Hydrogen Production Using an Electrocatalyst Fabricated from Environmentally Safe Chromium Plating Bath Based on a Deep Eutectic Solvent

V.S. PROTSENKO, L.S. BOBROVA, T.E. BUTYRINA, F.I. DANILOV
Ukrainian State University of Chemical Technology
Gagarin Ave., 5, Dnipro, 49005
UKRAINE
Vprotsenko7@gmail.com

Abstract: - The concept of using hydrogen as a reliable solution to the problems of planetary warming and pollution requires the development of high-performance and sustainable methods of H_2 production. The electrolysis of water seems to be a very promising approach to the hydrogen synthesis. In this context, there is an urgent need to create efficient, inexpensive and environmentally friendly electrocatalysts for the hydrogen evolution reaction. In this study, chromium-based coatings as a heterogeneous electrocatalyst for the hydrogen evolution process were electrodeposited from a trivalent chromium plating bath based on a deep eutectic solvent (a green and available analogue of room temperature ionic liquids). The plating bath contained a liquid mixture of chromium (III) chloride, choline chloride and extra water. The fabricated coatings were tested as electrocatalysts towards the hydrogen evolution reaction in an acidic medium (0.5 M H_2SO_4). The results of linear voltammetry and electrochemical impedance spectroscopy showed that the electrocatalytic activity of deposits fabricated from choline chloride-based bath towards the hydrogen evolution reaction is higher than that of Cr coatings deposited from common industrial hexavalent chromium plating bath.

Key-Words: - Hydrogen production, electrocatalysis, electrodeposition, coatings, trivalent chromium, deep eutectic solvent

1 Introduction

Hydrogen is nowadays considered as a promising energy carrier which forms the basis for the so-called "hydrogen economy" [1, 2]. The use of hydrogen can enhance the security of energy supply, appreciably mitigate the emission of greenhouse gases and create an inexhaustible source of energy. Thus, widespread adoption and implementation of technologies based on hydrogen will ensure reliable and sustainable energy production and satisfy all ecological and technical requirements.

Large-scale application of hydrogen requires development of efficient and safe ways for hydrogen production. Hydrogen can be synthesized by different methods, electrolysis of water being the most simple and viable technique with a low environmental impact [3]. Therefore, there is an urgent need to create available, high-performance and environmentally friendly electrocatalysts for the hydrogen evolution reaction (HER) [4].

It is known that electrocatalysts based on noble metals (Pt, Pd, etc.) exhibit good electrocatalytic activity but suffer from high cost and scarcity [4–6]. Therefore, the development of electrocatalysts for the HER using base metals attracts special attention of researchers [6–10]. In this context, chromium and its alloys seem to be promising materials. For example, chromium carbides of different composition showed a relatively high electrocatalytic activity towards the HER in acidic solutions [11, 12].

Various techniques can be applied to fabricate chromium carbides. Among these methods, the electrodeposition is the simplest and easiest one. The electrodeposition of Cr–C alloys was reported in a number of publications [13–15], aqueous Cr(III) electrolytes being commonly used to deposit metal layers. It should be noted that trivalent chromium electroplating is regarded as an environmentally friendly alternative to extremely hazardous hexavalent chromium deposition that is strictly restricted throughout the world.

However, aqueous trivalent chromium plating baths are characterized by some shortcomings [16, 17]. Non-aqueous chromium electrolytes based on the so-called deep eutectic solvents (DESs), a new generation of room temperature ionic liquids, are now considered as a feasible and "green" alternative to traditional aqueous electroplating baths [18–26]. DESs-based electrolytes are characterized by high performance and stability as compared with both aqueous systems and those based on organic solvents [27].

However, the electrocatalytic activity of coatings electrodeposited from DES-containing chromium plating bath towards the HER is poorly investigated. Only one our previous paper [28] reported the electrocatalytic performance of such coatings in an alkaline medium where oxide layers can be present on the electrode surface. It is important to ascertain the electrocatalytic characteristics of these coatings in an acidic medium. Therefore, the goal of this work was to characterize the electrocatalytic properties of Cr-containing electrodeposits fabricated from a DES-based plating bath in an acidic solution (0.5 M H_2SO_4).

2 Materials and Methods

The electrodeposition of coatings was performed using a gold plate as a cathode (S = 1.77 cm^2). The surface of the gold cathode was polished with filter paper, then treated in HCl solution (1:1 vol.) and thoroughly rinsed with bidistillate water.

