

UDC 537.6

STUDY OF ELECTROMOTIVE FORCE OF THE SYSTEM $Al-Al_2O_3$ – ELECTROLYTE

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Abstract: The paper examines the features of space charge formation in anodic oxide films of metals, in particular within the $Al-Al_2O_3$ – electrolyte system, which is essential for understanding physicochemical processes at phase boundaries. It is substantiated that anodic oxide films are characterized by the presence of space-charge regions that significantly affect the electrical and optical properties of the material.

The results of experimental studies aimed at investigating the electrical characteristics of the $Al-Al_2O_3$ system in contact with various types of electrolytes are presented. It has been established that when the samples are immersed in aqueous solutions of acids, salts, and alkalis, as well as in non-aqueous electrolytes, a potential difference spontaneously arises between the electrodes. Its magnitude depends on the nature of the electrolyte, its concentration, and the experimental conditions. The performed measurements made it possible to quantitatively assess the influence of the medium composition on the electromotive force of the system. The fundamental possibility of creating primary power sources based on the studied system has been established, opening prospects for their application in micro-power engineering and autonomous sensor devices. Particular attention is paid to the luminescent properties of oxide films: it has been found that the recombination of ions arriving from the electrolyte onto the Al_2O_3 surface is accompanied by light emission, the intensity of which strongly depends on the chemical composition and concentration of the electrolyte.

The obtained results indicate the potential use of anodic aluminum oxide films as sensitive elements of sensors for monitoring the composition of liquid media, which is of practical importance for environmental monitoring, chemical analysis, and technological processes.

Keywords: aluminum oxide films, electrolyte, potential difference, electromotive force (EMF), space charge.

ДОСЛІДЖЕННЯ ЕЛЕКТРОРУШІЙНОЇ СИСТЕМИ $Al-Al_2O_3$ - ЕЛЕКТРОЛІТ

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Анотація: У роботі розглянуто особливості формування просторового заряду в анодних оксидних плівках металів, зокрема в системі $Al-Al_2O_3$ – електроліт, що є важливою для розуміння фізико-хімічних процесів на межі поділу фаз. Обґрунтовано, що для анодних оксидних плівок характерна наявність просторово-заряджених областей, які суттєво впливають на електричні та оптичні властивості матеріалу.

Наведено результати експериментальних досліджень, спрямованих на вивчення електричних характеристик системи $Al-Al_2O_3$ при її контакті з різними типами електролітів. Встановлено, що при зануренні зразків у водні розчини кислот, солей і лугів, а також у неводні електроліти, між електродами самочинно виникає різниця потенціалів, величина якої залежить від природи електроліту, його концентрації та умов експерименту. Проведені вимірювання дозволили кількісно оцінити вплив складу середовища на електрорушійну силу системи.

Встановлено принципову можливість створення на основі досліджуваної системи первинних джерел струму нового типу, що відкриває перспективи їх використання в мікроенергетиці та автономних сенсорних пристроях. Окрему увагу приділено дослідженню люмінесцентних властивостей оксидних плівок: виявлено, що рекомбінація іонів, які надходять



з електроліту на поверхню Al_2O_3 супроводжується випромінюванням світла, інтенсивність якого істотно залежить від хімічного складу та концентрації електроліту.

Отримані результати свідчать про можливість використання анодних оксидних плівок алюмінію як чутливих елементів сенсорів для контролю складу рідких середовищ, що має практичне значення для екологічного моніторингу, хімічного аналізу та технологічних процесів.

Ключові слова: оксидні плівки алюмінію, електроліт, різниця потенціалів, ЕРС, просторовий заряд.

1 INTRODUCTION

Metal oxide films are objects with high catalytic surface activity. Adsorption of molecules and ions from the environment on the surface of the oxide is very active. As a result, energy levels of adsorption origin appear in the forbidden zone. This allows the use of oxide films as detectors of the composition of the environment. Anodic aluminum oxide is one of the promising materials for sensor applications. Anodic oxide films of many metals are characterized by the phenomenon of space charge formation. The presence of a space charge in these films, the nature of which remains uncertain, indicates the possibility of using aluminum oxide films as anode electrets, as well as sources of weak currents. In this regard, there is a need to find out the mechanism of space charge formation in aluminum oxide films. On the other hand, the task of creating current sources is based on the knowledge of this mechanism.

