

A.K. Abildina<sup>1,2</sup>, A.M. Agimbayeva<sup>1</sup>, D.A. Urazkeldiyeva<sup>1</sup>

<sup>1</sup>al-Farabi University, Almaty, Kazakhstan;

<sup>2</sup>Oldenburg University, Oldenburg, Germany

[ainaz@list.ru](mailto:ainaz@list.ru) [akmaral.argimbaeva@kaznu.kz](mailto:akmaral.argimbaeva@kaznu.kz) [urazkeldieva.97@list.ru](mailto:urazkeldieva.97@list.ru)

## REDUCTION OF MAGNESIUM ON A BISMUTH SUBSTRATE IN DIMETHYLFORMAMIDE SOLUTION

**Abstract.** A modified anode material was obtained by reducing magnesium on the surface of a bismuth electrode in an anhydrous  $\text{Mg}(\text{ClO}_4)_2$ /dimethylformamide (DMF) system. The structure and composition of the obtained anode material were determined using a scanning electron microscope and X-ray spectral microanalysis.

Analysis of the polarization curves revealed the electrochemical properties and the process of reversibility of the previously unexplored intermetallic compound consisting of Mg- Bi in  $\text{Mg}(\text{ClO}_4)_2$ /DMF system. Cyclic voltammograms showed that the processes in the system are quasi-reversible. It is proved that the process of electronic exchange is carried out by diffusion.

**Keywords:** magnesium-ion battery, bismuth, electrode, anode, dimethylformamide, reduction.

### Introduction

One of the modern scientific and technical research topical issues is the development of affordable, environmentally friendly, cheap types of energy [1]. In recent years, the use of lithium-ion batteries in the electrochemical industry has expanded and developed rapidly. However, the high cost of lithium, rare abundant in the earth's crust and the danger of dendrite formation make the use of lithium-ion batteries ineffective [2-4]. Therefore, magnesium-ion batteries with high energy density are proposed as an alternative to lithium-ion energy sources and studied their electrochemical properties [5-8]. However, the redox potential of the  $\text{Mg}^{2+}/\text{Mg}$  pair is greater than the potential of  $\text{Li}^+/\text{Li}$  pair, by about 1 V. In addition, the volume capacity of magnesium is lower than lithium,  $2061 \text{ mAh}\cdot\text{h}/\text{cm}^3$  [9, 10]. Consequently, magnesium-based batteries lag slightly behind lithium batteries. However, if cathodes with high productivity are used for such current sources, the specific energies can be up to  $100 \text{ W}\cdot\text{h}/\text{kg}$  [7]. It is much more than low-tech secondary batteries. In addition, magnesium as an anode material has many properties: low electrochemical potential, high volumetric specific capacity, large energy/power densities, most abundant in the Earth's crust, cheaper and environmentally friendly.

However, magnesium is corrosively unstable in simple electrolytes. Therefore, the replacement of metallic magnesium with other alternative materials is relevant. It also allows you to work with simple electrolytes. Recently, it was found that some p-elements in a low potential form an electrochemical reverse intermetallic with magnesium [11-13]. Magnesium ions have been found to penetrate and diffuse well into bismuth since it has a rhombohedral crystal structure [14]. Magnesium intercalated into bismuth forming magnesium bismuthide with a theoretical capacity of  $385 \text{ mAh/g}$  ( $3\text{Mg}^{2+} + 2\text{Bi} + 6\text{e} \rightarrow \text{Mg}_3\text{Bi}_2$ ) [15, 16]. W.Jin and other scientists [14] described the diffusion resistance of magnesium in bismuth. According to them, for one Mg atom in the bismuth, the most stable position is located between two layers of the Bi, where Mg has eight neighboring Bi atoms with Mg-Bi bond lengths of 3.00 and 3.07 Å. The calculated adsorption energy was -1.31 eV for one Mg atom adsorbed in Bi. According to the definition of adsorption energy, negative adsorption energy means a favorable exothermic reaction. The larger the

negative energy values are, the more favorable of the reactions are. Given this, we can conclude that bismuth can be a good adsorbate for magnesium ions. In addition, magnesium ions embedded in the bismuth crystal lattice form a weak bond, which allows quickly diffuse into the crystal lattice and have good current. For this reason, bismuth can be a promising anode material for magnesium-ion batteries.

