PHYSICS AND CHEMISTRY OF SOLID STATE
V. 23, No. 4 (2022) pp. 836-841

Section: Physics

DOI: 10.15330/pcss.23.4.836-841

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 23, № 4 (2022) С. 836-841

Фізико-математичні науки

PACS: 31.15.ac

ISSN 1729-4428

L.O. Solianyk

Influence of the melt composition on the cathode current density in electrode reactions

A.V. Dumansky Institute of Colloid and Water Chemistry, Kyiv, Ukraine, solianyk2017@gmail.com

Within the framework of the Dogonadze-Kuznetsov-Levich theory, with the replacement of the classical Boltzmann distribution by the Fermi-Dirac quantum distribution and the simplest dispersion law, an expression for the discharge of currents at the dielectric/electrolyte interface is provided. An approach to estimate the average density of electronic levels from which heterogeneous charge transfer is carried out is proposed. An expression for obtaining the numerical value of the cathode current density was found. The conditions for the occurrence of surface conductivity of a dielectric in a salt melt without its prior metallization are formulated. It is substantiated that the type of surface conductivity depends on the energy reorganization, energy reagents and product reaction in the electrode field, transmission coefficient and other quantities that have a value of the chemical composition of the electrolyte, and can be significantly calculated by analytical or quantum chemical methods. It was established that the adsorption of carbon dioxide on the surface of the dielectric leads to a significant polarization of the surface cluster to the side of the conduction zone. The width of the band gap decreases, but the dielectric character of the cluster does not change, there is no overlapping of the band, that is, the electrode does not acquire the semiconducting and semimetallic character of conductivity. At that time, the adsorption of BO^{2-} on the electrode surface leads to a strong polarization of the surface cluster towards the valence band. With this width of the band gap decreases slightly, less than in the case of carbon dioxide.

Keywords. Redox reactions, electrode, dielectric, semiconductor.

Received 02 September 2022; Accepted 20 December 2022.

Introduction

Hard materials that are particularly important from a technical perspective are divided into natural hard materials (diamond, corundum, and others) and synthetic hard materials (refractory carbides, borides, nitrides, and metal silicides). For metallurgy, industries of hard alloys and grinding materials, it is necessary that a hard material in addition to significant hardness (8-9 on the Mohs scale), a high melting point also feature a metallic character and be able to form alloys with metals of the iron group. These requirements are met, in particular, by carbides of transition metals of groups IV A - VI A of the periodic table. Among them, the most important carbides are WC, TiC, TaC, as well as VC, NbC and Mo_2C, cemented by cobalt or nickel [1-2].

The experimentally discovered [3] possibility of deposition of galvanic coatings on natural and synthetic diamond-dielectrics without prior formation of a conductive layer [4] showed an occurrence of conductivity of a diamond immersed in a carbonate-containing melt and lack of conductivity, for instance, in a boride-containing melt. Based on the experimental data, the authors [4] drew a phenomenological conclusion that surface conductivity of diamond in oxide melts is caused by the course of redox processes at interphacial boundary. Later, a model scheme of variation of diamond surface conductivity was proposed (based on the analysis of the results of quantum chemical calculations), which explains the occurrence of conductivity of a surface layer of diamond-dielectric. However, the problem of a type and a mechanism of occurence of the surface conductivity in this case remains debatable which served as a springboard for development and generalization of the Dogonadze-Kuznetsov-Lyvych theory regarding dielectric/electrolyte interphacial boundary in order to substantiate the possibility of occurence of surface conductivity of dielectric in saline melts.

I. The research methodology

According to the band theory of solids, density of electronic levels in metals is practically constant, at the same time for a dielectric and a semiconductor it depends weakly on energy of electron in the depth of the band, but in the vicinity of the band boundaries the dependence is complex and based on the choice of a particular dependence model $g = g(E)$. Since charge carriers located near the band boundaries contribute the most to discharge current, in order to establish the specificity of heterogeneous reactions at dielectric/electrolyte boundary, it is necessary to take into account the dependence of density of electronic levels on energy of an electron. In this work, a standard model [5] of the dependence of the density of electronic levels on the energy is chosen:

$$g(E) = A \cdot \sqrt{E} \qquad (1)$$

Where E - energy of an electron or a hole calculated from the boundary of a corresponding band, A – dimensional numerical parameter. Replacing $g(E) = \text{const}$ with $g(E) = \text{const}$ definitely takes into account the features of the band structure of solids in the best possible way to solve the given task.

