

ELECTROCHEMICAL SYNTHESIS OF PROTECTIVE CERIA LAYERS USING METHANESULFONATE ELECTROLYTES

TSURKAN A.V., VASIL'EVA E.A., PROTSENKO V.S., DANILOV F.I.
Ukrainian State University of Chemical Technology
annatsurkan@ukr.net

The work deals with a new electrochemical procedure for cerium oxide layer electrodeposition on iron surface to provide corrosion protection. A methanesulfonate electrolyte has been used for the first time to electrodeposit ceria layer. Methanesulfonate electrochemical systems based on methanesulfonic acid and its salts are now considered as a "green" alternative to common plating baths due to their environmental and technological advantages. The electrodeposition of ceria films was performed in a galvanostatic mode from electrolyte containing 0.5 M $\text{Ce}(\text{CH}_3\text{SO}_3)_3$, (pH 1.3) at cathodic current densities of 0.25 to 2.5 mA cm^{-2} at 298 K. The possible reaction scheme of CeO_2 films electrodeposition has been proposed. The local EDX analysis revealed the presence of cerium oxides on the Fe surface after cathodic treatment in cerium (III) methanesulfonate solutions. The thickness of the obtained ceria layers seems to be relatively small (about 60-70 nm). The electrochemical impedance spectroscopy (EIS) method was used to estimate the corrosion and protective behavior of CeO_2 films. Nyquist plots were recorded at the open circuit potentials in open to air solution of 3% NaCl as an aggressive environment. Two electrical equivalent circuits were developed to interpret the experimental data. The electrical equivalent circuits contain polarization resistance of the electrochemical reaction, constant phase element (CPE), and ohmic resistance of solution. In addition, the equivalent circuit for iron coating modified by ceria layer contains finite Warburg impedance resulted from diffusion behavior at lower frequencies. The surface modification of Fe matrix by ceria layer was shown to provide a significant increase in the corrosion stability.

It is well-known that ceria films are successfully used for the corrosion protection of iron and steels [1-3]. They are considered as a very promising alternative to the chromate coatings, which are extremely dangerous to human health and environment. Ceria layers can be obtained from various types of electrolytes: chloride [1-3], nitrate [4, 5], acetate [6]. In this work, the application of methanesulfonate systems for ceria electrodeposition is reported for the first time. Methanesulfonate electrolytes are based on methanesulfonic acid $\text{CH}_3\text{SO}_3\text{H}$ (MSA) and its

salts. MSA is now regarded as a "green acid" because of its environmental advantages [7]. Methanesulfonic acid is less corrosive and toxic than other "usual" inorganic acids used in industry. MSA is easily biodegradable [7]. Methanesulfonates of different metals are highly soluble in water, the conductivity of corresponding aqueous solutions being high. Due to these environmental and technological advantages, electrochemical systems containing methanesulfonic acid and its salts are very promising for different electrochemical engineering processes [8]. Thus we made a research effort to develop entirely environmentally friendly corrosion inhibitors for iron and its composites [9].

Research methodology

Iron electrodeposits obtained from a methanesulfonate plating bath [10] were used as a matrix on which ceria layer were deposited. Fe coatings were deposited on the mild steel plates ($S = 1 \text{ cm}^2$) placed in a plastic holder. Anodes were made of mild steel. The electrolysis was conducted at a steady current density in a thermostated glass cell ($T = 298 \text{ K}$) for 10 min. The methanesulfonate iron plating bath allows obtaining nanocrystalline Fe coatings with a high current efficiency (ca. 95%) and a relatively high deposition rate [10]. The composition of methanesulfonate electroplating bath and operating parameters are given in Table 1.

Table 1. Composition of Fe plating bath and deposition parameters

Fe(CH ₃ SO ₃) ₂	1.25 mol dm ⁻³
pH	1.3
Temperature	298 K
Current density	10 A dm ⁻²
Stirring	Magnetic stirrer, ~ 60 rev min ⁻¹
Cathode	Mild steel
Anode	Mild steel

Cerium (III) methanesulfonate solution was synthesized by chemical interaction between concentrated MSA solution and powdered cerium (III) carbonate. The electrolyte for ceria cathodic synthesis contained 0.5 M Ce(CH₃SO₃)₃, its pH value was adjusted to 1.3. The electrodeposition was performed in a galvanostatic mode by means of Potentiostat/Galvanostat Reference 3000 (Gamry). The ohmic potential drop was measured and automatically compensated using the built-in iR-compensator of the potentiostat. All potentials were measured with respect to the saturated Ag/AgCl-electrode and recalculated to the standard hydrogen electrode. The temperature of Ce(CH₃SO₃)₃ solution was maintained at 298 K during the electrochemical synthesis of ceria films.

