

## The Influence of Nanosized Active Particles of the Melt and the Electrode Surface on Charge Transfer Processes at the Electrode/Melt Interface

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By using methods of quantum chemistry, in order to study a mechanism of electrode processes at the electrode/melt interface, calculations of reorganization energy were made within a model of conductive ellipsoids, which generalizes the Marcus model for a case when reagents are substantially non-spheric. It was ascertained that a value of reorganization energy of a dissolvent hardly varies at all intervals of distances between an electrode surface and a reagent and decreases substantially with an increase in a reagent charge. The values of activation energy for charge transfer at the electrode/melt interface were calculated. A decrease in the values of activation energy for charge transfer between a cathode surface and particles of a melt was established. The values of molecular orbital energies were calculated for a fragment of an electrode surface and active complexes of model melts. Based on the analysis of activation energy values and values of energy of highest occupied and lowest unoccupied molecular orbitals of the interacting structures, a conclusion was made about the essential role of a cationic composition of an electrolyte in the processes of electroreduction at the cathode. The analysis of the obtained theoretical results allows us to formulate the conditions for the occurrence of surface conductivity of the dielectric in the salt melt. A presumption was made that a selection of an electrolyte composition allowed controlling the rate of redox reactions at the electrode/melt interface without prior metallization of the dielectric i.e., a targeted change in the cationic composition of a melt makes it possible to achieve concurrence of energy levels of the electrode surface and the active complex, thereby enabling control over the synthesis of nanoparticles at the cathode. It was established that the mechanism of electrode processes at the electrode/melt interface is based on a shift in the Fermi level of a cluster of a solid-state body surface as well as equality of energies of marginal molecular orbitals of a pre-reaction complex and a cluster, which are determining factors in heterogeneous redox reactions at the surface of a dielectric immersed in a corresponding ionic melt.

**Keywords:** Interfacial boundary electrode/melt, Reorganization energy, Activation energy, Heterogeneous reactions, *Ab initio* calculations.

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### 1. TOPICALITY OF THE PROBLEM

The theory of an elementary act of electron transfer reactions originates from Marcus's classical works, who succeeded in obtaining an equation expressing free energy of activation. According to his classic concept [1], the nature of the activation energy of charge transfer lies in a necessity to spend system energy on partial reorganization of an environment and a nuclear configuration of reagents in the process of electron transfer in polar solutions. However, Marcus did not manage to calculate the pre-exponential factor in the reaction rate constant. Thus, it remained unclear to what extent dynamic properties of a solvent affect the speed of an elementary act of an electron transfer reaction. The aforesaid factor was calculated in the works of Levich, Dogonadze and Kuznetsov by the method of quantum mechanical perturbation theory, in which the reaction rate constant is directly proportional to the square of the resonance integral, which characterizes a degree of overlap of donor and acceptor orbitals. In accordance with this theory, dynamic properties of a solvent do not have a significant effect on the reaction rate. However, when evaluating characteristics and parameters of the charge transfer process at the electrode/melt interface, this theory cannot provide complete and comprehensive information on

kinetic features of electrochemical behavior of particles at the interface. The question of the dependence of the work function on the change in the composition of the melt, the energy of the Fermi level of the solid-state electrode, the activation energy of charge transfer, etc., remains open. At the same time, the application of methods of the quantum theory of molecules (quantum-chemical methods, molecular dynamics methods, Monte Carlo methods, etc.) is an integral part of studies of physical and chemical characteristics of the interface.

### 2. PROBLEM DEFINITION. METHODS OF THE RESEARCH

One of the most important parameters in the charge transfer theory is the solvent reorganization energy  $E_S$ . In this work, the reorganization energy was calculated within the model of conductive ellipsoids, which generalizes the Marcus model [1, 2] for a case when reagents are substantially non-spheric [3, 4]. According to this model, for different orientations of ellipsoids, when one of the semi-axes is perpendicular and another is parallel, which corresponds to the perpendicular and parallel orientations of the dipole moment of the metal complex with respect to the surface (Fig. 1), the reorganization energy is calculated as follows [5, 6]:

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$$E_s^\perp = e^2 \left( \frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_{st}} \right) \left\{ \frac{1}{2r_{eff}} - \frac{1}{4x} \left( 1 - \frac{a^2 + (c_{eff})^2}{12x^2} \right) \right\}, \quad (1)$$

$$E_s^\parallel = e^2 \left( \frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_{st}} \right) \left\{ \frac{1}{2r_{eff}} + \frac{1}{4x} \left( 1 + \frac{a^2 + (c_{eff})^2}{24x^2} \right) \right\}. \quad (2)$$

the effective radius of the ellipsoid shape  $r_{eff}$  is calculated as follows:

$$r_{eff} = \frac{\sqrt{a^2 - c^2}}{F(\Theta, \phi)}, \quad (3)$$

where  $F(\Theta, \phi)$  is the elliptic integral of the first kind with parameters  $\Theta = \arcsin \sqrt{\frac{a^2 - c^2}{a^2}}$ ,  $\phi = \sqrt{\frac{a^2 - b^2}{a^2 - c^2}}$ ,