1.1. Calculation of cathodic current density through the conduction band

In order to calculate cathode current density within the framework of the Dogonadze-Kuznetsov-Levich theory at a single-electron transfer through the conduction band of a solid, let us presume that: 1) the redox reaction takes place at the distance of the maximum approach of a discharging ion to the electrode, 2) electron transfer is not accompanied by breaking or formation of chemical bonds, 3) in order to exclude electron tunneling in the band gap, the Debye shielding length in a solid body is taken as quite large, 4) total potential drop is concentrated in a solid body. Taking the aforesaid into account, within the Dogonadze-Kuznetsov-Levich theory [5], the cathode current density through the conduction band is equal to:

$$j_c = A \cdot F[c]\frac{\omega_{eff}}{2\pi}\kappa(\delta) \cdot \delta \int_{E_C+F\eta}^{\infty}\left(E - (E_C + F\eta)\right)^{\frac{1}{2}} \frac{1}{1+exp\frac{E-E_F}{RT}} exp\left(\frac{-(\Delta G(E)+\lambda)^2}{4RT\cdot\lambda}\right) dE \qquad (2)$$

where $[c]$ – the concentration of discharging ions, ω_{eff} – is the effective fluctuation frequency of all classic degrees of freedom, $\kappa(x)$ – a transmission coefficient, δ – thickness of the reaction zone, E_C – energy of conduction band minimum at the absence of overvoltage, η – overvoltage, $\Delta G(E) = F\eta + W_P - W_R + E_F - E$ - Gibbs energy of the reaction, W_P and W_R – the enegry of the reaction product and the reactant in electrode field; E_F – the Fermi energy, λ – total (outer- and inner-sphere) reorganization energy. The limits of integration of the integral are chosen under the assumption that the energy is counted from the minimum of the valence band. Since the integral in expression (2) cannot be evaluated precisely, we will rewrite it taking into account the asymptotic expansion of the integral by a large parameter $\beta = RT$:

$$\begin{aligned} j_c = A\chi\frac{\sqrt{\pi}}{3}\left(\frac{2RT\cdot\lambda}{\lambda+\Delta_C-W_P+W_R}\right)^{\frac{3}{2}} exp\left(\frac{-\Delta_C+F\eta}{RT}\right) \times exp\left(\frac{-(\lambda-\Delta_C+W_P-W_R)^2}{4RT\cdot\lambda}\right) \times \\ \times \sum_{m=0}^{\infty}\left(\frac{1}{m!}\prod_{i=0}^{m}\left(\frac{3}{2}+i\right)\left(\frac{2RT\cdot\lambda}{\lambda+\Delta_C-W_P+W_R}\right)^{m}\sum_{s=0}^{m} C_m^s f^{(s)}(E_C+F\eta)\frac{(-1)^{\frac{m-s}{2}}}{(4RT\cdot\lambda)^{\frac{m-s}{2}}}\frac{(m-s)!}{\left(\frac{m-s}{2}\right)!}\delta_{\left[\frac{m-s}{2}\right]}^{\frac{m-s}{2}}\right), \end{aligned} \qquad (3)$$

where $f(E) = \frac{1}{1+exp\frac{E_F-E}{RT}}$, $\chi = F[c]\frac{\omega_{eff}}{2\pi}\kappa(\delta)\cdot\delta$, $\Delta_C = E_C - E_F$ - distance from Fermi level to the minimum of the conduction band in equilibrium; $\delta_{\left[\frac{m-s}{2}\right]}^{\frac{m-s}{2}}$ - Kronecker delta; $[x]$ - the integral part of a number x.

Let us write out the first part of the obtained asymptotic series:

$$j_c \approx A\chi\frac{\sqrt{\pi}}{2}\left(\frac{2RT\cdot\lambda}{\lambda+\Delta_C-W_P+W_R}\right)^{\frac{3}{2}}\frac{1}{1+exp\frac{\Delta_C+F\eta}{RT}} exp\left(\frac{-(\lambda-\Delta_C+W_P-W_R)^2}{4RT\cdot\lambda}\right)$$

In the simplest case when homogeneous electron gas in an electrode is non-degenerate ($E - E_F \gg RT$), the Fermi–Dirac distribution approaches the Maxwell–Boltzmann distribution:

$$\left(1 + exp\frac{E-E_F}{RT}\right)^{-1} = exp\left(\frac{-E-E_F}{RT}\right).$$