The cerium oxide layers were deposited on fresh deposited Fe surface, the counter electrode was made of platinum sheet. After ceria layer electrodeposition, the samples were rinsed in double distilled water and dried in a hot air jet (ca. 80 °C) for 3 min.

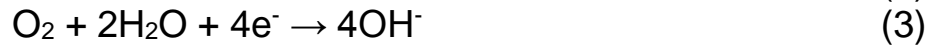
The surface morphology of the electrodeposits was investigated by scanning electron microscopy (Zeiss EVO 40XVP) in secondary (SE) electron regimes. The chemical composition of the surface layers was determined by energy dispersive X-ray spectroscopy (EDX) coupled with SEM microscope (Oxford INCA Energy 350).

The corrosion behavior of electrodeposits was studied by means of electrochemical impedance spectroscopy using open to air solution of 3% NaCl as an aggressive environment. A conventional three electrodes glass cell thermostated at 298 K was used for these corrosion experiments. The working electrodes (mild steel samples with electrodeposited layers as described above) were immersed in a test solution for approximately 30 min prior to each test in order to establish a stable open circuit potential. The counter electrode was iron gauze. The potentials were measured with respect to the saturated Ag/AgCl-electrode and recalculated to the scale of standard hydrogen electrode. Electrochemical impedance spectra were recorded in a potentiostatic mode (Potentiostat/Galvanostat Reference 3000 (Gamry)) at open circuit potentials. The applied sinuous potential amplitude was 10 mV, the frequency range was from 0.01 Hz to 100 kHz. The data of electrochemical impedance spectroscopy were processed (development of electrical equivalent circuits and determination of quantitative parameters of their elements) using a computer system with Gamry Elchem Analyst software package.

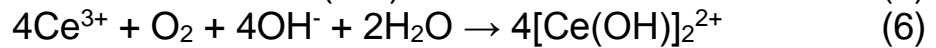
Results and Discussion

Fig. 1 presents the variation of electrode potential versus time during cathodic treatment of as-deposited Fe coatings at different current densities. As can be seen, an abrupt growth of cathode polarization is observed during ca. 50 seconds after turning on the electric current. Then the electrode potential reaches a minimum value and begins to increase. Finally, after about 300-400 seconds, the electrode potential again decreases slightly and stabilizes showing small oscillations. Other conditions being equal, an increase in cathode current density results in a decrease in electrode potential.

Such complex behavior of electrode potential with time can be related to diverse electrochemical and chemical reactions occurring on the electrode surface. First of all, hydrogen evolution reaction (HER) and electroreduction of oxygen dissolved in solution take place on the electrode in an aqueous medium [4]:



All these reactions are accompanied by an increase in pH value in the near electrode solution layer because MSA is a very strong acid [7] and its solutions do not show any pronounced buffering effect. As a result, the following reactions of Ce(III) hydroxides and hydroxo-complexes formation can occur on the electrode [4]:



In addition, the further oxidation of Ce(III) with the formation of Ce(IV) complex ions and cerium (IV) oxide layer becomes possible:

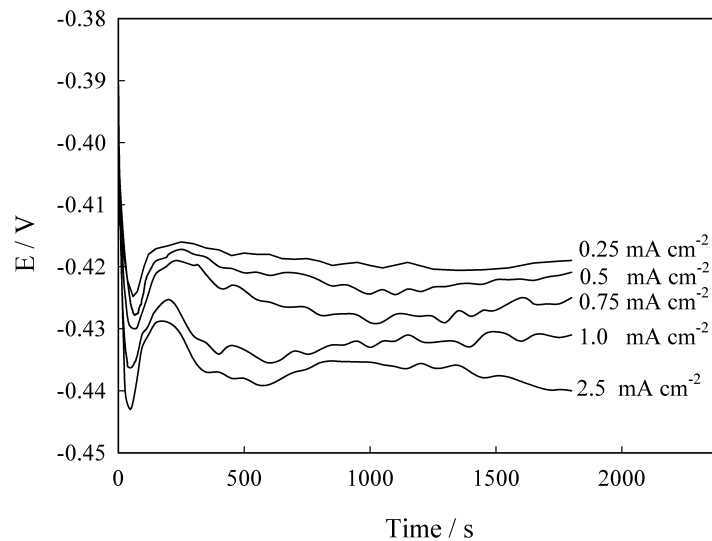
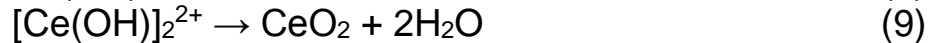
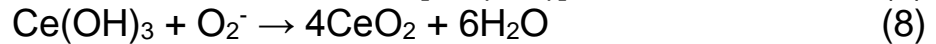
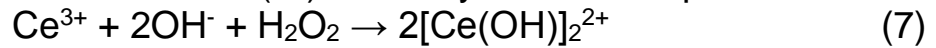


