

On the Contamination of Membrane–Electrode Assemblies of Water Electrolyzers with Solid Polymer Electrolyte by the Elements of Titanium Alloys¹

S. A. Grigoriev^{a, *}, D. G. Bessarabov^b, and A. S. Glukhov^{a, c}

^aNational Research University “Moscow Power Engineering Institute,” Krasnokazarmennaya st. 14, Moscow, 111250 Russia

^bHySA Infrastructure Center of Competence, North-West University, Potchefstroom, 2520 South Africa

^cNational Research Center “Kurchatov Institute”, Akad. Kurchatov sq. 1, Moscow, 123182 Russia

*e-mail: sergey.grigoriev@outlook.com

Received August 1, 2016; in final form, December 15, 2016

Abstract—The aspects of contamination of membrane–electrode assemblies of water electrolyzers with solid polymer electrolyte by the elements of titanium alloys (Ti and Fe) are considered. These alloys are used as the material for current collectors/gas-diffusion electrodes, bipolar plates, and other elements of electrolysis system. It is shown that titanium is one of the main impurities that contaminate the membrane and electrocatalytic layers of membrane–electrode assembly in the case that deionized water is used as the reagent. The membrane contamination can lead to the degradation of electrolyzer characteristics and its failure.

Keywords: water electrolysis, solid polymer electrolyte, membrane, electrocatalytic layer, titanium alloy, degradation of characteristics

DOI: 10.1134/S1023193517080067

INTRODUCTION

In the recent years, great attention has been paid to the problems of stability of characteristics of water electrolyzers with solid polymer electrolyte [1–3]. The aspects of the dissolution and migration of the catalyst particles [3–5], thermooxidative destruction of membranes [5, 6] and other factors that have a detrimental effect on the characteristics and service life of the electrolysis systems with solid polymer electrolyte have been studied. Here, the processes of contamination of membrane–electrode assemblies (MEAs) with the elements of titanium alloys (Ti and Fe), which are the structural materials for the current collectors/gas-diffusion electrodes, bipolar plates, and other elements of electrolysis system, are considered.

It should be noted that, since titanium alloys are rather expensive, the work is underway to replace them completely or partially by alternative materials, which are used, in particular, in the fuel cells with solid polymer electrolyte. For example, the composite bipolar plates based on stainless steel coated with a thin layer of titanium alloy are developed [7, 8]. However, in this case, titanium will be also washed away by the water-reagent from the coating of bipolar plate and will

deposit on the components of MEA. Thus, the dissolution of titanium and other elements of titanium alloys from the structural elements of electrolyzer and its hydraulic framing in the water and their subsequent deposition in the membrane and electrocatalytic layers is a problem that requires a detail study. In this work, the life tests of MEA and subsequent examination of structure and chemical composition of its membrane and electrocatalytic layers for the content of Ti and Fe with the use of the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS) were performed.

EXPERIMENTAL

Description of MEA Preparation and Testing

The MEA for the experiments was prepared with the use of Nafion® 117 membrane (EI. DuPont de Nemours Co., USA) and current collectors (gas-diffusion electrodes) coated with the electrocatalytic compositions. To exclude possible presence of impurity inclusions in the membrane, prior to the assembling, MEA was washed in isopropanol and nitric acid as it was described in [9]. Porous titanium TPP-7 (the plates 0.95 mm thick, porosity 37%) was used for the current collectors. It was also preliminarily washed according to [9].

¹ Published on the basis of a report delivered at the 13th International Meeting “Fundamental Problems of Solid State Ionics,” Chernogolovka, 2016.

The electrocatalytic layers were formed on the surface of current collectors by spraying. On the anode side, iridium powder was used (loading 1.5 mg/cm^2 with the addition of 5 wt % proton–exchange polymer Nafion® in the form of D521 dispersion (DuPont)). On the cathode side, we used platinum in the amount of 40 wt % on the Vulcan XC-72 carbon support (loading 1.0 mg/cm^2 Pt/XC-72 with the addition of 15 wt % proton–exchange polymer Nafion® in the form of aforementioned dispersion). The catalysts were synthesized in accordance with the procedures described in [10].

In the experiments, we used a thermally controlled electrolysis cell (active surface area was 25 cm^2) made of titanium alloy VT1-0. The hydrogen and oxygen separators were made of chemical glass. The silicon tubes were used as the connecting lines.