The DES-based trivalent chromium bath used in this work was formulated in our previous publications [23–26]. The bath contained choline chloride, chromium (III) chloride and extra water in 2.5:1:15 molar ratios, respectively [26]. Coatings were electrodeposited at the current density of 5 A dm^{-2} and the bath temperature of 40 °C. Platinum plate served as an anode.

Chromium coatings were also prepared using "conventional" hexavalent chromium electroplating bath containing 2.5 M CrO_3 and 0.025 M H_2SO_4. In these experiments, coatings were deposited at the current density of 40 A dm^{-2} and the temperature of 45 °C. Lead plates were used as anodes.

The deposits' thickness was controlled by gravimetric method. The electrodeposition duration was adjusted to achieve the thickness of the coatings of about 10 μm.

The electrocatalytic activity of the synthesized coatings towards the HER was investigated using 0.5 M H_2SO_4 water solutions at the temperature of 25 °C. The electrocatalytic performance was estimated by means of linear voltammetry method and electrochemical impedance spectroscopy (EIS). To this end, Potentiostat/Galvanostat Reference 3000 (Gamry, USA) was used.

The electrochemical behavior of the coatings was studied in a thermostatted glass three-electrode cell in which the electrode compartments were divided by a glass porous diaphragm. Porous graphite served as a counter electrode. The values of electrode potentials were measured towards the saturated Ag/AgCl electrode and recalculated to the scale of a standard hydrogen electrode. The potential sweep rate in linear voltammetry was 50 mV s^{-1}.

The electrochemical impedance spectra were obtained at constant values of the overvoltage of the hydrogen evolution reaction in a frequency range of 0.01 Hz to 100 kHz. The impedance spectra were recorded at AC voltage amplitude of 5 mV.

3 Results and Discussion

Fig. 1 demonstrates the electrochemical behavior of chromium deposits in 0.5 M H_2SO_4 solution in a wide range of electrode potentials. The anodic current peak at about –0.7 V recorded for the "common" chromium coating (obtained from Cr(VI) plating bath) can be associated with the active anodic dissolution of metallic chromium. However, there is no current peak of active dissolution of coating deposited from Cr(III) electroplating bath. This indicates an enhanced corrosion stability of chromium layers prepared from DES-based electrolyte as compared with those from hexavalent chromium one [26]. This feature is very important and favorable for a practical use since many other possible electrocatalytic materials containing base metals can easily corrode in acidic aqueous medium.

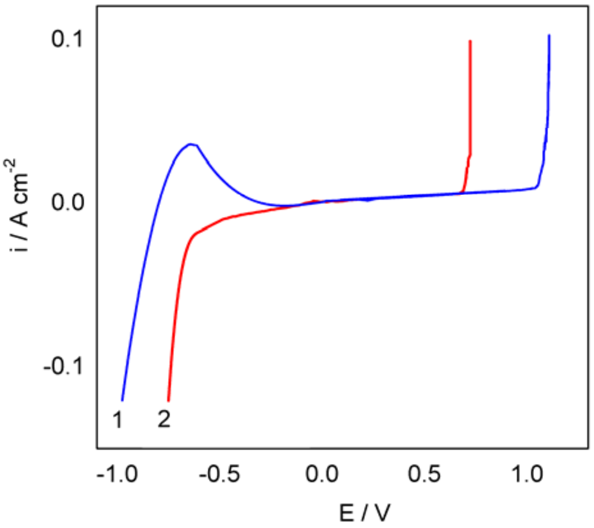

Fig. 1. Linear voltammograms of electrodeposits in 0.5 M H_2SO_4 aqueous solution: (1) Cr coating prepared using Cr(VI) plating bath, (2) Cr coating prepared using Cr(III) DES-based plating bath.

The cathodic segments of the recorded current waves evidently correspond to the HER occurring in a sulfuric acid solution. It is seen that the overvoltage of the HER on the coating deposited from DES-based electrolyte is less than that of Cr deposits from Cr(VI) bath. The cathodic segment of the polarization curves related to the HER was treated using the Tafel equation:

$$\eta = a + b\log|i| \tag{1}$$

where η is the value of overpotential, i is the current density, a is the Tafel intercept connected with the exchange current density (i_0), and b is the Tafel slope.

The exchange current density and transfer coefficient (α) were calculated by the following expressions:

$$\log i_0 = -\frac{a}{b} \tag{2}$$

$$\alpha = \frac{2.303RT}{bF} \tag{3}$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the thermodynamic temperature (K) and F is the Faraday constant (96,487 A s mol^{-1}).