Asymptotic series for (3) appears as follows:

$$j_c = A\chi\frac{\sqrt{\pi}}{3}\left(\frac{2RT\cdot\lambda}{\lambda+\Delta_C-W_P+W_R}\right)^{\frac{3}{2}} exp\left(\frac{-\Delta_C+F\eta}{RT}\right) exp\left(\frac{-(\lambda-\Delta_C+W_P-W_R)^2}{4RT\cdot\lambda}\right) \times$$

$$\times \sum_{m=0}^{\infty} \frac{(-1)^{\frac{m}{2}}}{\left(\frac{m}{2}\right)!} \prod_{i=0}^{m} \left(\frac{3}{2} + i\right) \frac{1}{(4RT \cdot \lambda)^{\frac{m}{2}}} \left(\frac{2RT \cdot \lambda}{\lambda + \Delta_C - W_P + W_R}\right)^{m} \delta_{\left[\frac{m}{2}\right]}^{\frac{m}{2}} \quad (4)$$

The first part of the expression (4) appears as follows:

$$j_c \approx A\chi \frac{\sqrt{\pi}}{2} \left(\frac{2RT \cdot \lambda}{\lambda + \Delta_C - W_P + W_R}\right)^{\frac{3}{2}} exp\left(\frac{-\Delta_C + F\eta}{RT}\right) exp\left(\frac{-(\lambda - \Delta_C + W_P - W_R)^2}{4RT \cdot \lambda}\right) \quad (5)$$

It should be noted that in [5], due to the choice of the simplest law of variance in the final formulas for discharge currents, the value $g(E)$ remained a parameter that could not be calculated precisely, which diminished the importance of received results. The approach proposed in this work, as shown by the calculations, allows to present the average density of electronic levels, from which the heterogeneous charge transfer is carried out, as follows:

$$g_{sr} \approx A \cdot \frac{\sqrt{\pi}}{2} \left(\frac{2RT \cdot \lambda}{\lambda + \Delta_C - W_P + W_R}\right)^{\frac{1}{2}} \quad (6)$$

Thus, the proposed option of evaluation of the expression (4) enables obtaining a numerical value of cathode current density. Thus, taking into account (5), formula (6) appears as follows:

$$j_c \approx \chi \cdot g_{sr} \frac{2RT \cdot \lambda}{\lambda + \Delta_c - W_p + W_r} exp\left(\frac{-\Delta_c + F\eta}{RT}\right) exp\left(\frac{-(\lambda - \Delta_c + W_p - W_r)^2}{4RT \cdot \lambda}\right). \quad (7)$$

If we take values of reorganization energy which satisfy the inequality $\lambda \gg |\Delta_c - W_p + W_r|$ for a non-adiabatic reaction in the Point Particle Model, formula (7) turns into similar formulas for cathode current density through the conduction band obtained in [5] for the interfacial boundary semiconductor/electrolyte.

The analysis of the expression (5) regarding a possibility of an appearance of discharge currents at the interfacial boundary “dielectric/electrolyte” showed that concentration $\frac{1}{1+exp\frac{\Delta_C + F\eta}{RT}}$ and activation $exp\left(\frac{-(\lambda - \Delta_C + W_P - W_R)^2}{4RT \cdot \lambda}\right)$ components contribute the most into the value of cathode current density through the conduction band. Knowing that for a dielectric in standard conditions $\frac{\Delta_C + F\eta}{RT} \gg 1$, therefore $\frac{1}{1+exp\frac{\Delta_C + F\eta}{RT}} \to 0$ and as it is derived from (5.3.4), $j_C = 0$, which indicates the absence of redox processes at the interphacial boundary. It is obvious that current density may be non-zero if $\frac{\Delta_C + F\eta}{RT} \sim 1$. However, the following conditions are required for this ratio to be realized: 1) high temperature of the environment; 2) significant cathodic overvoltages; 3) appropriate physical and chemical properties of the electrolyte which contacts with the electrode surface, capable of affecting (e.g. due to adsorption), the change in the distance from Fermi level to the minimum of conduction band. In reality, these conditions can be fulfilled only in saline melts, where the adsorption of melt ions can occur, which leads to the appearance of significant induced dipole moments in the adsorbate particles due to the redistribution of electron density between adsorbent and adsorbate. As a result of the aforesaid redistribution, a position of Fermi level changes, and, as a consequence, it approaches the minimum of conduction band (or the boundary of valence band) transforming surface layer of dielectric into a conductive state. Alteration in cationic-anionic composition of a melt leads to a change in the values $\lambda, \Delta_C, \chi, W_P, W_R$ and allows both to influence the particle interaction mechanism in the volumetric phase of a melt and to control the rate of redox reactions at the interfacial boundary ”dielectric/melt”. It obviously leads to the fact that in melts of a certain chemical composition, dielectric begins to show an electrode function, and, as a consequence, acts as an active base in high-temperature electrochemical synthesis. It is possible to establish the type of surface conductivity (electron or hole) only based on: 1) specifying the type of particles in saline melt; 2) numerical calculation (analytical or quantum chemistry methods) of reorganization energy, energy of reactants and reaction products in electrode field, transmission coefficient, etc.

