrolitów w obszarze małych nadpotencjałów katodowych. W obszarze tym proces redukcji metanolu hamowany jest tworzeniem powierzchniowego produktu będącego rezultatem równoległej do redukcji metanolu reakcji utleniania niklu z udziałem cząsteczek CH_3OH. Konkurencyjne procesy tworzenia produktu powierzchniowego (reakcja powierzchni z metanolem) i roztwarzania (reakcja produktu powierzchniowego z czynnikiem kompleksującym), decydują o obszarze swobodnej powierzchni na której zachodzi redukcja metanolu. Obecność czynników kompleksujących – anionów CH_3O^- oraz Cl^- powoduje „oczyszczanie" powierzchni z produktu anodowego i ułatwia tym samym redukcję katodową metanolu (reakcje 3,5,6,7). Proces usuwania produktu powierzchniowego jest procesem kontrolowanym dyfuzją anionów do powierzchni elektrody.