The anodic supply of water preliminarily twice distilled and purified on an ion-exchange filter was organized. The MEA tests were carried out at the electrolysis cell temperature of 60°C and the atmosphere pressure in the electrode chambers. The water–reagent circulation through the anodic compartment of the cell was provided by gas–lift.

The electrolysis system worked under the aforementioned conditions for 4000 h with regular measurements of the voltammetric characteristics. Then, the structure and chemical composition of MEA were studied. In the course of life tests, the water exchange was performed several times, when the water resistance exceeded $18 \text{ M}\Omega \text{ cm}$.

Studies of the MEA Structure and Chemical Composition

The structure and chemical composition of the membrane and electrocatalytic layers were studied by the SEM and EDXS. The MEA under investigation was fixed with epoxy resin and, then, it was cross-cut by means of an ultramicrotome with a diamond knife. The SEM micrographs of MEA cross-sections were obtained by means of Tescan Vega II LSU setup with an IMAX detector (Oxford Instruments, Great Britain). The elemental analysis of membrane fragments and electrocatalytic layers was performed by means of the system of energy-dispersive microanalysis Oxford Instruments Inca EDS (Great Britain).

RESULTS AND DISCUSSION

During the life tests, the voltage of the electrolysis cell increased monotonically at an average rate of approximately $35.5 \text{ }\mu\text{V/h}$. After 4000-h work of the electrolysis system, the experiment was stopped, and the aforementioned structural and chemical studies of MEA were performed.

Figure 1 gives a micrograph of a cross-section of the MEA cathodic region obtained by SEM. The site,

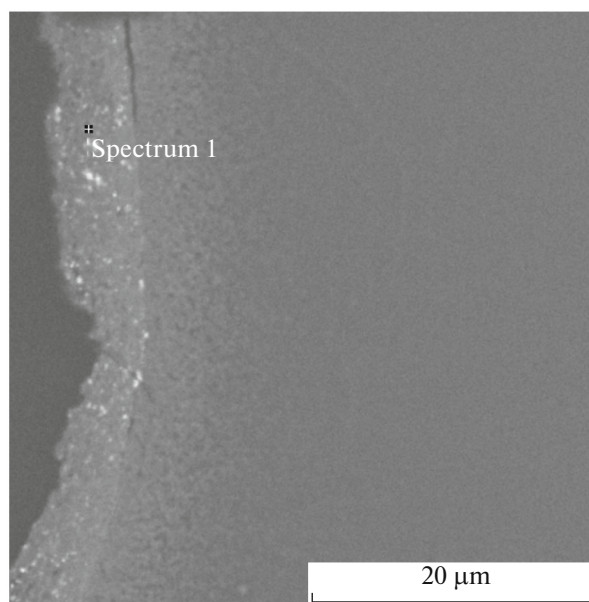


Fig. 1. SEM image of cross-section of MEA cathodic region.

where the elemental analysis was performed (Spectrum 1), is shown on the micrograph. Table 1 lists the results of the elemental analysis.

Figures 2a and 2b give the distributions of concentrations of the elements across the MEA width in its cathodic region that were measured by the EDXS with linear scanning (the concentrations of the elements in wt % are given along the ordinate axis). In the course

Table 1. Results of elemental analysis of MEA fragment indicated on Fig. 1 (Spectrum 1)

Element	wt %	at %
C	45.30	61.48
O	12.74	12.98
F	22.61	19.40
S	0.41	0.21
Cl	1.27	0.58
Ti	5.48	1.86
Cr	7.23	2.27
Fe	3.81	1.11
Pt	1.15	0.10
Total	100.00	100.00