Thus, within the framework of Dogonadze-Kuznetsov-Levich theory, having replaced the classic Maxwell–Boltzmann distribution with the quantum Fermi–Dirac distribution and the simplest law of variance $g(E) = const$ with $g(E) = A \cdot \sqrt{E}$, an expression for discharge currents at the interfacial boundary dielectric/electrolyte was obtained.

1.2. Quantum-chemical calculations of particle parameters

Quantum-chemical calculations [6,7] were done in order to assess a possibility of appearance of surface conductivity. Electrode surface was modeled by a $C_{70}H_{24}$ cluster (Fig. 1); as melt structural particles for modeling a charge transfer stage at reduction of electrochemically active complexes (EACs) and receiving carbides and tungsten borides - isoelectronic molecules CO_2 i BO_2^- together with an $[WO_4]^2$ anion surrounded by two singly charged cations of the same type Ca^{2+} or Mg^{2+}, or by four singly charged cations Li^+.

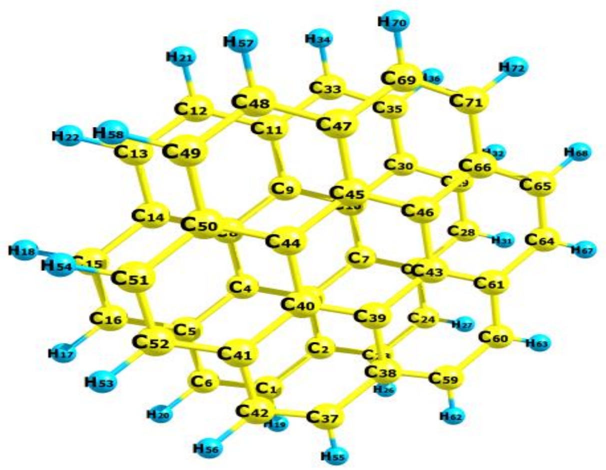

Fig. 1. The structure of an electrode surface fragment $C_{70}H_{24}$.

II. Results and their discussion

Having calculated and analyzed the received values of enegries of highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO), it is established that a presence of the particles CO_2 and BO_2^- in the proximity of the cluster $C_{70}H_{24}$, firstly, does not affect the HOMO values of the cluster $C_{70}H_{24}$ radically. Secondly, involvement of $[WO_4]^{2-}$ anions cause an insignificant rise of HOMO values of the cluster, the rise is greater in the case with BO_2^-. Finally, when an EAC $\{M_n^{m+}[WO_4]^{2-}\}^{(nm-2)+}$ (Fig. 2) is involved, it, on the contrary, decreases significantly (approximately twofold) the HOMO values of the cluster. However, these values decrease insignificantly for the clusters in the presence of BO_2^-. At the same time there is a downward trend of energy gap values of the marginal molecular orbitals, the trend is more substantial for carbonate melts. Reactivity alteration of the surface of a dielectric electrode at the alteration of cationic composition of a melt reflects both the specificity of chemical interaction of particles in saline melts and the course of heterogeneous redox reactions on the surface of dielectric.

The essence of this effect (transition of the surface layer of a dielectric into a conductive state) is caused by the redistribution of electronic density between an adsorbent and an adsorbate, which leads to corresponding changes in values of Fermi energy of electrons on the electrode surface, as well as energies of marginal molecular orbitals of an EAC. It is obvious that the greatest plus side of this effect is equalizing Fermi energy levels of a cathode material and LUMO energies of an EAC.