On this basis, in the present work, bismuth is proposed to use as an anode for magnesium-ion batteries instead of non-corrosive metallic magnesium. Accordingly, was carried out the recovery of magnesium ions on the surface of the bismuth electrode and were investigated possible processes on the metal surface.

### Experimental part

Electrochemical cells in a three-electrode configuration were used for deposition experiments (high-surface area Pt-mesh counter-electrode, Ag/AgCl-reference, and pure bismuth ( $D=0.17 \text{ cm}^2$  Aldrich, 99.9% purity) as working electrodes. Before measurements metal electrode was first mechanically polished with fine emery papers (5-7  $\mu\text{m}$ ) and then wired with ethanol.

Electrolyte and electrochemical cell preparations were carried out in an Ar-filled glove box ( $\text{O}_2$  and  $\text{H}_2\text{O} < 1 \text{ ppm}$ ). For the electrolyte preparation  $\text{Mg}(\text{ClO}_4)_2$  (99.5%) was used as conductive salt. Salt  $\text{Mg}(\text{ClO}_4)_2$  was dried in a vacuum oven at  $1000^\circ \text{C}$  for 12 hours, at  $1600^\circ \text{C}$  for 6 hours, at  $2100^\circ \text{C}$  for 4 hours. Dimethylformamide (DMF, anhydrous, 99.9%) was vacuum dried before use. DMF was annealed at  $1000^\circ \text{C}$  and dried in an inert atmosphere for one week. The precipitate was filtered and twice distilled in a vacuum (at a pressure of 3-5 mm mercury column)

Cyclic voltammetry (CV), chronopotentiometry (CP) measurements were recorded on a potentiostat-galvanostat Autolab PGstat 30 potentiostat (Brinkmann Instruments Co.). The morphology of bismuth electrodes before and after tests was analyzed by Quanta 200i 3D (FEI Company, USA) scanning electron microscope (SEM). The electrodeposited alloys were characterized by X-ray diffraction (XRD) with  $\text{Cu K}\alpha$  radiation. Scanning electron microscopy (SEM) images were taken to observe the morphology of the alloy anodes.

### Results and discussion

#### *Reduction of magnesium ions on the surface of bismuth*

The deposition of magnesium to bismuth was performed by chronoamperometry. The calculation of the given potential in the potentiometric mode for the recovery of magnesium ions to a bismuth electrode, we used the Nernst equation, with recalculation to the silver chloride reference electrode:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{Ox}}}{C_{\text{Red}}} = E^\circ + \frac{0.059}{n} \lg \frac{C_{\text{Mg}^{2+}}}{1} = -2,37 - 0,02 = -2,4\text{B} \quad (1)$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = -2,4 - E_{\text{Ag}^+/\text{Ag}}^\circ = -2,4 - 0,212 = -2,6\text{B} \quad (2)$$

The theoretically calculated potential value represents the stationary potential of magnesium relative to the silver chloride electrode for an aqueous medium in the standard case. However, since the experiment is carried out in an anhydrous dimethylformamide medium, the potential activity may vary depending on the nature of the solvent. Therefore, in order to find favorable conditions for the deposition and dissolution of magnesium on the surface of the bismuth electrode were removed cyclic voltammograms in  $0.1 \text{ mol/l Mg}(\text{ClO}_4)_2/\text{DMF}$ . The reduction potential of magnesium ions was determined from the voltammograms. The deposition was carried out for 1 minute and 5 minutes. To remove the chronoamperometric curves were chosen -1.5 V and -2.6 V potentials. These potentials were taken from the calculated data and cyclic voltammograms.