Using Eqs. (2) and (3), the Tafel parameters for the HER in an acidic solution were calculated (Table 1); the coefficients of determination R^2 were not less than 0.97.

Table 1. Tafel parameters of the HER in 0.5 M H_2SO_4

Kinetic parameter	Electrolyte	
	Cr(VI)-based bath	Cr(III) DES-based bath
a, V	1.251	1.115
b, mV dec^{-1}	173	160
α	0.34	0.37
i_0, A cm^{-2}	0.59×10^{-7}	1.08×10^{-7}

Hydrogen evolution reaction in an acidic water solution can be considered as a combination of several elementary steps as follows [29]:

$$\text{M–H}_{ads}+\text{H}^{+}+\text{e}^{-}\rightarrow\text{H}_2+\text{M} \quad \text{(Heyrovsky step)} \tag{4}$$

$$\text{M–H}_{ads}+\text{M–H}_{ads}\rightarrow\text{H}_2+2\text{M} \quad \text{(Tafel step)} \tag{5}$$

$$\text{M}+\text{H}^{+}+\text{e}^{-}\rightarrow\text{M–H}_{ads} \quad \text{(Volmer step)} \tag{6}$$

where M denotes the surface metal atoms on which hydrogen atom is adsorbed.

It is known that the Tafel slope (i.e. the value of b) is about 40 and 30 mV dec^{-1} when electrochemical desorption (Heyrovsky step) or chemical desorption (Tafel step) are rate-determining steps, respectively. Meanwhile, the Tafel slope is about 118 mV dec^{-1} if electrochemical reduction (Volmer step) is a rate-determining step. The data presented in Table 1 indicates that the Tafel slopes are closer to 118 mV dec^{-1} rather than to 30 or 40 mV dec^{-1}. Therefore, the electrochemical reduction is a rate-determining step when the HER occurs on chromium coatings under study in an aqueous solution of H_2SO_4. Some excess of the calculated Tafel slopes over their theoretical value can be associated with the possible presence of relatively resistive oxide films on the cathode surface.

It is kwon that the electrocatalytic activity is explicitly characterized by the value of exchange current density [4, 5]. It is clearly seen that the electrocatalytic properties of coatings deposited from Cr(III) DES-based bath are higher than of those fabricated from "common" hexavalent chromium bath.

In order to get more comprehensive information on the kinetics and mechanism of the HER on Cr electrodes, electrochemical impedance spectroscopy (EIS) was used. The recorded Nyquist plots obtained for the HER in 0.5 M H_2SO_4 solution are shown in Fig. 2. Their shape is a flattened semicircle, which indicates that the electrochemical process is controlled by the charge transfer step and occurs on the inhomogeneous electrode surface. An equivalent circuit was developed to interpret the experimental impedance data (the inset in Fig. 2). The equivalent circuit contains a constant phase element characterizing the interface of "solid electrode/solution" (*CPE*), a polarization resistance of electrochemical reaction (R_{ct}) and an ohmic resistance of solution (R_s).

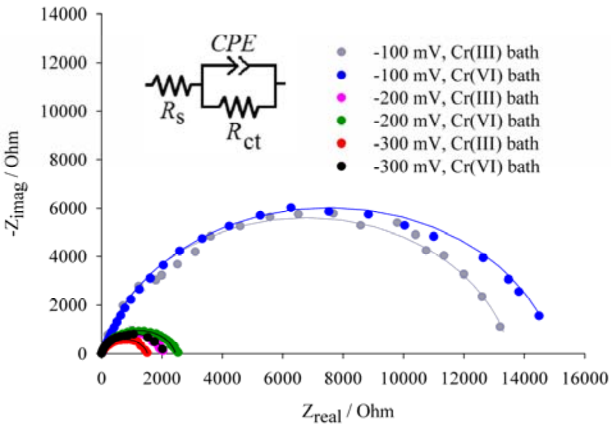

Fig. 2. Nyquist plots of chromium electrodeposits in 0.5 M H_2SO_4 aqueous solution. The type of the plating bath and the values of overpotential are shown in legend. The inset depicts electrical equivalent circuit used to simulate the electrochemical impedance data.

The electrochemical impedance of the *CPE* is usually given by the following equation [9, 10]:

$$Z_{CPE} = \left[Q(i\omega)^n\right]^{-1} \tag{7}$$

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 related to the phase deviation and associated with the inhomogeneity of the electrode surface.