The points on the charts correspond to the following interactions: 1- BO_2^- or CO_2; 2- CO_2 (or BO_2^-)…$[WO_4]^2$; 3- CO_2 (or BO_2^-)… $\{Li_4^+[WO_4]^{2-}\}^{2+}$; 4 - CO_2 (or BO_2^-)… $\{Ca_2^{2+}[WO_4]^{2-}\}^{2+}$; 5- CO_2 (or BO_2^-)… $\{Mg_4^+[WO_4]^{2-}\}^{2+}$; 6- $C_{70}H_{24}$; 7- $C_{70}H_{24}$… CO_2 (or BO_2^-); 8- $C_{70}H_{24}$…CO_2 (or BO_2^-)…$[WO_4]^{2-}$; 9 $C_{70}H_{24}$… CO_2 (or BO_2^-) … $\{Li_4^+[WO_4]^{2-}\}^{2+}$; 10- $C_{70}H_{24}$… CO_2 (or BO_2^-)… $\{Ca_2^{2+}[WO_4]^{2-}\}^{2+}$; 11 - $C_{70}H_{24}$… CO_2 (or BO_2^-) … $\{Mg_2^{2+}[WO_4]^{2-}\}^{2+}$. The calculation of cathode current was done at single-electron charge transfer through the conduction band of a dielectric [8,9] using the selected model of the dependence of electron level density on the energy

$$g(E) = 4\pi(2m/h^2)^{2/3} \tag{8}$$

which showed:

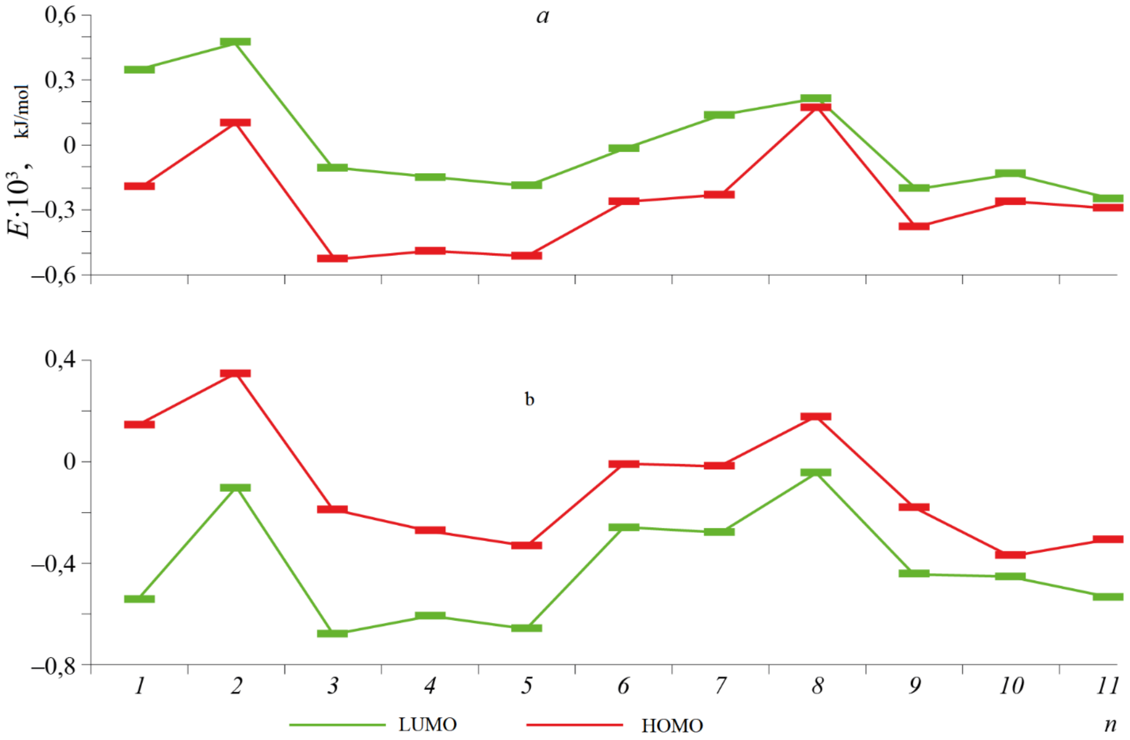

Fig. 2. A line chart of LUMO and HOMO values for interactions $C_{70}H_{24}…CO_2$ i $C_{70}H_{24}…BO_2^-$, in the presence of the particles $\{M_n^{m+}[WO_4]^{2-}\}^{(nm-2)+}$, where M=$Li^+$, Ca^{2+}, Mg^{2+} in the presence of a) BO_2^- b) – CO_2.

$$\frac{j_{\text{д}}}{j_{\text{м}}} = const\,\frac{1}{2}\left(\frac{h^2}{2\pi m_n}\right)^{\frac{3}{2}}\sqrt{\frac{\lambda-\Delta G}{2kT\cdot\lambda}} \qquad (9)$$

where $j_{м}$ – current density in the model g(E) = const, λ – general reorganization energy, ΔG – Gibbs energy of electron transfer reaction.