#### *The structure of the formed compounds on the surface of the bismuth electrode*

To show the morphological changes in the surface of bismuth were taken micrographs by using scanning electron microscopy. And also, to confirm the presence of magnesium done an elemental analysis of the surface. Figure 1a shows a micrograph of the surface of pure bismuth. In Figures 1 b, c - the micrographs of the bismuth electrode surfaces after magnesium reduction in different time and at



different potentials. In the cathodic polarization of the electrode, there is a thick layer of non-homogeneous surface formation on the bismuth electrode surface at the microelements shot at the potentials of -1.5V and -2.6V in 5 minutes. In figures 1 (b, c) showed the formations in the form of films.

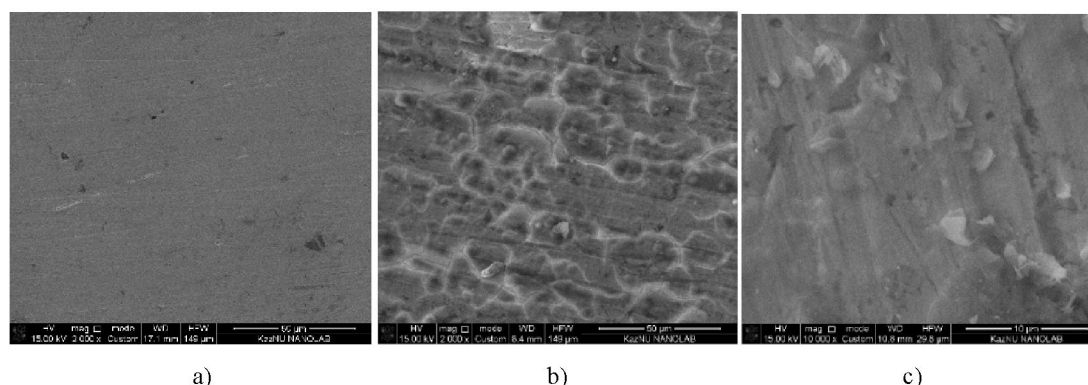


Figure 1 - Micrographs of the surface of the pure bismuth electrode (a) and after the reduction of magnesium from 0.1 mol/l  $\text{Mg}(\text{ClO}_4)_2/\text{DMF}$  solution at a potential of -1.5 V (b) and -2.6 V (c),  $\tau = 5$  minutes

In addition, the results of X-ray spectroscopy show that on the surface of metallic bismuth is contained some amount of magnesium (12.45%) after its deposition (Table 1).

Table 1 - Results of X-ray spectral microanalysis of the bismuth electrode surface after the deposition of magnesium ions from 0.1 mol/l  $\text{Mg}(\text{ClO}_4)_2/\text{DMF}$

Element	Wt, %			
	-1,5 V		-2,6 V	
	1 minute	5 minute	1 minute	5 minute
Bi	77,05	49,84	81,05	65,50
Mg	2,64	12,45	1,63	6,47
O	17,81	34,05	13,98	24,83

According to X-ray microanalysis, the bismuth electrode has the following elements: Mg, O, Bi. According to the results of the analysis, a large amount of film consists of a metallic coating (40-80%). This can be explained by the fact that during the scan caught the substrate under the film. However, the pictures clearly show the presence of the film. In our opinion, the metal substrate can be included in the film. The presence of oxygen in the composition of the film on the surface can be explained by the oxidation of Mg to  $\text{MgO}$ , as a result of the decomposition of the solvent. The presence of a large amount of magnesium in the composition indicates that it is well penetrated by the bismuth crystal lattice. This has a significant effect on the electrode potential of bismuth. To confirm this, it was taken curves dependence time from the potential of the bismuth electrode before and after the reduction of magnesium (Fig. 2).

The standard electrode potential of bismuth in aqueous media is 0.23 V versus a standard hydrogen electrode. However, given that the study is carried out in an anhydrous dimethylformamide system, the theoretically calculated potential for the silver chloride electrode used should change to 0.018 V. The changing of bismuth electrode potential from a time before magnesium deposition corresponds to the theoretically calculated potential (Fig. 2).