2 ANALYSIS OF LITERARY DATA AND RESOLVING THE PROBLEM

Aluminum oxide films are used to create structures metal dielectric semiconductor, capacitors, humidity sensors, development of functional micro- and nanomaterials. Due to the properties of the porous structure, the development of nanoporous anodized materials is interesting from the point of view of obtaining membranes for the removal of toxic and valuable components from liquids. [1, 2]. The work [3] describes the development of the technology of thin-film sensor coatings made of porous anodic aluminum oxide grown on aluminum films on glass substrates. Metal oxide nanostructures are promising electrode materials for lithium ion batteries and supercapacitors due to their high specific capacity [4]. Structures based on oxide films exhibit characteristic reactions when interacting with light. This makes such structures an attractive material for the development of optically active devices [5, 6]. Amorphous Al_2O_3 films obtained using pulsed laser deposition can serve as materials with high dielectric constant for electronic devices of the new generation [7].

Anodic oxide films of many metals are characterized by the phenomenon of space charge formation. It was shown [8] that the Al/Nanosilicon/Al thin-film structure with a porous upper contact can spontaneously generate EMF when interacting with water vapor in the surrounding atmosphere. The main cause of EMF generation is the reaction of water with silicon nanoparticles. Water is necessary for chemical reactions and proton conduction that lead to EMF generation. The generation of electric current by nanoporous hydrocells based on metal oxide by water dissociation has been thoroughly investigated [9]. The generation of current due to the dissociation of water on the surface has been confirmed as a distinctive property of all metal oxide hydrocells.

Earlier [6, 10] we discovered that if the resulting $Al - Al_2O_3 - SnO_2$ structure is placed in an atmosphere containing water vapor, a potential difference of 0.4 - 0.8 V occurs between the electrodes. The value of this potential difference and current depend on the technology of preparing the oxide film, as well as on the concentration of water vapor and temperature. It is shown that the EMF arises as a result of the dissociation of water molecules adsorbed on the surface of the micropores of the oxide. It is obvious that the emergence of EMF should be expected even when dissociation does not occur on the water surface, and charged ions come from the external environment, for example, the electrolyte. Negatively charged ions are able to supply electrons to the film, which, due to their greater mobility compared to ions, are able to charge the aluminum electrode negatively, leading to the emergence of EMF in the $Al - Al_2O_3$ --electrolyte system. Despite the widespread use of anodic oxide films on aluminum in various fields of technology, their rich functional properties remain little studied and not fully understood. Due to the need to expand the functionality of microelectronic

devices based on aluminum oxide films, it was of interest to find out the specific mechanism of space charge formation in these films.

3 PURPOSE AND TASKS OF THE STUDY

The purpose of the work is to study the occurrence of EMF in the $Al - Al_2O_3 - \text{electrolyte}$ system and clarify the mechanism of space charge formation.

4 RESEARCH RESULTS

The paper studied aluminum oxide films obtained by electrochemical oxidation of aluminum foil in a 3% aqueous solution of oxalic acid [6]. The non-oxidized part of the aluminum foil was used as a contact. The second contact was a layer of SnO_2 applied to the oxide film by pyrolysis of $SnCl_4$. The contact area was approximately 1 cm². The SnO_2 layer served as an ohmic contact, in addition, this layer has significant porosity and does not prevent water vapor from the surrounding atmosphere from penetrating to the surface of the micropores of the oxide film.

It was found that if the resulting $Al - Al_2O_3 - SnO_2$ structure is placed in an atmosphere containing water vapor, a potential difference of 0.4 - 0.8 V occurs between the electrodes. The value of this potential difference and current depend on the technology of preparing the oxide film, as well as on the concentration of water vapor and temperature. It is shown that the EMF arises as a result of the dissociation of water molecules adsorbed on the surface of micropores of the oxide and the spatial separation of the charge along the film thickness due to the difference in the values of the diffusion coefficients of charged particles of the opposite sign, which are formed during dissociation.

We further proposed that the occurrence of EMF should also be expected when dissociation of water on the surface does not occur, and charged ions come from the external environment, for example, the electrolyte. In this case, not neutral molecules, but charged ions of the electrolyte of both signs, reach the surface of the film from the electrolyte. Charged ions of the electrolyte interact with the surface of the oxide film. Negatively charged ions are able to supply electrons to the film, which, due to their greater mobility compared to ions, are able to charge the aluminum electrode negatively, leading to the emergence of EMF in the $Al - Al_2O_3 - \text{electrolyte}$ system. Thus, the EMF should also appear when the oxide film is placed in the electrolyte solution.

To confirm that EMF in aluminum oxide films occurs in contact with the electrolyte, we performed measurements when the investigated films were immersed in aqueous solutions of acids, salts, and bases, as well as non-aqueous electrolytes. Indeed, it was found that the EMF appeared when the system of oxide films was immersed in these electrolytes, and the magnitude of the EMF depended on the nature of the electrolyte. In all cases, the aluminum electrode with an oxide film on it acquired a negative potential.