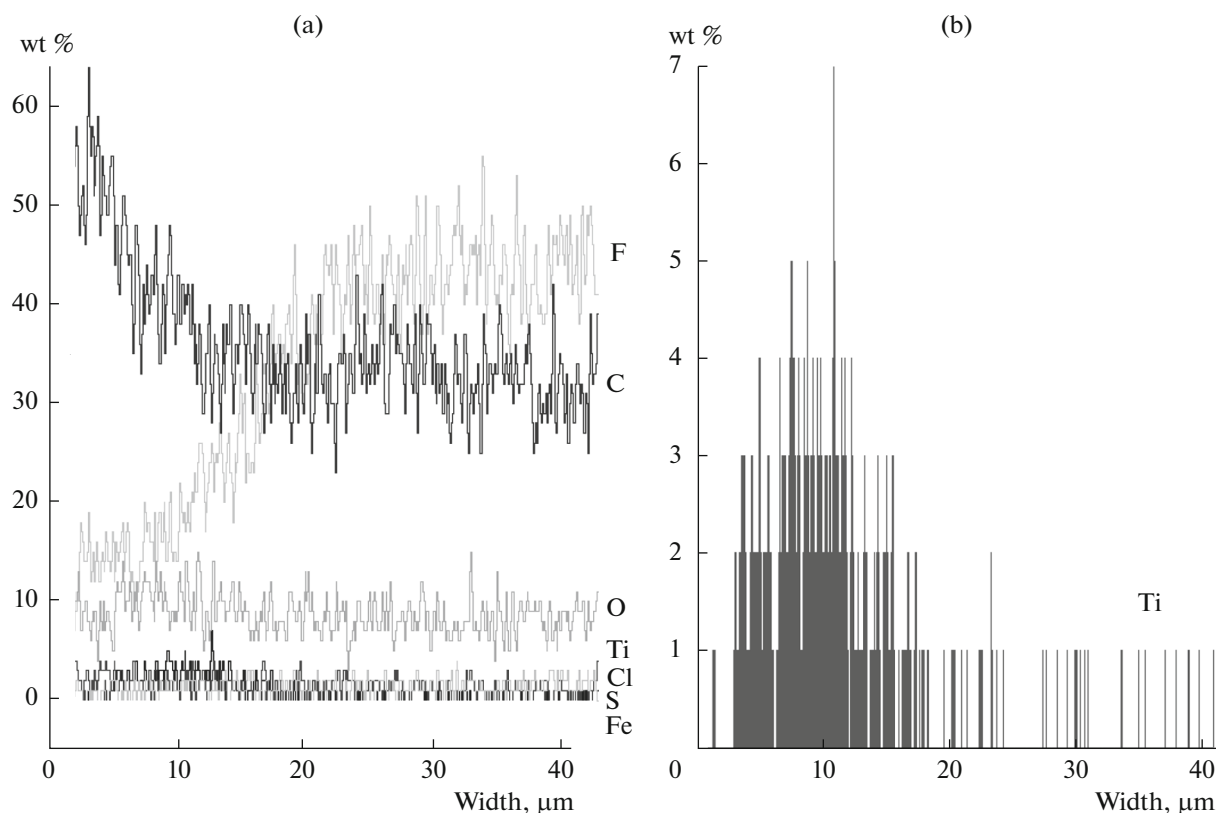


Fig. 2. Spectra of distribution of concentrations of the elements across the MEA width in the cathodic region: (a) Fe, Ti, Cl, S, F, O, C and (b) Ti.

of scanning of the regions of MEA cross-section, the sensing element of the analyzer passes different zones:

—the cathodic electrocatalytic layer, which consists of platinum nanoparticles on the carbon support, the ionomer, and porous system, and also includes the ions and nanoparticles of accumulated impurity inclusions;

—the membrane with impurity inclusions.

The highest concentrations are recorded for carbon, fluorine, and oxygen (Fig. 2a). The next most intense signal is given by titanium. Figure 2b gives the distribution of titanium concentration across the MEA width in a scale increased compared to Fig. 2a and without the spectra of other elements. The pronounced peaks of titanium are observed in Fig. 2b. In particular, in the point on the abscissa axis remote at a distance of 10.8 μm from the origin of coordinates (corresponds to the membrane zone bordering with the cathode active layer), the concentration of titanium reaches 7 wt %. The spectrum also contains the zones with zero concentration of titanium (in this case, the sensing element of analyzer passes the zones of active layer and membrane, where titanium ions and particles are absent, but other elements are present; their spectra, in particular, are presented on

Fig. 2a). The error of determination of element concentration is less than 1 wt %.

As is seen from Fig. 2, the presence of titanium was detected predominantly in the cathodic active layer and membrane zone adjacent to it. Thus, the analysis of the micrograph and the results of EDXS allow us to make an initial conclusion that the cathode is the center of attraction of titanium impurity ions and the formation of clusters in the membrane.