After deposited magnesium ions on the bismuth electrode surface electrode potential moves to the negative value. In the chronopotentiogram, which was taken after the reduction of magnesium ions on the surface of bismuth, began at -2.0 V. That is, the proximity of the standard potential of standard metallic magnesium can be explained by the relatively complete coverage of the surface of the bismuth electrode. As time increases (up to 400 seconds), the potential immediately shifts to a positive value. Magnesium on the surface of bismuth is redissolved and the potential value approaches the potential of pure bismuth. After 400 seconds, the potential value gradually stabilizes and reaches a plateau.

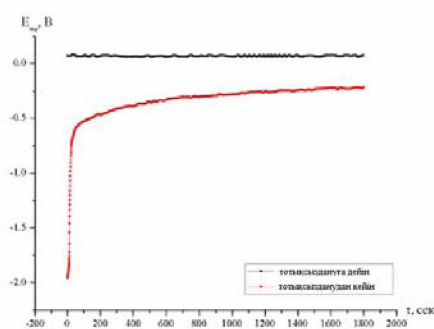


Figure 2 - Dependence of the stationary potential of the bismuth electrode on the time before and after the reduction of magnesium

### Analysis of cyclic voltammetry curves

In fig. 5a shows cyclic voltammograms of the bismuth electrode in a 0.1 mol/l  $\text{Mg}(\text{ClO}_4)_2/\text{DMF}$  solution at different scan rates (10-100 mV/s). As can be seen from the curves, magnesium is deposited on the surface of the electrode starting at a potential of -1.2 V. As the scan rate increases, the current value decreases, and the magnesium reduction potential shifts to the negative region. In addition, polarization in the opposite direction shows the oxidation peak of magnesium at a potential of -0.4 V.

According to the classical law of electrochemistry, if the sum of the potential peaks of the forward and reverse directions is  $E_0$ , and the potential difference of these peaks is  $2.2 \text{ RT/F}$  (56.5 mV), then for this region is used the Nernst equation, that is, the reaction in the system is reversible. However, in our case, the potential difference is 450 mV at  $25^\circ \text{C}$ . This means the irreversibility of the processes occurring in the system. In addition, cyclic voltammetry curves were taken at different potential scan rates. From voltammograms, it is seen that the potential difference in the direct and inverse peaks increases.

An analysis of the effect of time and potential scan rate on the direction of a cyclic voltammogram showed that the potential values for cathodic and anodic processes shift to a more negative direction as the potential scan rate and time increase. This is due to the irreversibility of the process in the system. However, due to the presence of the anode peak, the process is quasi-reversible.

Analyzing cyclic voltammograms and relying on other studies [15, 16], we can assume that the following electrochemical process will occur in the system:



### Effect of various factors on magnesium reduction

For reversible reactions, the reduction peak potential does not depend on the scan rate. For irreversible electrode reactions, the relationship between the potential of the oxidation peak and the scan rate is expressed by the following equation:

$$E_p = E_{1/2} - \left( \frac{RT}{\alpha n_a F} \right) \left[ 0,780 + \ln \left( \frac{D^{1/2}}{k_s} \right) + \ln \left( \frac{\alpha n_a F v}{RT} \right)^{1/2} \right] =$$

$$E_{1/2} - \frac{RT}{\alpha n_a F} \left[ 0,780 + \ln \left( \frac{D^{1/2}}{k_s} \right) + \ln \left( \frac{\alpha n_a F v}{RT} \right)^{1/2} \right] - \frac{RT}{\alpha n_a F} \ln v^{1/2} \quad (5)$$

Here,  $E_{1/2}$  - half-wave potential,  $n_a$  - the number of electrons,  $D^{1/2}$  - diffusion coefficient,  $\alpha$  - exchange coefficient,  $F$  - Faraday constant (C/mol),  $T$  - absolute temperature (K),  $R$  - gas constant ( $\text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $v$  - scanning rate (V/s).