When using electrolytes containing strong acids, bases and salts, although the EMF value was large, intense dissolution of the aluminum electrode was observed. Obviously, the oxide film, due to the presence of micropores in it, is not able to fully protect the aluminum electrode from its destruction, so the choice of electrolyte was determined by less active substances, for example, salts of weak acids and bases. Aluminum was used as the second counter electrode. In this case, due to the flow of electrochemical processes in the studied system, one should expect either the absence of a potential difference, or the electrode without a film should be negatively charged, since it should dissolve more strongly than the one covered with an oxide film. In fact, the experiment observed the presence of a potential difference, and the aluminum electrode with an oxide film is negatively charged. This speaks in favor of the fact that the formation of EMF goes largely by the proposed mechanism.

Measurements were made with aluminum oxide films immersed in a 3% solution of ammonium sulfate salt. The area of the part of the oxide film immersed in the electrolyte was 3 cm², and its mass was 93 g. Since the dissolution of the aluminum counter-electrode was still observed during the operation of the system, a more chemically stable graphite rod was used as the second counter-electrode. EMF was observed on all samples, the value of which was 0.1-0.6 V. In fig. 1 shows typical dependences of the current strength in the $Al - Al_2O_3$ - electrolyte system from the time of testing (16 months) at a load resistance of 1 k Ω .

After the tests, the samples were freed from the electrolyte, dried, and their weight loss was determined, which is obviously related to the flow of electrochemical processes in the system under study. Weight loss was determined by weighing and amounted to 3 mg for the sample shown in Fig. 1, curve 1, and 7 mg for the sample shown in Fig. 1, curve 2.

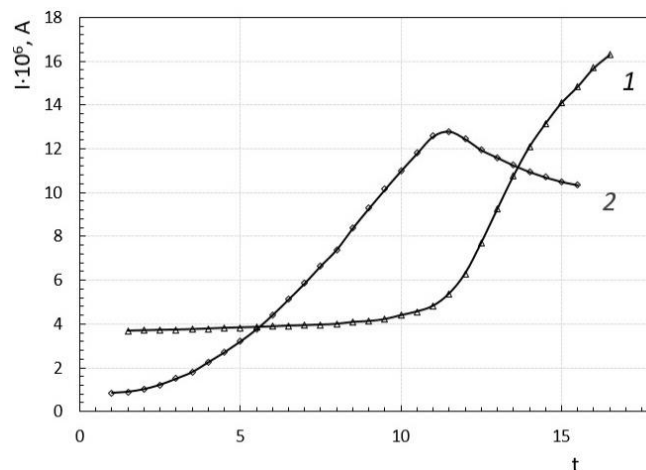


Fig. 1. Dependence of the current strength in the $Al - Al_2O_3$ - system - electrolyte from the time of testing (16 months) at a load resistance of 1 k Ω .

The total amount of electricity passed through the system and the amount of electricity passed due to electrolysis was evaluated. The total amount of electricity that passed through the $Al - Al_2O_3$ - electrolyte system was determined from Fig. 1 by the area under the curve and was approximately 400-450 C for each sample. The amount of electricity passed due to electrolysis was determined by the weight loss of the sample, taking into account the value of the electrochemical equivalent, which for aluminum is equal to $9,3 \cdot 10^{-5}$ g/C, and was 30 C for sample 1, and 70 C for sample 2.

A comparison of the total amount of electricity passed through electrolysis shows that electrolysis contributes much less than the total amount of electricity. This fact suggests that electrolysis is not the main process responsible for the flow of current in the system.

It is obvious that the occurrence of EMF and the appearance of stationary current in the $Al - Al_2O_3$ - electrolyte system occur in this way. Positively charged ions coming from the electrolyte lead to charging as a result of adsorption of the surface of the oxide film adjacent to the electrolyte. Negatively charged ions ensure the arrival of electrons to the film, which then diffuse to the aluminum electrode, as a result of which it acquires a negative potential. The neutral radicals formed at the same time leave the surface of the film, enabling the entry of other ions to it, which ensures the stationary nature of the current flow when the circuit is closed due to the resistance of the load. The recombination of ions coming from the electrolyte to the surface of the oxide film leads to the appearance of luminescence, the intensity of which also depends significantly on the concentration of certain substances in the electrolyte [6].