From Table 1, it is seen that Ti and Fe, which are the components of titanium alloys, are present in the control site of cathodic electrocatalytic layer (Spectrum 1) in the amounts of 5.48 and 3.81 wt %, respectively. According to Fig. 2, the highest concentration of Ti is observed in the boundary region of the membrane, it is approximately 7 wt %. Thus, the presence of the elements of titanium alloys in MEA is evidenced qualitatively and quantitatively.

We can suppose that the main mechanism of impurity ion transport in the membrane is associated with the water flow, which is initiated by hydrogen ions in the course of electrolysis and is directed from the anode towards the cathode. As the cathode is approached, the reduction of the impurity ions occurs, which promotes their deposition. This process

can be caused by the interaction of the ions with hydrogen and already partially reduced impurity ions.

Titanium and iron, which were detected in MEA, are involved in the composition of titanium alloys and are present in the material of current collectors and electrolysis cell. For instance, porous current collector is made of titanium alloy TPP-7; according to *TU* (Technical Conditions) 1715-449-05785388-99, it can contain up to 1.1 wt % iron. Technical titanium alloy VT1-00 used as the electrolysis cell material, according to the *GOST* (State Standard) 19807-91, contains 0.15% iron. A high purity of water-reagent is confirmed by the absence of Ca, Mg, Na, K and other impurities, which are present in tap water.

According to the equilibrium potential—pH (Pourbaix) diagram for the titanium—water system [11], in the cathodic potential range of electrolysis cell, titanium is passive with the formation of TiO_2 passivating oxide. Being a valve metal, titanium forms very stable oxide layer; however, the oxide film formed on the cathode is much less compact than that on the anode. Thus, in the course of dynamic formation of oxide film on the cathode, titanium ions can pass to the near-cathode region of the membrane, which, as is known, is equivalent to 10% sulfuric acid in its acidic properties. In the sulfuric acid solution, the oxide film is reduced to Ti(III) ions, which pass to the solution [12]. In addition, as a result of on—off cycles of the electrolysis cell, short-term polarity reversal of the electrodes can take place. This assists the penetration of Ti ions into the matrix of polymer membrane. The cathodic dissolution of titanium oxide films is explained by the formation of TiOOH by the reaction: $\text{H}_{\text{ads}} + \text{TiO}_2 = \text{TiOOH}$ [13, 14].

From the potential—pH diagram, we can conclude that, for the anode that operates in the potential range of 1.4 to 2.0 V, the electrochemical corrosion of titanium with the formation of hydroxides and oxide TiO_2 and titanium repassivation as a result of anodic polarization are thermodynamically possible. Consequently, in the course of electrolysis cell operation, the anodic current collector may be prone to corrosion; as a result, Ti^{2+} ions pass to water and, then, are oxidized to Ti^{3+} . Thereafter, the electroosmotic flow of water with dissolved titanium ions moves through the membrane from the anode towards cathode, and titanium ions are reduced in the membrane and cathodic electrocatalytic layer to form clusters. Thus, the emergence of ions and reduced titanium nanoparticles in the membrane matrix can proceed by two mechanisms, which are associated with its cathodic and anodic dissolution. These mechanisms require further investigation.

According to [15], the incorporation of nanoparticles of inorganic substances into the ion-exchange membranes leads to a significant change in the system of pores and channels, as well as in the transport properties of the membranes. In particular, with increasing

concentration of impurity metal particles in the membrane, its protonic conductivity decreases [16] and the probability of the local overheating and burnout of the membrane due to the ohmic heating of closed metal clusters increases [1]. We can suppose that an increase in the voltage of electrolysis in the course of the life tests of MEA is associated with these two factors. According to the theory of percolation, the short circuit of the anodic and cathodic electrocatalytic layers occurs at approximately 30% volume concentration of impurity particles in the membrane [17, 18]. When such a high degree of membrane metallization is reached, its burnout is highly probable [1]. According to [3, 4], the accumulated impurities (Pt, Ir, Fe, etc.) can be removed from MEA by its boiling in the sulfuric acid solution; as a result, the characteristics of MEA are almost completely restored to the initial level.

