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*V.S. Protsenko, L.S. Bobrova, T.E. Butyrina, F.I. Danilov***HYDROGEN EVOLUTION REACTION ON Cr–C ELECTROCATALYSTS
ELECTRODEPOSITED FROM A CHOLINE CHLORIDE BASED TRIVALENT
CHROMIUM PLATING BATH****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

Electrocatalytic activity of chromium-carbon electrodes towards hydrogen evolution reaction was studied in this work. Chromium-carbon coatings were electrodeposited from a trivalent chromium plating bath on the basis of a deep eutectic solvent. The plating electrolyte contained choline chloride, chromium(III) chloride and water. The electrocatalytic behavior was studied by means of linear voltammetry method and electrochemical impedance spectroscopy in an alkali medium (1 M NaOH). Our findings showed that the exchange current density of the hydrogen evolution reactions for Cr–C electrodeposited electrocatalysts was higher than that for Cr coatings. The results of linear voltammetry and electrochemical impedance spectroscopy revealed that the electrochemical reduction (i.e. Volmer step) is a rate-determining step of the hydrogen evolution reaction occurring on Cr and Cr–C electrodes in an alkaline solution. The changes in the electrocatalytic properties may be associated with the changes in the electronic structure. Thus, the electrodeposited chromium-carbon coatings fabricated from a deep eutectic solvent seem to be very promising to develop new electrocatalysts in the hydrogen evolution reaction for water-splitting devices.

Keywords: kinetics, hydrogen evolution reaction, electrocatalysis, chromium-carbon coatings, deep eutectic solvents, trivalent chromium electrodeposition.

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Introduction

The development of new and effective electrocatalysts for hydrogen evolution reaction (HER) is an important task of contemporary theoretical and applied electrochemistry [1]. Various metals can be used as a base for electrocatalysts: Pt, Ni, Fe, etc. [1,2]. Although pure chromium is hardly considered as a possible electrocatalyst for the HER, chromium-based alloys look as very promising materials to this effect. Chromium-carbon alloys (chromium carbide) attract special attention in this connection. For instance, Schmuecker et al. showed that chromium carbide Cr_7C_3 exhibits a relatively high electrocatalytic activity towards the hydrogen evolution reaction in sulfuric acid solution [3]. Chromium carbide demonstrated high hydrogen evolution activity in 100% phosphoric acid [4].

Chromium carbides can be synthesized by various methods, electrodeposition being a simple, available and convenient approach to fabricate Cr–C layers. A number of papers reported the electrodeposition of Cr–C coatings with enhanced

corrosion resistance and improved electrocatalytic activity using aqueous chromium plating baths [5–9]. However, it is known that aqueous chromium electroplating baths suffer from a number of shortcomings. In this context, non-aqueous chromium electrolytes based on deep eutectic solvents (DESs), a new generation of room temperature ionic liquids, seem to be very promising [10–16]. Electroplating electrolytes prepared using DESs are considered as a «green» alternative to both aqueous systems and those based on organic solvents; such plating baths are characterized by high performance and stability. It is important that DESs-based chromium plating electrolytes allow depositing coatings with a relatively high thickness [14,15]. Our preliminary investigations showed that these chromium coatings include some carbon and exhibit reduced overvoltage of the HER [15]. As far as we know, there is no detailed information on the electrocatalytic behavior of Cr–C coatings deposited from DESs-based trivalent chromium electrolyte. Therefore, this work was aimed to determine the

electrocatalytic properties of these chromium-carbon electrodeposits as compared to Cr coatings in an alkali medium.

Experimental

The coatings were electrodeposited on a plate of gold ($S=1.77 \text{ cm}^2$) fixed in a plastic holder. Prior to each experiment, the gold surface was polished with filter paper, then treated by HCl aqueous solution (1:1 vol.) and thoroughly rinsed with distillate water.