The value of EMF arising in the $Al - Al_2O_3$ -- electrolyte system is the same as in the $Al - Al_2O_3 - SnO_2$ structures located in the atmosphere of water vapor, however, their internal resistance is different, and therefore the currents that can be removed during the operation of such structures on an order of magnitude higher than for $Al - Al_2O_3 - SnO_2$ structures. It was found that the specific capacity is $200 - 300 Ah / kg$, the specific energy is $10 Wh / dm^3$.

5 DISCUSSION OF THE RESULTS OF THE STUDY

The systems considered by us can obviously be used as primary elements of current sources. Since the magnitude of the current depends significantly on the nature of the electrolyte, aluminum oxide films have sensory properties and can be used to determine the concentration of certain substances in the electrolyte. Also, these films can be used to create sensors in aqueous solutions of some inorganic substances.

For the practical use of current sources, it is necessary that aluminum oxide films do not break down during operation, that is, they should be able to function for a long time. One of the ways to improve these elements of current sources is to replace the aqueous electrolyte with a chemically less active, non-aqueous electrolyte.

6 CONCLUSIONS

The results of studies of aluminum oxide films obtained by electrochemical oxidation of aluminum foil are given. It was found that if the resulting $Al - Al_2O_3$ - electrolyte system is placed in an electrolyte solution, a potential difference occurs between the electrodes. The total amount of electricity passed through the system and the amount of electricity passed due to electrolysis was evaluated. It is shown that electrolysis is not the main process responsible for current flow in the system. The mechanism of formation of EMF in the studied system is proposed. An important possibility of creating primary elements of current sources has been established. It is shown that the $Al - Al_2O_3$ - electrolyte system can be used to determine the concentration of certain substances in the electrolyte. The resulting aluminum oxide films can be used to create sensors for aqueous solutions of some inorganic substances.

7 ETHICS DECLARATIONS

The author has no relevant financial or non-financial interests to disclose.

References

1. Kudelko K. O., Rozhdestvenska L. M., Borysenko Yu. V., Mikhniuk A. O., Barsukov V. Z. Formuvannia ta kharakteryzatsiia porystoho anodovanoho oksydu aliuminiuu, syntezovanoho elektrokhimichno u prysutnosti okslenoho hrafenu. Tekhnolohii ta inzhynirynh, № 2, 2021. <https://vistnuk.knutd.edu.ua/wp-content/uploads/sites/2/2021/12/48-59-2-2021.pdf>
DOI: [10.30857/2786-5371.2021.2.5](https://doi.org/10.30857/2786-5371.2021.2.5)
2. Rozhdestvenska L.M., Kudelko K.O., Ohenko V.M., Chanh M. Membranni materialy na osnovi porystoho anodnoho oksydu aliuminiuu. Ukrainskyi khimichnyi zhurnal, 86(12), (2020). 67-102. <https://doi.org/10.33609/2708-129X.86.12.2020.67-102>
3. Voitovych, T. S. Lebedeva, P. B. Shpylevoi, N. V. Bednov Pokrytyia yz nanoporystoho anodnoho oksyda aliumyniia dlia sensornykh pryumenenyi // Nanosystemy, nanomaterialy, nanotekhnolohii Nanosystems, Nanomaterials, Nanotechnologies 2014, t. 12, № 1, S. 169–180
4. Jian Jiang, Yuanyuan Li, Jinping Liu, Xintang Huang, Changzhou Yuan, and Xiong Wen (David) Lou. Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage Adv. Mater. 2012, 24, 5166–5180. <https://pubmed.ncbi.nlm.nih.gov/22912066/>

5. Burlak H.M., Vylynskaia L.N. Vliyanye perekysy vodoroda na yntensyvnost liumynestsentsyy poluprovodnykovykh plenok. //Sensor electronics and microsystem technologies. №4. 2008. S.53-56.
6. Burlak G.M., Vilinskaya L.N. Luminescence properties of oxide films aluminum and tantalum in contact with an electrolyte // Photoelectronics №21, 2012. R. 65- 68.
7. Katiyar P., Jin C., Narayan R.J. Electrical properties of amorphous aluminum oxide thin films. Acta Materialia 53 (2005) 2617–2622.
8. Dorofeev S., Kononov N., Bubenov S., Kotin P., Zolotykh A., Grigoriev D. Spontaneous Generation of Electromotive Force in Thin Film Al/Nanosilicon/Al Structures. Batteries 2017, 3, 31; doi:10.3390/batteries3040031
9. Kotnala R. K., Rekha Gupta, Abha Shukla, Shipra Jain, Anurag Gaur, Jyoti Shah Metal Oxide Based Hydroelectric Cell for Electricity Generation by Water Molecule. Dissociation without Electrolyte/Acid J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.8b04999 • Publication Date (Web): 24 Jul 2018 Downloaded from <http://pubs.acs.org> on July 25, 2018
10. Mykho.V.V., Koleboshyn V.Ya., Semeniuk L.M. Heneratsiia ERS u plivkakh oksydu aliuminiuu // Ukrainskyi fizychnyi zhurnal, 1995.-Т.40.-№11-12.-S.1209-1211.
11. Maslieieva N.V., Bohdan O.V., Brytavskiy Ye.V., Tarasevych D.V., Shuharov V.V. Vplyv rezhymiv sulfidnoi modyfikatsii poverkhni na mekhanizmy prokhozhenia strumiv ta morfolohiiu poverkhni u perekhodakh na osnovi GaAs // Zhurnal fizychnykh doslidzhen №25, 3 (2021). S. 3705-3708.