Fig. 1. Variation of electrode potential with deposition time for different applied current densities in 0.5 M $\text{Ce}(\text{CH}_3\text{SO}_3)_3$ solution; pH 1.3; temperature 298 K [9].

It is evident that in the initial stage of deposition (first several tens seconds) the nucleation and the growth of nuclei of new solid phase CeO_2 occur on the electrode surface [4]. The formation of some blocking surface layer on Fe matrix hinders both the HER and other electrochemical processes. This causes shifting the electrode potential towards more negative values.

If the current density exceeds the value of about 3 mA cm^{-2} , the electrodeposition experiments show the formation of a brownish spongy deposit of CeO_2 practically without any adhesion to the substrate.

Therefore, the electrochemical synthesis of ceria layer was performed in all further experiments at current densities less than 3 mA cm^{-2} .

The cathodic treatment of Fe coatings in methanesulfonate electrolyte leads to the change in their visible surface appearance. If before treating they are light grey, they become greyish-blue with a sheen resembling temper colors on oxidized steel surface after the formation of ceria films. At the same time, the SEM images of Fe electrodeposits presented do not show any noticeable differences between electrodeposits with and without ceria films. There is a superficial network of cracks on the surface of "pure" iron (Fig. 2). No visible specific features of surface morphology appear in SEM images after the cathodic treatment of samples with Fe coatings in methanesulfonate electrolytes. This behavior may be connected with a very small thickness of the obtained ceria layer. Indeed, gravimetric measurements do not show any weight gain of the samples even after 30 minutes of electrochemical treatment in methanesulfonate solutions. If we take into account the sensitivity of the utilized analytical balance ($5 \cdot 10^{-5} \text{ g}$), the density of CeO_2 (7.65 g cm^{-3}) and the surface area of the sample (1 cm^2), then we can easily estimate the upper limit of the thickness of cerium oxide layer which is close to 60-70 nm. Earlier the deposition of nanometer-thick ceria films has been reported in a number of publications [6].

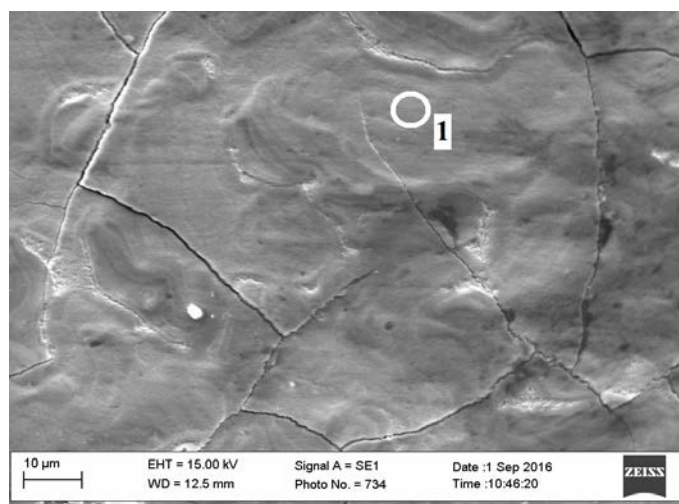


Fig. 2. SEM image of iron coating with electrodeposited ceria layer [9].

Although the SEM images did not show any changes in the surface morphology of Fe coatings after cathodic treatment in methanesulfonate electrolyte, the EDX investigations clearly revealed the presence of cerium oxides on the surface. The local EDX analysis performed at the point marked as 1 in Fig. 2 shows that the content of Ce, O and Fe is equal to 0.57, 16.64, and 82.79 at.%, respectively. No other elements have been detected.

Despite a relative small thickness of the synthesized cerium oxide layers, their adhesion to the substrate seems to be satisfactory. At least, according to the obtained EDX data, these ceria films cannot be removed from the surface after rinsing by water.