$c_{eff} = \frac{b+c}{2}$ ,  $\varepsilon_{opt}$ ,  $\varepsilon_{st}$  are the optical and static dielectric constants (relative permittivity),  $e$  is the value of the transferred charge;  $a$ ,  $b$ ,  $c$  are the semiaxes of ellipsoids,  $x$  is the distance from the center of the reagent to the surface of the electrode (Fig. 1).<sup>†</sup>

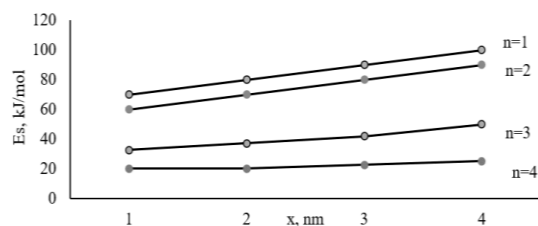
Formulas (1) and (2) use the geometric parameters of nanoparticles of tungsten-containing and niobium-containing melts  $\{M_n z^+ [WO_4]^{2-}\}_{(zn-2)^+}$ ,  $\{M_n z^+ [NbF_7]^{2-}\}_{(zn-2)^+}$ , where  $M = Li^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ( $n = 1-4$  is the coordination number of a cation), obtained as a result of quantum chemical *ab initio* calculations with full geometry optimization for all considered interactions [7, 8].

### 3. RESULTS AND THEIR DISCUSSION

Let us consider the interaction of nanoparticles of a tungsten-containing melt with the electrode surface. Since the values of the dielectric constants (relative permittivity)  $\varepsilon_{st}$  and  $\varepsilon_{opt}$  differ significantly for highly polar solvents and there are no reliable experimental data on the numerical values of  $\varepsilon_{st}$  for the considered melts and temperatures, the value of  $1/\varepsilon_{st}$  in the calculations was equal to zero. This contributes to the expected additive increase of  $E_s$  with the variables specified in (1) and (2) by approximately 5 %.

Fig. 1 presents the calculated data on the dependence of the outer sphere reorganization energy on the distance of a nanoparticle to the electrode surface, when the coordination number of cations in the solvate shell of the anion changes and when mass-to-charge ratio in a row  $Li^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  varies as well. The analysis of the aforementioned trends shows that the amount of solvent reorganization energy increases insignificantly with the growth of  $x$ , reaching a saturation state at the maximum distance from the electrode surface, regardless of parallel or perpendicular orientation of particles, indicating the invariance of the obtained results with respect to the mutual orientation of particles and the electrode surface, and increases with distance from the surface. When the coordination number  $n$  grows, a sharp (two-fold or

three-fold) decrease in the reorganization energy is observed for all considered interactions, which indicates the possibility of anion dissociation under the influence of cations, through a stage of formation of nanosized electrochemically active particles (EAP).



**Fig. 1** – Dependence of the outer sphere reorganization energy on the distance  $x$  (EAP/ electrode surface), on the example of a nanoparticle  $\{Mg_n z^+ [WO_4]^{2-}\}_{(2n-2)^+}$

An increase in the cation mass-to-charge ratio also leads to a decrease in the reorganization energy of the solvent, although less significant than in case if  $n$  alters. Thus, the calculated values of the outer-sphere reorganization energies showed the effect of cationic melt impurities on charge transfer in the near-electrode layer.

In accordance with the Marcus model [1], the activation energy can be represented as follows:

$$E^{\ddagger} = \frac{(\Delta H_{if} + E_z)^2}{4E_s}, \quad (4)$$

where  $\Delta H_{if} = E_z - E_0$  is the thermal effect, which can be obtained by the quantum-chemical method as the difference between the total energies of EAP in the transition and equilibrium states during the transfer of a one-electron charge from the electrode surface.

When simulating electrochemical reactions for niobium-containing systems, the values of the reorganization energy  $E_r$  of the solvate shell of EAP were calculated in the same way as for tungstate-containing systems. Analysis of the values of activation energies (for the sake of convenience/activation barriers  $\delta$ ) for  $[Nb(V)F_7]^{2-} + e = [Nb(IV)F_7]^{3-}$  (in accordance with the experiment [9, 10]) shows a significant influence of the acid-base properties of an environment on the reactivity of EAP, indicating the advantage of electroreduction of  $\{Mnm + [NbF_7]^{2-}\}_{(mn-2)^+}$  particles, compared to the direct reduction of the heptafluoronioabate-ion.