Symbols in Fig. 2 present experimentally measured values of electrochemical impedance. These results were fitted by means of the adapted electrical equivalent circuit (continuous lines in Fig. 2). The calculated parameters of the electrochemical impedance are summarized in Table 2.

Table 2. Parameters of the electrochemical impedance of the HER in 0.5 M H_2SO_4

Electrolyte	Electrode overpotential, mV	Parameter			
		R_s, Ω	R_{ct}, kΩ cm^2	$Q\times10^6$, Ω^{-1} s^n cm^{-2}	n
Cr(VI)-based bath	–100	2.2	15.1	80	0.86
	–200	2.2	2.5	95	0.85
	–300	2.2	2.1	182	0.84
Cr(III) DES-based bath	–100	2.2	13.6	60	0.88
	–200	2.2	2.1	78	0.87
	–300	2.2	1.5	102	0.85

The obtained data show that the value of the polarization resistance decreases with an increase in the overpotential due to the acceleration of electrochemical process. Other conditions being equal, the polarization resistance of the HER occurring on deposits from Cr(III) DES-based plating bath is less than in the case of Cr(VI) aqueous plating bath. This confirms an enhanced electrocatalytic activity of Cr layers obtained in DES. The data on the polarization resistance of the HER are in good agreement with the results of calculation of the exchange current density (see above).

The value of n in Eq. (7) reflects the extent of surface heterogeneity [9, 10]. It is equal to unity if the surface is ideally smooth and homogeneous. The more inhomogeneous the electrode surface, the less is the value of n. In our opinion, there is no appreciable differences in the values of n for two different kinds of electrocatalytic coatings investigated in this work (deposited from Cr(VI) and Cr(III) electrolytes), although the surface seems to be rather heterogeneous in both cases. The constant Q characterizes the real (total) surface area of an electrode, which is available for an electrochemical reaction [9, 10]. It follows from the data presented in Table 2 that the real surface area of coatings prepared in electrolyte based on Cr(III) DES is less than that of coatings obtained in conventional Cr(VI) water electrolyte. Therefore, an enhanced electrocatalytic performance of chromium coatings from Cr(III) DES-based bath is associated with a "true" electrocatalytic effect rather than with a simple enlargement of the electrode surface area.

As concerns the reasons for the improved electrocatalytic activity of the coatings under consideration, they can be connected with the introduction of carbon into electrodeposited layers. Indeed, the results of EDX analysis showed the presence of some carbon (together with Cr, Cl and O) in the coatings fabricated using Cr(III) DES-based plating bath (Fig. 3). Evidently, the source of carbon is an organic component of the electrolyte. The inclusion of carbon in the chromium coatings deposited from Cr(III) plating baths has been observed in a number of previous publications [13–15]. It was earlier stated that Cr–C materials exhibited high electrocatalytic activity towards the HER due to the presence of excess carbon and corresponding increase in the density of states at the Fermi energy level [11].

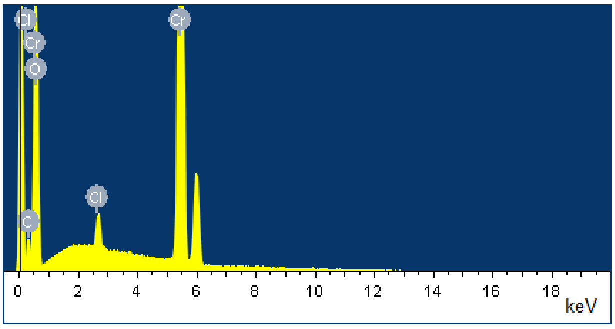

Fig. 3. EDX spectrum of the surface of coating prepared using Cr(III) DES-based plating bath.

If we compare the electrocatalytic characteristics of Cr-based coatings under consideration reported in the present work for an acidic medium (0.5 H_2SO_4) with those typical of an alkaline medium (1 M NaOH) [28], then we can conclude that they are very similar in exchange current densities, transfer coefficients and polarization resistances. Thus, Cr-containing electrocatalysts fabricated from the DES-based plating bath seem to be universal: they can be successfully used both in acidic and alkaline water solutions. An improved corrosion resistance of Cr–C electrodeposits in acidic media together with their good electrocatalytic performance in the HER allow considering them as a promising alternative to those fabricated using expansive noble metals.