The calculation outcomes of solid/metal exchange current ratio in accordance with (9) for alternative interactions $C_{70}H_{24}\ldots CO_2$ i $C_{70}H_{24}\ldots BO_2^-$, in the presence of the particles $\{M_n^{m+}[WO_4]^{2-}\}^{(nm-2)+}$, where M=$Li^+$, Ca^{2+}, Mg^{2+}, at n=0, n=4 – for the case of the cations Li^+, n=2 – Ca^{2+}, Mg^{2+} based on the data received from quantum-chemical calculations are presented in the table below:

Table 1

Received results of solid ($C_{32}H_{21}$)/metal cathodic currents ratio.

Echange currents	$j_{\partial}/ j_{м}$	
Type of interaction	Y=CO_2	Y=BO_2^-
$C_{70}H_{24}\ldots Y$	0.0427	0.0044
$C_{70}H_{24}\ldots Y\ldots WO_4^{2-}$	0.0452	0.0048
$C_{70}H_{24}\ldots Y\ldots\{Li_4^+[WO_4^{2-}]\}^{2+}$	0.0781	0.0054
$C_{70}H_{24}\ldots Y\ldots\{Ca_2^{2+}WO_4^{2-}]\}^{2+}$	0.0803	0.0056
$C_{70}H_{24}\ldots Y\ldots\{Mg_2^{2+}WO_4^{2-}]\}^{2+}$	0.0779	0.0057

The analysis the above data shows the presence of non-zero exchange currents on the surface of $C_{32}H_{21}$, which interact with structural particles of the melt. For instance, when a diamond cluster interacts with CO_2 particles, the ratio is by far greater than in interactions with BO_2^-. This trend remains when an EAC $\{M_n^{m+}[WO_4]^{2-}\}^{(nm-2)+}$ is involved, at the same time in interactions with particles of a tungsten-containing melt, the ratio $j_{\partial}/ j_{м}$ rises almost twofold. For the entire range of interactions of the cluster in the presence of BO_2^- the ratio $j_{\partial}/j_{м}$ remains almost the same, this fact does not allow us to assert the presence of heterogeneous electron exchange reactions on diamond surface for boron-containing melts, even with a qualitative comparison of values of the exchange current values in a carbonate-containing melt. In addition, it can be seen from expression (9) that in a general case, the ratio depends both on the features of the band structure of a solid and on the physicochemical characteristics of the structural particles of the polar liquid. For values of the Gibbs free energy ΔG that satisfy the condition λ >> ΔG, of the expression (9) it is directly obtained that $j_{\partial} = j_{м}$.

Conclusions

Thus, the model g(E)=const can be used to calculate the rate of redox processes at solid/polar liquid boundary only for Gibbs free energy values which satisfy the condition λ >> ΔG. In a general case, in order to calculate exchange currents at semiconductor/polar liquid interphacial boundaries, it is necessary to use other dependences of variance law on the energy in accordance with the features of a band structure of a solid. Also, the analysis of the obtained results provides grounds for substantiating the possibility of joint electroreduction of melt particles on dielectric surface, which is achieved in the presence, firstly, of carbonate-containing melt particles - CO_2. Secondly, the mere presence of CO_2 particles in a tungsten-containing melt is not enough for tungsten reduction. In order to implement joint electroreduction of carbon and tungsten during the high-temperature electrochemical synthesis of tungsten carbides, the presence of strongly polarizing cations Li^+, Ca^{2+}, Mg^{2+} is necessary, i.e. the course of heterogeneous redox reactions is possible only for particles of the type $M_n^{m+}[WO_4]^{2-}\}^{(nm-2)+}$ in the presense of CO_2 which in practice enables joint electroreduction by combining the potentials of carbon and tungsten reduction (achieved through changing melt acidity - cationic catalysis), as well as alteration of phase composition of electrolysis products and their nanostructure.