Література

1. Куделко К. О., Рождественська Л. М., Борисенко Ю. В., Міхнюк А. О., Барсуков В. З. Формування та характеристика пористого анодованого оксиду алюмінію, синтезованого електрохімічно у присутності окисленого графену. *Технології та інжиніринг*, № 2, 2021. <https://vistnuk.knutd.edu.ua/wp-content/uploads/sites/2/2021/12/48-59-2-2021.pdf>
DOI:10.30857/2786-5371.2021.2.5
2. Рождественська Л.М., Куделко К.О., Огенко В.М., Чанг М. Мембранні матеріали на основі пористого анодного оксиду алюмінію. *Український хімічний журнал*, 86(12), (2020). 67-102. <https://doi.org/10.33609/2708-129X.86.12.2020.67-102>
3. Войтович, Т. С. Лебедева, П. Б. Шпилевой, Н. В. Беднов Покрытия из нанопористого анодного оксида алюминия для сенсорных применений // Наносистемы, наноматериалы, нанотехнології Nanosystems, Nanomaterials, Nanotechnologies 2014, т. 12, № 1, С. 169–180
4. Jian Jiang , Yuanyuan Li, Jinping Liu, Xintang Huang, Changzhou Yuan, and Xiong Wen (David) Lou. Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage Adv. Mater. 2012, 24, 5166–5180. <https://pubmed.ncbi.nlm.nih.gov/22912066/>
5. Бурлак Г.М., Вилинская Л.Н. Влияние перекиси водорода на интенсивность люминесценции полупроводниковых пленок. //Sensor electronics and microsystem technologies. №4. 2008. С.53-56.
6. Burlak G.M., Vilinskaya L.N. Luminescence properties of oxide films aluminum and tantalum in contact with an electrolyte // Photoelectronics №21, 2012. P. 65 – 68.
7. Katiyar P., Jin C., Narayan R.J. Electrical properties of amorphous aluminum oxide thin films. Acta Materialia 53 (2005) 2617–2622
8. Dorofeev S., Kononov N., Bubenov S., Kotin P., Zolotykh A., Grigoriev D. Spontaneous Generation of Electromotive Force in Thin Film Al/Nanosilicon/Al Structures. Batteries 2017, 3, 31; doi:10.3390/batteries3040031
9. Kotnala R. K., Rekha Gupta, Abha Shukla, Shipra Jain, Anurag Gaur, Jyoti Shah Metal Oxide Based Hydroelectric Cell for Electricity Generation by Water Molecule. Dissociation without Electrolyte/Acid J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.8b04999 • Publication Date (Web): 24 Jul 2018 Downloaded from <http://pubs.acs.org> on July 25, 2018
10. Михо В.В., Колебошин В.Я., Семенюк Л.М. Генерація ЕРС у плівках оксиду алюмінію // Український фізичний журнал, 1995.-Т.40.-№11-12.-С.1209-1211.



11. Маслєва Н.В., Богдан О.В., Бритавський Є.В., Тарасевич Д.В., Шугаров В.В. Вплив режимів сульфідної модифікації поверхні на механізми проходження струмів та морфологію поверхні у переходах на основі GaAs // Журнал фізичних досліджень №25, 3 (2021). С. 3705-3708.

Стаття надійшла до редакції 10.11.2025

Стаття прийнята до друку 05.01.2026

Дата публікації статті 26.03.2026

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For references:

L. Vilinskaya, G. Burlak (2026). Study of electromotive force of the system Al-Al₂O₃-electrolyte. Mechanics and Mathematical Methods. VIII (1). 108 –115.

Для посилань:

Вілінська Л. М., Бурлак Г. М. Дослідження електрорушійної сили системи Al-Al₂O₃-електроліт. Механіка та математичні методи, 2026. Т. VIII. №. 1. С. 108-115.

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