4 Conclusion

The need to create high-performance and available ways for the production of hydrogen, that is considered as a promising green energy carrier, stimulates the development of new electrocatalysts for the hydrogen evolution reaction. Cr-based layers electrodeposited from environmentally friendly trivalent chromium plating baths seem to be a good alternative to expansive and scarce electrocatalysts based on the noble metals.

We reported the electrodeposition of chromium coatings using trivalent chromium plating bath based on a deep eutectic solvent, a new kind of room temperature ionic liquids. The electrodeposited Cr coatings showed an improved electrocatalytic activity in the hydrogen evolution reaction occurring in 0.5 M H_2SO_4 solution that was argued by the results of linear voltammetry and electrochemical impedance spectroscopy methods. An enhanced electrocatalytic activity was associated with the introduction of carbon into coatings structure. Thus, coatings electrodeposited from Cr(III) DES-based plating baths seem to be a very promising material to the development of new electrocatalysts for the hydrogen evolution reaction.

References:

[1] Bockris J.O'M., The origin of ideas on a Hydrogen Economy and its solution to the decay of the environment, *International Journal of Hydrogen Energy*, Vol.27, 2002, pp. 731-740.

[2] Kim J.W., Boo K.J., Cho J.H., Moon I., Key challenges in the development of an infrastructure for hydrogen production, delivery, storage and use. In: A. Basile and A. Iulianelli (eds.) *Advances in Hydrogen Production, Storage and Distribution*, Woodhead Publishing, 2014, pp. 3-31.

[3] Xu D., Dong L., Ren J., Introduction of hydrogen routines (Chapter 2). In: A. Scipioni, A. Manzardo and J. Ren (eds.) *Hydrogen Economy*, Academic Press, 2017, pp. 35-54.

[4] Safizadeh F., Ghali E., Houlachi G., Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions – a review, *International Journal of Hydrogen Energy*, Vol.40, 2015, pp. 256-274.

[5] McCrory C.C.L., Jung S., Ferrer I.M., Chatman S.M., Peters J.C., Jaramillo T.F., Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices, *Journal of the American Chemical Society*, Vol.137, 2015, pp. 4347-4357.

[6] Jamesh M.I., Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electrocatalyst for overall water splitting in alkaline media. *Journal of Power Sources*, Vol.333, 2016, pp. 213-236.

[7] Boiadjieva-Scherzer T., Kronberger H., Fafilek G., Monev M., Hydrogen evolution reaction on electrodeposited Zn–Cr alloy coatings. *Journal of Electroanalytical Chemistry*, Vol.783, 2016, pp. 68-75.

[8] Nady H., Negem M., Ni-Cu nano-crystalline alloys for efficient electrochemical hydrogen production in acid water, *RSC Advances*, Vol.6, 2016, pp. 51111-51119.

[9] Danilov F.I., Tsurkan A.V., Vasil'eva E.A., Protsenko V.S., Electrocatalytic activity of composite Fe/TiO_2 electrodeposits for hydrogen evolution reaction in alkaline solutions, *International Journal of Hydrogen Energy*, Vol.41, 2016, pp. 7363-7372.

[10] Protsenko V.S., Tsurkan A.V., Vasil'eva E.A., Baskevich A.S., Korniy S.A., Cheipesh T.O., Danilov F.I., Fabrication and characterization of multifunctional Fe/TiO_2 composite coatings, *Materials Research Bulletin*, Vol.100, 2018, pp. 32-41.

[11] Schmuecker S.M., Clouser D., Kraus T.J., Leonard B.M., Synthesis of metastable chromium carbide nanomaterials and their electrocatalytic activity for the hydrogen evolution reaction, *Dalton Transactions*, Vol.46, 2017, pp. 13524-13530.

[12] Томбs-Garcна A.L., Jensen J.O., Bjerrum N.J., Li Q. Hydrogen evolution activity and electrochemical stability of selected transition metal carbides in concentrated phosphoric acid, *Electrochimica Acta*, Vol.137, 2014, pp. 639-646.

[13] Safonova O.V., Vykhodtseva L.N., Polyakov N.A., Swarbrick J.C., Sikora M., Glatzel P., Safonov V.A., Chemical composition and structural transformations of amorphous chromium coatings electrodeposited from Cr(III) electrolytes, *Electrochimica Acta*, Vol.56, 2010, pp. 145-153.

[14] Danilov F.I., Protsenko V.S., Gordiienko V.O., Baskevich A.S., Artemchuk V.V., Electrodeposition of nanocrystalline chromium-carbon alloys from electrolyte based on

trivalent chromium sulfate using pulsed current, *Protection of Metals and Physical Chemistry of Surfaces*, Vol.48, 2012, pp. 328-333.