I would like to express my gratitude to PhD in physical and chemical sciences, S. Kovalenko for discussing the obtained results.

Solianyk L.O. – Candidate of Chemical Sciences, Associate Professor, Senior Research Fellow.

[1] K. Liu, Z. Wang, Z. Yin, L. Cao, J. Yuan, *Effect of Co content on microstructure and mechanical properties of ultrafine grained WC-Co cemented carbide sintered by spark plasma sintering*, Ceram. Int. 44, 18711 (2018); https://doi.org/10.1016/j.ceramint.2018.07.100.

[2] J. Garcia, V.C. Cipres, A. Blomqvist, B. Kaplan, *Cemented carbide microstructures: a review*, Int. J. Refract. Met. Hard Mater. 80, 40 (2019); https://doi.org/10.1016/j.ijrmhm.2018.12.004.

[3] V.I. Shapoval. H.B. Kushkhov, V.V. Malyshev et al., *Deposition of Molybdenum Carbide onto the Diamond Surface by Electrolysis of Ionic Melts*, Powder metallurgy. 7, 43 (1986).

[4] V.V. Solovyov, V.V. Malyshev, A.I. Gab, *Physicochemical processes at the dielectric/oxide melt interface and their application in the electrocoating of diamond powders*, Theoretical foundations of chemical technology. 38(2), 219 (2004).

[5] R.R. Dogonadze, Yu.A. Chizmadzhev, *Kinetics of some electrochemical redox reactions in semiconductors*, Dokl. AN SSSR, 150(2), 333 (1963).

[6] Firefly and PC GAMESS /Firefly version 8.0.1. Access mode. [Electronic resource]. Alex A. Granovsky. http://classic.chem.msu.su/gran/games/forum/discussion.html.

[7] In memory of Alex A. Granovsky. [Electronic resource]. http://classic.chem.msu.su/gran/gamess/index.html.

[8] S. Kovalenko, V. Soloviev, *Kinetics of the Elementary Act of Electrochemical Reactions at the Semiconductor–Electrolyte Solution Interface*, Zeitschrift fuer Naturforschung, A: Physical Sciences. 69a. 654. (2014); https://doi.org/10.5560/ZNA.2014-0063.

[9] V.V. Malyshev, V.V. Soloviev, L.A. Chernenko, V.N. Rozhko, *Management of composition cathodic products in the electrolysis of molybdenum-, tungsten- and carbon-bearing halogenide-oxide and oxide melts,* Mat.–wiss. u. Werkstofftech, 46(1), 5 (2015); https://doi.org/10.1002/mawe.201400331.

Л.О. Соляник

Вплив складу розтопу на густину катодного струму в електродних реакціях

Інститут колоїдної хімії та хімії води ім. А.В. Думанського НАН України, м. Київ, solianyk2017@gmail.com,

У рамках теорії Догонадзе-Кузнецова-Левича із заміною класичного розподілу Больцмана на квантовий розподіл Фермі-Дірака й найпростішого закону дисперсії одержано вираз для струмів розряду на міжфазній межі діелектрик/електроліт. Запропоновано підхід оцінки середньої густини електронних рівнів, з яких відбувається гетерогенний перенос заряду. Знайдено вираз для отримання чисельного значення густини катодного струму. Сформульовано умови виникнення поверхневої провідності діелектрика в сольовому розтопі без попередньої його металізації. Обґрунтовано, що тип поверхневої провідності залежить від енергії реорганізації, енергій реагентів і продуктів реакції в полі електрода, трансмісійного коефіцієнта й інших величин, значення яких визначаються хімічним складом електроліту й можуть бути чисельно розраховані аналітичними або квантовохімічними методами. Встановлено, що адсорбція діоксиду вуглецю на поверхні діелектрика приводить до значної поляризації кластера поверхні убік зони провідності. Ширина забороненої зони зменшується, але діелектричний характер кластера не змінюється, не відбувається перекривання зон, тобто електрод не набуває напівпровідникового й напівметалевого характеру провідності. В той час адсорбція BO_2^- на поверхні електрода приводить до сильної поляризації кластера поверхні у бік валентної зони. При цьому ширина забороненої зони незначно зменшується, менше ніж у випадку діоксиду вуглецю.

Ключові слова. Окислювально-відновні реакції, електрод, діелектрик, напівпровідник.