According to (5) equation, the relationship between  $E_p$  and  $v^{1/2}$  is shown in Fig. 4. This relationship shows a linear relationship.

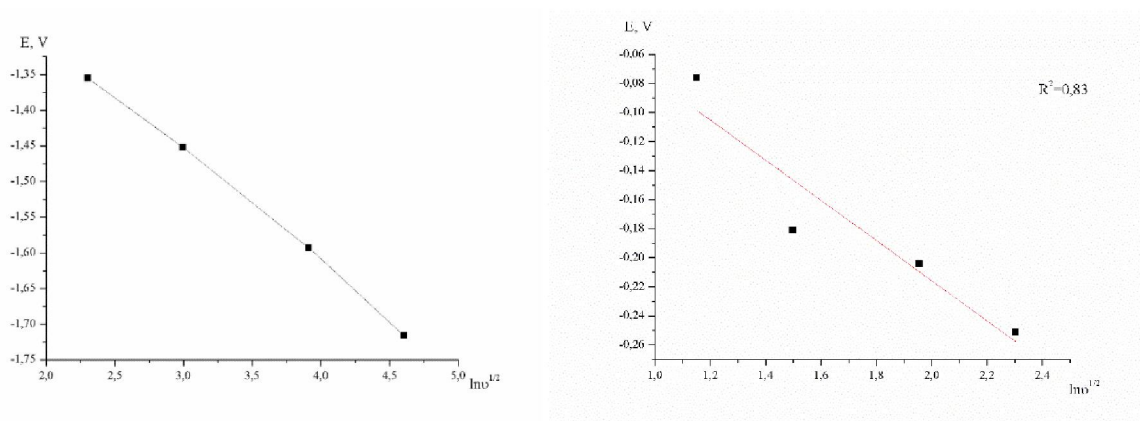


Figure 4 - The dependence of the scan rate on the currents of the anodic and cathodic peaks in 0.1 mol/l  $Mg(ClO_4)_2/DMF$

As shown in fig. 5 for this electrode reaction, the dependence of the peaks of the reduction current ( $I_p$ ) on the square root value of the sweep speed ( $v^{1/2}$ ) is observed a linear dependence. However, the linear dependence does not intersect with the origin point, so it can be predicted that the nature of the process will be quasi-reversible.

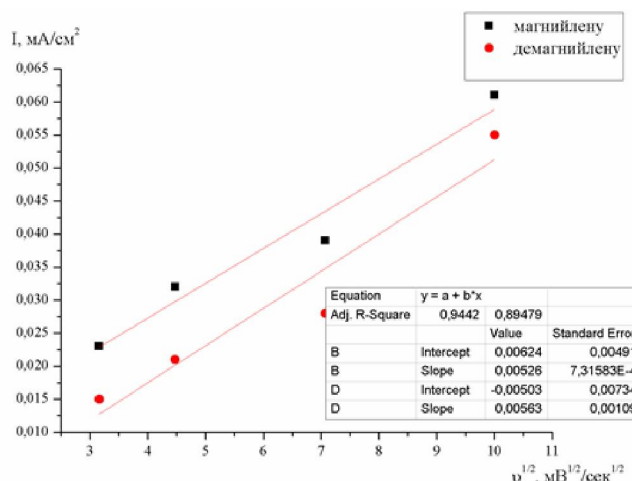


Figure 5 - Dependence of the potential scan rate on the peaks of the anodic and cathodic currents in 0.1M  $Mg(ClO_4)_2/DMF$

This satisfies the Rendles-Shevchyk equation (6) for quasi-reversible processes, which expresses the electrochemical reduction of magnesium as a diffusion process:

$$I_p = 2,69 \cdot 10^5 S n_a C_0 D_0^{1/2} v^{1/2} \quad (6)$$

Here,  $D_0$  - diffusion coefficient ( $cm^2/s$ ),  $n_a$  - number of electrons,  $v$  - scanning speed (V/sec),  $C$  - concentration of solute ( $mol/cm^3$ ),  $S$  - electrode area ( $cm^2$ ).