CONCLUSIONS

It is shown that, during the operation of water electrolyzer with solid polymer electrolyte, its MEA is contaminated with titanium and iron that are a part of the titanium alloys. As a result of corrosion of current collectors and bipolar plates, titanium and iron ions pass to the water-reagent and are reduced in the membrane and active layers leading to an increase in the ohmic resistance of the membrane and a decrease in its protonic conductivity. To reduce the contamination of MEA, it can be recommended to use filters and/or to exchange regularly water in the electrolysis system. The accumulated impurities can be removed from MEA and its characteristics can be almost completely restored to the initial level by treating it in the sulfuric acid solution. However as applied to titanium, this problem requires a detail investigation.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Education and Science of the RF within the framework of government task in the field of scientific activities (project no. 16.7113.2017/6.7).

REFERENCES

1. Millet, P., Ranjbari, A., de Guglielmo, F., Grigoriev, S.A., and Aupretre, F., *Int. J. Hydrogen Energy*, 2012, vol. 37, p. 17478.
2. Rakousky, C., Reimer, U., Wippermann, K., Carmo, M., Lueke, W., and Stolten, D., *J. Power Sources*, 2016, vol. 326, p. 120.
3. Wei, G., Wang, Y., Huang, C., Gao, Q., Wang, Z., and Xu, L., *Int. J. Hydrogen Energy*, 2010, vol. 35, p. 3951.
4. Sun, S., Shao, Z., Yu, H., Li, G., and Yi, B., *J. Power Sources*, 2014, vol. 267, p. 515.
5. Grigoriev, S.A., Dzhus, K.A., Bessarabov, D.G., and Millet, P., *Int. J. Hydrogen Energy*, 2014, vol. 39, p. 20440.

6. Grigor'ev, S.A., Dzhush', K.A., Bessarabov, D.G., Markelov, V.V., and Fateev, V.N., *Elektrokhim. Energetika*, 2014, vol. 14, p. 187.
7. Gago, A.S., Ansar, S.A., Saruhan, B., Schulz, U., Lettenmeier, P., Canas, N.A., Gazdzicki, P., Morawietz, T., Hiesgen, R., Arnold, J., and Friedrich, K.A., *J. Power Sources*, 2016, vol. 307, p. 815.
8. Langemann, M., Fritz, D.L., Muller, M., and Stolten, D., *Int. J. Hydrogen Energy*, 2015, vol. 40, p. 11385.
9. Grigoriev, S.A., Bessarabov, D.G., and Fateev, V.N., *Russ. J. Electrochem.*, 2017, vol. 53, no. 3, p. 318.
10. Grigoriev, S.A. and Kalinnikov, A.A., *Int. J. Hydrogen Energy*, 2017, vol. 42, p. 1590.
11. Fokin, M.N., Ruskol, Yu.S., and Mosolov, A.V., *Titan i ego splavy v khimicheskoi promyshlennosti. Spravochnoe posobie* (Titanium and Its Alloys in Chemical Industry. A Handbook), Leningrad: Khimiya, 1978.
12. Ohtsuka, T., Masuda, M., and Sato, N., *J. Electrochem. Soc.*, 1987, vol. 134, p. 2406.
13. Dyer, C.K. and Leach, J.S.L., *J. Electrochem. Soc.*, 1978, vol. 125, p. 23.
14. Zeng, Y., Noel, J.J., Norton, P.R., and Shoesmith, D.W., *J. Electroanal. Chem.*, 2010, vol. 649, p. 277.
15. Safronova, E.Yu. and Yaroslavl'tsev, A.B., *Membr. Membr. Tekhnol.*, 2016, vol. 6, p. 3.
16. Ehteshami, S., Mohsen Mousavi, Taheri Amirhooshang, and Chan, S.H., *J. Industr. Eng. Chem.*, 2016, vol. 34, p. 1.
17. Baranov, I.E., Grigoriev, S.A., Ylitalo, D., Fateev, V.N., and Nikolaev, I.I., *Int. J. Hydrogen Energy*, 2006, vol. 31, p. 203.
18. Baranov, I.E., Grigoriev, S.A., Nikolaev, I.I., and Fateev, V.N., *Russ. J. Electrochem.*, 2006, vol. 42, p. 1325.

Translated by T. Kabanova