The obtained decrease in the values of the activation barriers is confirmed by the data on the values of the energies ( $E'$ ) of the lowest unoccupied molecular orbital (LUMO) for the entire row of EAP. When comparing the  $E'$  values, it is clearly seen that cationic additives significantly reduce the LUMO energy of  $NbF_7^{2-}$ , indicating an important role of cationic environment in increasing the electroreduction ability of EAP. At the same time, the effect of lowering the value of  $E'$ , as well as changes in  $\delta$ , strengthens as the cation charge goes up and the coordination number for cations of the same type rises. For the considered coordination compounds, the maximum decrease in  $E'$  is caused by  $Mg^{2+}$  cations.

<sup>†</sup> Here, all values are given in The Atomic Units System, when using the SI system, a coefficient  $N_a/8\pi\epsilon_0$  is introduced.

#### 4. CONCLUSIONS

Thus, the obtained calculations of the reorganization and activation energies of charge transfer for tungstate- and niobium-containing melts indicate the catalytic nature of cation influence on the charge transfer process from the electrode surface onto EAP at the electrode/

melt interface. It is proven by equalizing the energy values of electrons located in the vicinity of the Fermi level of the cathode material and vacant orbitals of EAP and the change in the energies of the marginal MOs of the EAP, which is achieved by constructing EAP of different types and shapes.

#### REFERENCES

1. Yao Wang, Yu Su, Rui-Xue Xu, Xiao Zheng, Yi Jing Yan, *Chin. J. Chem. Phys.* **34**, 462 (2021).
2. M. Noppe, *Int. J. Geosci.* **11**, 84 (2020).
3. A. Atxabal, *Nat. Commun.* **10**, 2089 (2019).
4. L. Yuan, *Nat. Nanotechnol.* **13**, 322 (2018).
5. S. Kovalenko, V. Soloviev, *Zeitschrift fuer Naturforschung, A: Physical Sciences* **69a**, 654 (2014).
6. L.O. Solyanyk, *Fizyka ta Novitni Tekhnologii* **1**, 122 (2022).
7. Alex A. Granovsky, *Firefly and PC GAMESS /Firefly version 8.0.1. Access mode.*
8. *In memory of Alex A. Granovsky.*
9. V.V. Soloviev, L.A. Chernenko, V.G. Kremenetsky, et al., *Zeitschrift fuer Naturforschung, A: Physical Sciences* **65a**, 245 (2010).
10. V.G. Kremenetsky, S.A. Kuznetsov, O.V. Kremenetskaya, V.V. Soloviev, L.A. Chernenko, A.D. Fofanov, *Zeitschrift fuer Naturforsch* **65a**, 1020 (2010).

### Вплив нанорозмірних активних частинок розплаву та поверхні електрода на процеси перенесення заряду на межі розділу електрод/розплав

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Методами квантової хімії з метою дослідження механізму електродних процесів на межі розділу електрод/розплав проведено розрахунки енергії реорганізації в рамках моделі провідних еліпсоїдів, яка узагальнює модель Маркуса на випадок, коли реагенти є, по суті, несферичними. Встановлено, що величина енергії реорганізації розчинника практично не змінюється на всіх інтервалах відстаней між поверхнею електрода і реагентом і суттєво зменшується зі збільшенням заряду реагенту. Розраховано значення енергії активації перенесення заряду на межі розділу електрод/розплав. Встановлено зменшення значень енергії активації перенесення заряду між поверхнею катода та частинками розплаву. Розраховано значення молекулярних орбітальних енергій для фрагмента поверхні електрода та активних комплексів модельних розплавів. На основі аналізу значень енергії активації та значень енергії найвищих зайнятих і найнижчих незаповнених молекулярних орбіталей взаємодіючих структур зроблено висновок про істотну роль катіонного складу електроліту в процесах електровідновлення на катоді. Аналіз отриманих теоретичних результатів дозволяє сформулювати умови виникнення поверхневої провідності діелектрика в сольовому розплаві. Було зроблено припущення, що підбір складу електроліту дозволяє контролювати швидкість окислювально-відновних реакцій на міжфазній межі електрод/розплав без попередньої металізації діелектрика: тобто цілеспрямована зміна катіонного складу розплаву дає змогу досягти збігу енергетичних рівнів поверхні електрода та активного комплексу, що дозволяє контролювати синтез наночастинок на катоді. Встановлено, що в основі механізму електродних процесів на міжфазній межі електрод/розплав лежить зсув рівня Фермі кластера поверхні твердого тіла, рівність енергій граничних молекулярних орбіталей передреакційного комплексу і кластер, які є визначальними факторами гетерогенних окисно-відновних реакцій на поверхні діелектрика, зануреного у відповідний іонний розплав.

**Ключові слова:** Міжфазна межа електрод/розплав, Енергія реорганізації, Енергія активації, Гетерогенні реакції, *Ab initio* розрахунки.