One of the factors that affect the size of the Mg placed on the bismuth electrode surface is the rate of potential transfer. In fig. 6a shows the reverse direction of the cyclic voltammetric curve, where the current value is 0 at various scan rates. The dependence of the potential value of the post-polarization potential on the potential scan rate is shown in Figure 6b.



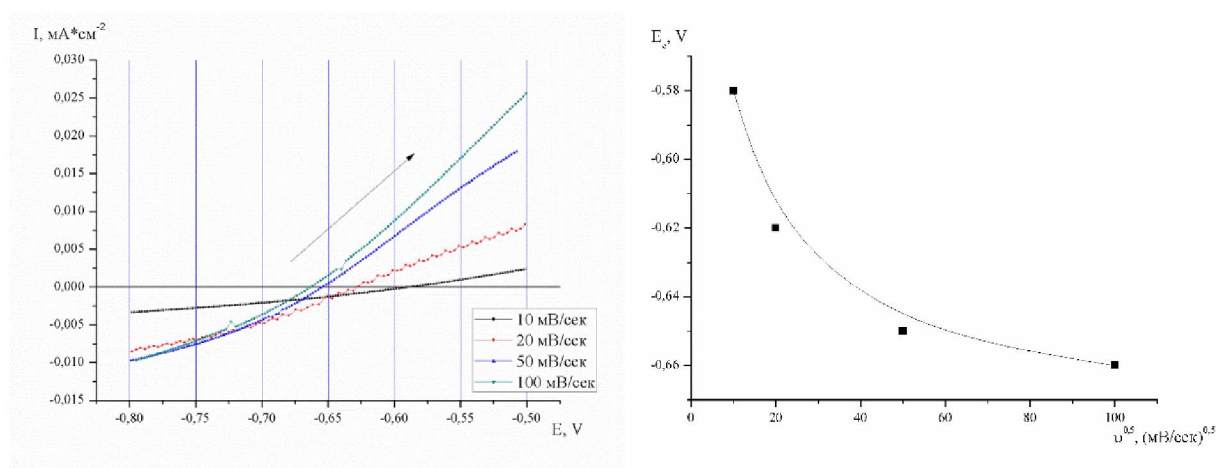


Figure 6 - a) Reverse polarization curves depending on the rate of different potential transfer of electrode of the Bi electrode 0.1M  $\text{Mg}(\text{ClO}_4)_2/\text{DMFA}$ ; b) The dependence of the rate of potential transfer on the potential potential

As the potential scan rate increases, the potential value changes from the negative direction to 50 mV / s, and then its change is not noticeable. As the scanning speed increases, the anode process takes a short time. Therefore, the oxidation reaction of magnesium does not come to an end.

### Conclusion

- The bismuth rhombohedral structure allows magnesium ions to penetrate into its crystal lattice since their diffusion rate is high, Bi was chosen as the anode material for Mg-ion batteries.
- As a result of the deposition of magnesium, the formations of bismuth electrode surfaces was detected by the scanner electron microscope (Quanta 200i 3D), and the composition was determined by energy density X-ray spectroscopy.
- Analysis of cyclic voltammograms showed that the processes in the system are quasi-reversible.
- It is proved that the process of electronic exchange is carried out by diffusion.
- As the potential scan rate increases, the cathode processes proceed quickly and magnesium is not fully reduced.