Chromium-carbon coatings were deposited from a plating bath containing choline chloride, chromium (III) chloride and water in 2.5:1:15 molar ratios, respectively [12–15]. The bath formulation and preparation were reported in detail elsewhere [12,13]. The electrodeposition was conducted at the current density of 5 A dm^{-2} and the bath temperature of 40°C . Pt electrode was used as an anode without separation of electrodes compartments. According to the results of our previous study [15], the chromium-based coatings deposited under such conditions contain ca. 5 wt.% of carbon.

The «pure» chromium coatings were electrodeposited from a conventional hexavalent chromium plating bath containing 2.5 M CrO_3 and 0.025 M H_2SO_4 . The electrodeposition was carried out at the current density of 40 A dm^{-2} and the temperature of 45°C . Lead anodes were used to deposit Cr coatings from the hexavalent chromium plating bath. The electrolysis duration in all cases was adjusted to achieve the average thickness of deposits of ca. $10 \mu\text{m}$.

The electrocatalytic behavior of coatings deposited on Au surface was studied by means of linear voltammetry method and electrochemical impedance spectroscopy (EIS) using a Potentiostat/Galvanostat Reference 3000 (Gamry, USA). The investigation of electrocatalytic activity was performed in 1 M NaOH aqueous solution at the temperature of 25°C . A common thermostatted glass three-electrode cell was used in these experiments; the electrode compartments being divided by a glass porous diaphragm. Porous graphite was used as a counter electrode. Dissolved atmospheric oxygen was removed by purging purified electrolytic hydrogen.

The potential scan rate in voltammetric measurements was 50 mV s^{-1} . Electrochemical impedance spectra were recorded at constant values of the overvoltage of the HER ($\eta=-100, -200$ and -300 mV) in the frequency range of 0.01 Hz to 100 kHz, the AC voltage amplitude was equal to 5 mV. To set a specified value of the overvoltage, the equilibrium potential of the HER was calculated on the basis of Nernst equation taking into account the

measured value of solution pH.

The results of EIS measurements were processed (that means the development of electrical equivalent circuits and the determination of quantitative parameters of their elements) using Gamry Elchem Analyst software.

Results and discussion

Fig. 1 shows the polarization curves of the electrodeposits under consideration recorded in 1 M NaOH solution. The polarization curve of Au substrate is also given for the sake of visualization. There are no current peaks of active dissolution of both Cr and Cr–C coating as would be expected in an alkaline electrolyte. The cathodic segments of the recorded current waves correspond to the HER occurring in NaOH solution. It is clearly seen that the overvoltage of the HER on Cr–C coatings is less than that of Cr deposits which indicates an improved electrocatalytic activity of chromium-carbon films fabricated from DES-based plating bath. The overvoltage of the HER proceeding on gold substrate is less than on «usual» chromium but higher than on Cr–C coating.

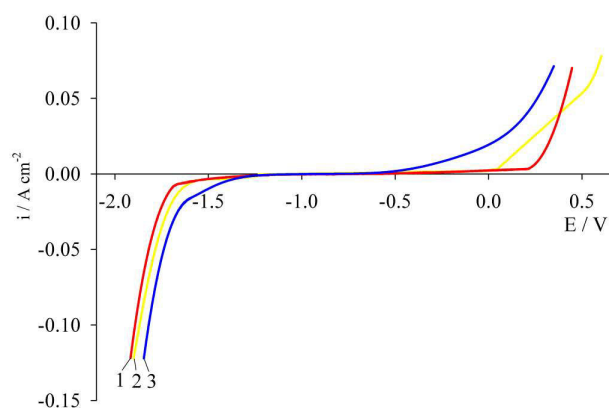


Fig. 1. Polarization curves of gold substrate and electrodeposited coatings recorded in 1 M NaOH aqueous solution: (1) Cr coating deposited from Cr(VI) plating bath, (2) Au substrate, (3) Cr–C coating deposited from Cr(III) plating bath

The polarization curves in the region corresponding to the HER proved to obey well the Tafel equation:

$$\eta = a + b \log|i|, \quad (1)$$

where η is the overpotential; i is the current density; b is the Tafel slope; and a is the Tafel intercept related to the exchange current density (i_0).