In order to estimate the kinetics of corrosion properties of ceria layers obtained, we used the electrochemical impedance spectroscopy (EIS) method. Nyquist plots (imaginary values Z_{imag} versus real values Z_{real}) were recorded at the OCP for the "pure" Fe coatings and electrodeposits with ceria layer on their surface (Fig. 3). Nyquist plot of as-deposited iron coating without CeO_2 film looks like conventional depressed semicircles, which indicates that the electrochemical reaction is controlled by the charge transfer step and occurs on inhomogeneous surface.

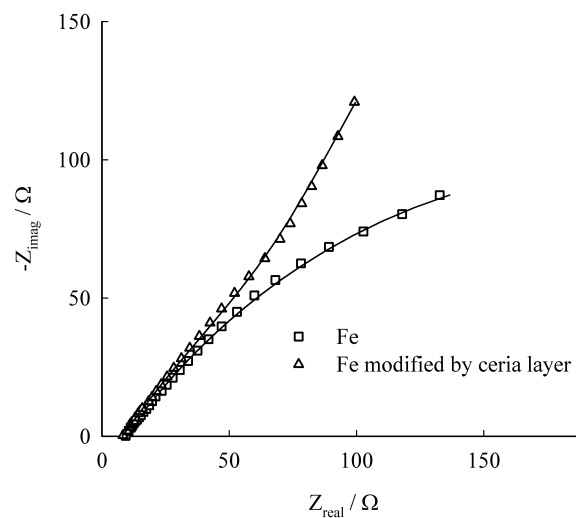


Fig. 3. Nyquist plots of Fe coatings with and without modification by ceria layer in 3% NaCl solution at OCP and temperature of 298 K. Cathodic treatment in 0.5 M $Ce(CH_3SO_3)_3$ was performed at 1 mA cm^{-2} during 1800 s. The symbols denote the measured (experimental) impedance spectra and solid lines represent fitted results [9].

Nyquist plot obtained for iron coating with electrodeposited film of cerium oxide is more complicated. In addition to capacitive loop at higher frequencies, the electrochemical impedance spectra show diffusion behavior at lower frequencies indicating Warburg impedance. One can conclude that the impedance values measured at the high-frequencies range only responded to the surface characteristics of the corroded Fe matrix whereas the precipitation of CeO_2 films forms a thin passive barrier layer which is responsible for diffusion behavior resulted in Warburg resistance at lower frequencies.

Taking into account the above arguments, two typical electrical equivalent circuits were used to fit experimental data as shown in Fig. 4. The first equivalent circuit (Fig. 4A) contains polarization resistance of the electrochemical reaction (R_{ct}), constant phase element (CPE) characterizing the interface of "solid electrode/solution", and ohmic resistance of solution (R_{sol}). The introduction of constant phase elements

into the electrical equivalent circuits is related to the energy and geometric heterogeneity of the electrode surface [11].

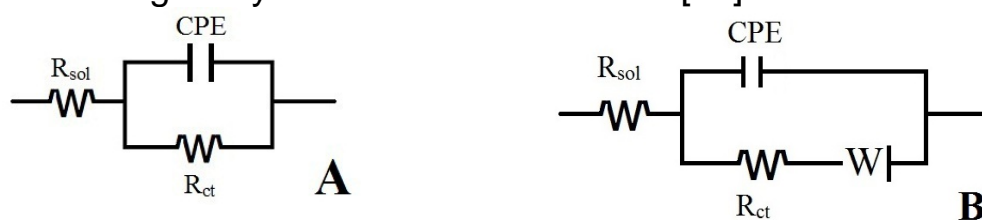


Fig. 4. Electrical equivalent circuits modeling the solid electrode/solution interface: (A) for as-deposited coatings without surface ceria modification, and (B) for coatings modified by ceria layer.

The first electrical equivalent circuit shown in Fig. 4A was employed for the description of the corrosion behavior of as-deposited coatings without surface ceria modification. The second equivalent circuit (Fig. 4B) used for the modeling of electrochemical impedance spectra recorded for the corrosion of the coatings with CeO_2 layer additionally contains the so-called finite Warburg impedance. The experimental data in Fig. 3 are presented as symbols and the continuous lines are obtained by curves fitting using the electrical equivalent circuits shown in Fig. 4. The calculated kinetic parameters are summarized in Table 2.