ӨОК 544.653.3

А.К. Абильдина<sup>1,2</sup>, А.М. Аргимбаева<sup>1</sup>, Д.А. Уразгельдиева<sup>1</sup>

<sup>1</sup>эл-Фараби атындағы Қазақ Ұлттық Университеті, Алматы, Қазақстан;

<sup>2</sup>Олденбург университеті, Олденбург, Германия

### ДИМЕТИЛФОРМАМИД ЕРІТІНДІСІНЕН ВИСМУТ ТӨСЕМЕСІНДЕ МАГНИЙДІҢ ТОТЫҚСЫЗДАНУЫ

**Аннотация.** Сусыз  $\text{Mg}(\text{ClO}_4)_2$ /диметилформамид (ДМФА) жүйесінде магнийді висмут электроды бетіне тотықсыздандыру арқылы модифицирленген анодтық материал алынды. Алынған анодтық материалдың құрылысы мен құрамы сканерлеуші электронды микроскоп және рентген-спектрлі микроталдау көмегімен анықталды.

Поляризациялық қисықтарды талдау нәтижесінде, бұрын зерттелмеген  $\text{Mg}(\text{ClO}_4)_2/\text{ДМФА}$  жүйесіндегі Mg-Bi интерметаллидің электрохимиялық қасиеттері, ондағы үдерістердің қайтымдылығы зерттелді. Циклдік вольтамперограммаларды талдау арқылы жүйеде өтетін үрдістердің квази-қайтымсыз екендігі анықталды. Электрон алмасу үдерісі диффузия арқылы жүзеге асатындығы дәлелденді.

**Түйін сөздер:** магний-ион батареясы, висмут, электрод, анод, диметилформамид, тотықсыздану.

## ВОССТАНОВЛЕНИЕ МАГНИЯ НА ВИСМУТОВОМ ПОДЛОЖКЕ В ДИМЕТИЛФОРМАМИДНОЙ СРЕДЕ

**Аннотация.** Было получено модифицированный анодный материал методом восстановления магния на висмутовый электрод  $\text{Mg}(\text{ClO}_4)_2$ /диметилформамид (ДМФА) системе. Структура и состав полученного анодного материала определялись с помощью сканирующего электронного микроскопа и рентгено-спектрального микроанализа. Анализ поляризационных кривых выявил электрохимические свойства интерметаллида  $\text{Mg-Bi}$  в ранее неизученной системе  $\text{Mg}(\text{ClO}_4)_2$ /ДМФА и процесс обратимости. Циклические вольтамперограммы показали, что процессы в системе квазиобратимы. Доказано, что процесс электронного обмена осуществляется путем диффузии.

**Ключевые слова:** магний-ионные батареи, висмут, электрод, анод, диметилформамид, восстановление.

### Information about authors:

Abildina A.K. – Ph.D. student, al Farabi University, Almaty, Kazakhstan. Tel: +77073986531. e-mail: [ainaz@list.ru](mailto:ainaz@list.ru), ORCID: <https://orcid.org/0000-0003-1761-7691>

Agimbayeva A.M. – Candidate of technical science, al Farabi University, Almaty, Kazakhstan. Tel: +77777279836 e-mail: [akmaral.argimbaeva@kaznu.kz](mailto:akmaral.argimbaeva@kaznu.kz), ORCID: <https://orcid.org/0000-0002-2467-8241>

Urazkeldiyeva D.A. – Student, al Farabi University, Almaty, Kazakhstan. Tel: +77783446197, e-mail: [urazkeldieva.97@list.ru](mailto:urazkeldieva.97@list.ru), ORCID: <https://orcid.org/0000-0001-7825-6995>