The exchange current density and transfer

coefficient (α) can be determined by the following formulae:

$$\log i_0 = -\frac{a}{b}; \quad (2)$$

$$\alpha = \frac{2.303RT}{bF}, \quad (3)$$

where R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the thermodynamic temperature (K) and F is the Faraday constant ($96487 \text{ A s mol}^{-1}$).

Table 1 summarizes the calculated Tafel parameters for the HER in an alkaline solution.

Table 1
Kinetic parameters of the HER obtained from Tafel dependences recorded in 1 M NaOH at 25°C

Kinetic parameter	Electrode	
	Cr (deposited from Cr(VI)-based electrolyte)	Cr-C (deposited from Cr(III)-based electrolyte)
$a, \text{ V}$	1.057	0.857
$b, \text{ V dec}^{-1}$	0.146	0.139
α	0.40	0.43
$i_0, \text{ A cm}^{-2}$	$0.60 \cdot 10^{-7}$	$6.58 \cdot 10^{-7}$

It is well known that the Tafel slope can give information about the mechanism of hydrogen evolution reaction. When electrochemical desorption (Heyrovsky step, $\text{M}-\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^- + \text{M}$, where M denotes the surface metal atoms on which hydrogen atom is adsorbed) or chemical desorption (Tafel step, $\text{M}-\text{H}_{\text{ads}} + \text{M}-\text{H}_{\text{ads}} \rightarrow \text{H}_2 + 2\text{M}$) are rate-determining steps, the Tafel slope is about 40 and 30 mV dec^{-1} , respectively. However, the Tafel slope is ca. 116 mV dec^{-1} , when electrochemical reduction (Volmer step, $\text{M} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{M}-\text{H}_{\text{ads}} + \text{OH}^-$) is a rate-determining step. The data given in Table 1 clearly show that the Tafel slopes are close to 116 mV dec^{-1} rather than to 30 or 40 mV dec^{-1} ; therefore, the charge transfer is a rate-determining step of the HER occurring on Cr and Cr-C electrodes in an alkaline solution.

It should be noted that the calculated Tafel slopes exhibit somewhat higher values as predicted theoretically. Such behavior was observed earlier [4]; it can be explained by the fact that a possible presence of relatively resistive oxide layers on the electrode surface can increase the apparent Tafel slope.

It is accepted that the value of exchange current density can serve as a criterion of electrocatalytic activity [1,2]. Inspection of the data presented in

Table 1 shows that the electrocatalytic properties of Cr-C coatings are substantially better than those of «usual» chromium deposits (the current exchange densities differ more than ten times).

Electrochemical impedance spectroscopy is known to be a non-destructive and convenient technique which may provide detailed and valuable information on the kinetics and mechanism of an electrochemical reaction. Fig. 2 shows the Nyquist plots obtained for the HER proceeding on Cr and Cr-C electrodeposited coatings in 1 M NaOH solution. The measurements were performed at the following values of electrode overpotential (with respect to the equilibrium electrode potential of the HER calculated using Nernst equation): $\eta = -100 \text{ mV}$; -200 mV and -300 mV . As can be seen, the impedance plots look like a depressed semicircle, which indicates that the electrochemical process is controlled by the charge transfer step and occurs on inhomogeneous electrode surface. Such behavior can be interpreted by the so-called constant phase element (CPE). An equivalent circuit describing experimental impedance data is shown in Fig. 3. It includes polarization resistance of electrochemical reaction (R_{ct}), constant phase element characterizing the interface of «solid electrode/solution» (CPE), and ohmic resistance of solution (R_s).