[15] Protsenko V.S., Danilov F.I., Gordiienko V.O., Baskevich A.S., Artemchuk V.V., Improving hardness and tribological characteristics of nanocrystalline Cr-C films obtained from Cr(III) plating bath using pulsed electrodeposition, *International Journal of Refractory Metals and Hard Materials*, Vol.31, 2012, pp. 281-283.

[16] Survilienй S., Nivinskienй O., Češuniené A., Selskis A., Effect of Cr(III) solution chemistry on electrodeposition of chromium, *Journal of Applied Electrochemistry*, Vol.36, 2006, pp. 649-654.

[17] Protsenko V.S., Danilov F.I., Chromium electroplating from trivalent chromium baths as an environmentally friendly alternative to hazardous hexavalent chromium baths: comparative study on advantages and disadvantages, *Clean Technologies and Environmental Policy*, Vol.16, 2014, pp. 1201-1206.

[18] Abbott A.P., Al-Barzinjy A.A., Abbott P.D., Frish G., Harris R.C., Hartley J., Ryder K.S., Speciation, physical and electrolytic properties of eutectic mixtures based on $CrCl_3 \cdot 6H_2O$ and urea, *Physical Chemistry Chemical Physics*, Vol.16, 2014, pp. 9047-9055.

[19] Ferreira E.S.C., Pereira C.M., Silva A.F., Electrochemical studies of metallic chromium electrodeposition from a Cr(III) bath, *Journal of Electroanalytical Chemistry*, Vol.707, 2013, pp. 52-58.

[20] Sun L., Brennecke J.F., Characterization of imidazolium chloride ionic liquids plus trivalent chromium chloride for chromium electroplating, *Industrial & Engineering Chemistry Research*, Vol.54, 2015, pp. 4879-4890.

[21] Zhang J., Gu C., Tong Y., Gou J., Wang X., Tu J., Microstructure and corrosion behavior of Cr and Cr–P alloy coatings electrodeposited from a Cr(III) deep eutectic solvent, *RSC Advances*, Vol.5, 2015, pp. 71268-71277.

[22] McCalman D.C., Sun L., Zhang Y., Brennecke J.F., Maginn E.J., Schneider W.F., Speciation, conductivities, diffusivities, and electrochemical reduction as a function of water content in mixtures of hydrated chromium chloride/choline chloride, *Journal of Physical Chemistry B*, Vol.119, 2015, pp. 6018-6023.

[23] Bobrova L.S., Danilov F.I., Protsenko V.S., Effects of temperature and water content on physicochemical properties of ionic liquids containing $CrCl_3 \cdot xH_2O$ and choline chloride, *Journal of Molecular Liquids*, Vol.223, 2016, pp. 48-53.

[24] Protsenko V.S., Bobrova L.S., Danilov F.I., Physicochemical properties of ionic liquid mixtures containing choline chloride, chromium (III) chloride and water: effects of temperature and water content, *Ionics*, Vol.23, 2017, pp. 637-643.

[25] Protsenko V.S., Bobrova L.S., Baskevich A.S., Korniy S.A., Danilov F.I., Electrodeposition of chromium coatings from a choline chloride based ionic liquid with the addition of water, *Journal of Chemical Technology and Metallurgy*, Vol.53, 2018, pp. 906-915.

[26] Protsenko V., Bobrova L., Danilov F., Trivalent chromium electrodeposition using a deep eutectic solvent, *Anti-Corrosion Methods and Materials*, Vol.65, 2018, pp. 499-505.

[27] Smith E.L., Abbott A.P., Ryder K.S., Deep eutectic solvents (DESs) and their applications, *Chemical Reviews*, Vol.114, 2014, pp. 11060-11082.

[28] Protsenko V.S., Bobrova L.S., Butyrina T.E., Danilov F.I., Hydrogen evolution reaction on Cr–C electrocatalysts electrodeposited from a choline chloride based trivalent chromium plating bath, *Voprosy Khimii i Khimicheskoi Tekhnologii*, No.1, 2019, pp. 61-66.

[29] Fekry A.M., Ameer M.A., Electrochemical investigation on the corrosion and hydrogen evolution rate of mild steel in sulphuric acid solution, *International Journal of Hydrogen Energy*, Vol.36, 2011, pp. 1207-1215.