## REFERENCES

- [1] A.K. Bayeshova, S.Molaigan, A.B. Bayeshov (2018) News of the national academy of sciences of the republic of kazakhstan, Series chemistry and technology, Volume 5, Number 431, 107 – 116, <https://doi.org/10.32014/2018.2518-1491.14>, ISSN 2224-5286 (in Eng).
- [2] P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon (2012) Li-O-2 and Li-S batteries with high energy storage, Nature Materials, 11 (1), p.19-29. <http://dx.doi.org/10.1038/nmat3191> (in Eng).
- [3] J.-I. Yamaki and S.-I. Tobishima, in Handbook of Battery Materials, ed. C. Daniel and J. O. Bessenhard (2011) Wiley-VCH Verlag & Co. KGaA, Weinheim, Germany, ch. 13. (in Eng).
- [4] C. Wang, D. L. Wang and C. S. Dai (2008) J. Electrochem. Society, 155, A390. (in Eng).
- [5] T. Gregory, R. J. Hoffman and R. C. Winterton (1990) Nonaqueous electrochemistry of magnesium - applications to energy-storage, J. Electrochem. Soc., 137, 775. (in Eng).
- [6] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi (2000) Prototype systems for rechargeable magnesium batteries, Nature, 407, 724 <http://dx.doi.org/10.1038/35037553> (in Eng).
- [7] P. Novak, R. Imhof and O. Haas (1999) Magnesium insertion electrodes for rechargeable nonaqueous batteries - a competitive alternative to lithium? Electrochim. Acta, 45, 351. [http://dx.doi.org/10.1016/S0013-4686\(99\)00216-9](http://dx.doi.org/10.1016/S0013-4686(99)00216-9) (in Eng).
- [8] J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Zajicek, and Y. Kotani (2012) Electrolyte roadblocks to a magnesium rechargeable battery, Energy and Environmental Science, 5, 5941. <http://dx.doi.org/10.1039/c2ee03029b> (in Eng).
- [9] Matsui M. (2011) Study on electrochemically deposited Mg metal, J. Power Sources, 196:7048–55. <http://dx.doi.org/10.1016/j.jpowsour.2010.11.141> (in Eng).
- [10] J.M. Tarascon, M.Armand (2001) Issues and challenges facing rechargeable lithium batteries, Nature, 414, 359 DOI: 10.1038/35104644 (in Eng).
- [11] Timothy S. Arthur, Nikhilendra Singh, Masaki Matsui. (2012) Electrodeposited Bi, Sb and Bi<sub>1-x</sub>Sb<sub>x</sub> alloys as anodes for Mg-ion batteries, Electrochemistry Communications 16, p.103–106 DOI:10.1016/j.elecom.2011.12.010 (in Eng).
- [12] Roberta A. DiLeoQing Zhang, Amy C. Marschlok, Kenneth J. Takeuchi and Esther S. Takeuchi (2015) Composite Anodes for Secondary Magnesium Ion Batteries Prepared via Electrodeposition of Nanostructured Bismuth on Carbon Nanotube Substrates, ECS Electrochemistry Letters, 4 (1) A10-A14, DOI:10.1149/2.0081501eel (in Eng).
- [13] D.-T. Nguyen, S.-W. Song (2017) Magnesium stannide as a high-capacity anode for magnesium-ion batteries, Journal of Power Sources 368 11-17 <http://dx.doi.org/10.1021/acs.nano.8b01847> (in Eng).
- [14] W. Jin, Z. Li, Z. Wang, Y.Q. Fu (2016) Mg ion dynamics in anode materials of Sn and Bi for Mg-ion batteries, Materials Chemistry and Physics, p.1-6 <http://dx.doi.org/10.1016/j.matchemphys.2016.07.019> (in Eng).
- [15] M. Ramanathan, A. Benmayza, J. Prakash, N. Singh, F. Mizuno (2016) A porous model for the magnesiation and demagnesiation of bismuth electrode in rechargeable magnesium-ion cells, Journal of the electrochemical society, 163 (3) A477-A487 <http://dx.doi.org/10.1149/2.0581603jes> (in Eng).
- [16] Y.-H. Tan, W.-T. Yao, T. Zhang, T.Ma, L.-L Lu, F.Zhou, H.-B.Yao, S.-H. Yu () High voltage magnesium-ion battery enabled by nanocluster Mg<sub>3</sub>Bi<sub>2</sub> alloy anode in the noncorrosive electrolyte, ACS Nano, 12 (6), 5856-5865 <http://dx.doi.org/10.1021/acs.nano.8b01847> (in Eng).