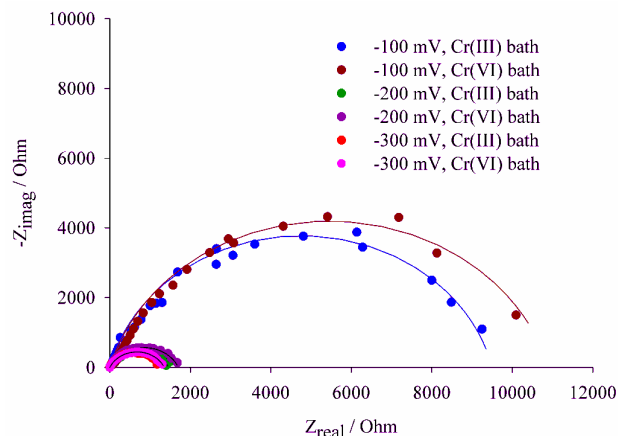


Fig. 2. Nyquist plots of coatings recorded in 1 M NaOH aqueous solution. The type of the plating bath and the values of overpotential are shown in the figure

The electrochemical impedance of the CPE can be expressed by the following formula:

$$Z_{\text{CPE}} = \left[Q(j\omega)^n \right]^{-1}, \quad (4)$$

where Q is a constant; $j = \sqrt{-1}$ is the imaginary

unit; ω is the angular frequency of alternating current; and n is the dimensionless empirical exponent corresponding to phase deviation and associated with inhomogeneity of the electrode surface.

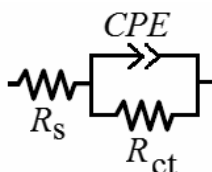


Fig. 3. Electrical equivalent circuit used to simulate the impedance of the HER on electrodeposited coatings

The experimentally measured values in Fig. 2 are shown as symbols and the continuous lines are drawn as a result of fitting using the electrical equivalent circuit shown in Fig. 3. The calculated parameters of the electrochemical impedance of the HER are given in Table 2.

The obtained results indicate that the polarization resistance of the electrochemical reaction, R_{ct} , diminishes with increasing the overpotential as can be expected. The value of R_{ct} in the case of Cr coatings prepared from Cr(VI) electrolyte is higher than that of Cr-C coatings from trivalent chromium bath other conditions being equal. This is in good agreement with the data on polarization measurements (see Fig. 1 and Table 1) and additionally confirmed an enhanced electrocatalytic activity of chromium-carbon electrodeposits.

As concerns the exponent n in the CPE, it can possess the value from 0.5 (porous electrode) to 1 (ideally planar electrode, i.e. a perfect capacitor) characterizing energy and geometric heterogeneity of the electrode surface. The higher the n value, the greater is the extent of heterogeneity of electrode surface. The calculated values of n are lower than unity showing appreciable heterogeneity of electrodeposited Cr and Cr-C layers. We think that the values of n for Cr and Cr-C coatings do not

differ substantially in a first approximation.

The value of Q in Equation (4) is often associated with the surface area of an electrode which is available for electrochemical reaction, because it is directly related to average double layer capacitance. The comparison of the calculated Q values shows that the real surface area of coatings deposited from Cr(III)-based electrolyte is less than of coatings fabricated in conventional Cr(VI) plating bath. This observation is very important, since it indicates that the improved catalytic properties of Cr-C coatings are connected with a real electrocatalytic effect rather than with the expansion of the electrode surface area (an increase in surface roughness).

Thus, there is an enhanced electrocatalytic activity of Cr-C electrodeposits as compared with Cr coating, although the mechanism of the HER remains the same. It was reported [4] that the highest catalytic activity for the HER is achieved when binding energy of the adsorbed hydrogen atoms takes some intermediate value. Seemingly, the H binding energy on chromium carbides is closer to this optimum than that on «pure» chromium. According to the conclusion drawn in work [3], the catalytic activity of metastable chromium carbides well correlates with differences in the density of states and different types of bonding within the structure. The higher the density of states at the Fermi energy level, the higher is the electrocatalytic activity.

Conclusions

In this work, the electrocatalytic properties of chromium-carbon electrodes prepared from the plating bath on the basis of a deep eutectic solvent have been investigated for the first time. The exchange current density of the hydrogen evolution reaction for Cr-C electrodeposited electrocatalysts is higher than that of Cr coatings although the mechanism of the HER remains the same on both investigated electrodes. The observed changes in the electrocatalytic behavior can be related to the changes in the electronic structure rather than to the expansion of the real surface area of the electrode.