Table 2. Calculated electrochemical impedance parameters

Electrode	R_{sol} (Ω)	R_{ct} (Ω cm^2)	$Q \cdot 10^3$ ($\Omega^{-1} \text{s}^n \text{cm}^{-2}$)	n	$Y_W \cdot 10^3$ ($\Omega^{-1} \text{s}^{1/2}$)	$B \cdot 10^3$ ($\text{s}^{1/2}$)
Fe coating	9.74	354.1	25.6	0.603	-	-
Fe coating modified by CeO_2	8.01	587.9	24.7	0.583	284.4	52.7-

As can be seen in Table 2, the values of parameter n are appreciably less than unity. This means a relatively high extent of fractal roughness of the electrode [11]. In the adopted electrical equivalent circuits, the value of R_{ct} can be considered as a parameter which can define the corrosion resistance of a coating in a general way. It is clear that the electrodeposition of ceria layers has a great influence on the values of R_{ct} for iron coatings. All these results indicate that the modification of the deposits surface by cerium oxide films considerably enhances the corrosion stability and provides high protective properties.

Conclusions

Thus, we reported the preparation of CeO_2 film on Fe coatings via electrodeposition technique to obtain a protective layer. The application of methanesulfonate electrolytes for the cathodic deposition of cerium oxide films has been reported [9]. MSA-based plating baths proved to be

very promising since they are considered a "green" electrolyte with relatively few environmental storage and disposal problems. A study on corrosion-electrochemical behavior revealed that the electrodeposition of ceria film on the surface of Fe matrix improves the corrosion resistance.

References

[1] Aldykiewicz A.J., Davenport A.J., Isaacs H.S., Studies of the formation of cerium-rich protective films using X-ray absorption near-edge spectroscopy and rotating disk electrode methods. *J. Electrochem. Soc.*, 143, 147-154, 1996.

[2] Stoychev D., Corrosion protective ability of electrodeposited ceria layers. *J. Solid State Electrochem.*, 17, 497-509, 2013.

[3] Yang L., Pang X., Fox-Rabinovich G., Veldhuis S., Zhitomirsky I., Electrodeposition of cerium oxide films and composite. *Surf. Coat. Technol.*, 206, 1-7, 2011.

[4] Hamlaoui Y., Pedraza F., Remazeilles C., Cohendoz S., Reber C., Tifouti L., Creus J., Cathodic electrodeposition of cerium-based oxides on carbon steel from concentrated cerium nitrate solutions. Part I. Electrochemical and analytical characterisation. *Mater. Chem. Phys.*, 113, 650-657, 2009.

[5] Hamlaoui Y., Tifouti L., Remazeilles C., Pedraza F., Cathodic electrodeposition of cerium based oxides on carbon steel from concentrated cerium nitrate. Part II: Influence of electrodeposition parameters and of the addition of PEG. *Mater. Chem. Phys.*, 120, 172-180, 2010.

[6] Kulp E.A., Limmer S.J., Bohannon E.W., Switzer J.A. Electrodeposition of nanometer-thick ceria films by oxidation of cerium(III)-acetate. *Solid State Ionics*, 178, 749-757, 2007.

[7] Gernon M.D., Wu M., Buszta T., Janney P., Environmental benefits of methanesulfonic acid: Comparative properties and advantages. *Green Chem.*, 1, 127-140, 1999.

[8] Walsh F.C., Ponce de León C., Versatile electrochemical coatings and surface layers from aqueous methanesulfonic acid. *Surf. Coat. Technol.*, 259, 676-697, 2014.

[9] Protsenko V.S., Vasil'eva E.A., Tsurkan A.V., Kityk A.A., Korniy S.A., Danilov F.I., Fe/TiO₂ composite coatings modified by ceria layer: Electrochemical synthesis using environmentally friendly methanesulfonate electrolytes and application as photocatalysts for organic dyes degradation. *J. Environ. Chem. Eng.*, 5, 136-146, 2017.

[10] Protsenko V.S., Vasil'eva E.A., Smenova I.V., Baskevich A.S., Danilenko I.A., Konstantinova T.E., Danilov F.I., Electrodeposition of Fe and composite Fe/ZrO₂ coatings from a methanesulfonate bath. *Surf. Eng. Appl. Electrochem.*, 51, 65-75, 2015.

[11] Rammelt U., Reinhard G., On the applicability of a constant phase element (CPE) to the estimation of roughness of solid metal electrodes. *Electrochim. Acta*, 35, 1045-1049, 1990.