Table 2
Calculated parameters of the HER obtained from electrochemical impedance spectra recorded in 1 M NaOH at 25°C

Electrode	Electrode overpotential η , mV	Parameters			
		R_s , Ω	R_{ct} , $k\Omega\text{ cm}^2$	$Q \cdot 10^6$, $\Omega^{-1}\text{ s}^n\text{ cm}^{-2}$	n
Cr (deposited from Cr(VI)-based electrolyte)	-100	2.2	10.9	120.5	0.835
	-200	2.1	1.70	200.0	0.750
	-300	2.1	1.35	260.0	0.740
Cr-C (deposited from Cr(III)-based electrolyte)	-100	2.2	9.50	66.5	0.855
	-200	2.2	1.45	150.0	0.755
	-300	2.1	1.25	190.0	0.749

Thus, the electrodeposited chromium-carbon coatings fabricated from a deep eutectic solvent can be used to develop new electrocatalysts for the hydrogen evolution reaction for water-splitting devices.

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РЕАКЦІЯ ВИДІЛЕННЯ ВОДНЮ НА Cr–C ЕЛЕКТРОКАТАЛІЗАТОРІ, ОСАДЖЕНОМУ З ЕЛЕКТРОЛІТУ НА ОСНОВІ ХОЛІН ХЛОРИДУ ТА ТРИВАЛЕНТНОГО ХРОМУ

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У роботі досліджена електрокаталітична активність хром-карбонівих електродів стосовно реакції виділення водню. Хром-карбоніві покриття були електроосаджені з електроліту на основі сполук тривалентного хрому та низькотемпературного евтектичного розчинника. Електроліт містив холін хлорид, хром(III) хлорид та воду. Електрокаталітична поведінка вивчалася за допомогою методів лінійної вольтамперометрії та електродного імпедансу у лужному середовищі (1 М NaOH). З отриманих результатів випливає, що густина струму обміну реакції електровиділення водню для електроосадженого Cr–C електрокаталізатора була вищою, ніж для Cr покриття. Дані лінійної вольтамперометрії та спектроскопії електродного імпедансу свідчать про те, що на Cr та Cr–C електродах у лужному середовищі швидкість визначальною стадією процесу виділення водню є перенесення заряду (стадія Фольмера). Зміни електрокаталітичних властивостей можуть бути пов'язані зі змінами у електронній структурі. Отже, електроосаджені хром-карбоніві покриття, отримані з електроліту на основі низькотемпературного евтектичного розчинника є вельми перспективними для розробки нових елект-

рокаталізаторів реакції виділення водню при електролізі води.

Ключові слова: кінетика; реакція виділення водню; електрокаталіз; хром-карбоніві покриття; низькотемпературні евтектичні розчинники; тривалентний хром; електроосадження.

HYDROGEN EVOLUTION REACTION ON Cr–C ELECTROCATALYSTS ELECTRODEPOSITED FROM A CHOLINE CHLORIDE BASED TRIVALENT CHROMIUM PLATING BATH

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Electrocatalytic activity of chromium-carbon electrodes towards hydrogen evolution reaction was studied in this work. Chromium-carbon coatings were electrodeposited from a trivalent chromium plating bath on the basis of a deep eutectic solvent. The plating electrolyte contained choline chloride, chromium(III) chloride and water. The electrocatalytic behavior was studied by means of linear voltammetry method and electrochemical impedance spectroscopy in an alkali medium (1 M NaOH). Our findings showed that the exchange current density of the hydrogen evolution reactions for Cr–C electrodeposited electrocatalysts was higher than that for Cr coatings. The results of linear voltammetry and electrochemical impedance spectroscopy revealed that the electrochemical reduction (i.e. Volmer step) is a rate-determining step of the hydrogen evolution reaction occurring on Cr and Cr–C electrodes in an alkaline solution. The changes in the electrocatalytic properties may be associated with the changes in the electronic structure. Thus, the electrodeposited chromium-carbon coatings fabricated from a deep eutectic solvent seem to be very promising to develop new electrocatalysts in the hydrogen evolution reaction for water-splitting devices.

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