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Influence modeling of cationic composition melt on structural features of the electrochemically active particles during simultaneous and sequential electron transfer

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ABSTRACT

Based on analysis results of the *ab initio*-calculation influence of a cationic composition tungstate containing melt on the structural features of the electrochemically active particles, were discovered differences in the structure of the outer coordination spheres while implementing a sequential and simultaneous 6-electron's transfer. The priority was justified for simultaneous transfer over the sequential for all cationized tungastate ion forms. Based on the analysis of *ab initio*-calculation of the effect of cation composition tungstate-containing melt structural characteristics electrochemically active particles detect a difference in the structure of the outer coordination spheres in the implementation of sequential and simultaneous 6-electrons transfer, and justified the priority of simultaneous transport of cationized consistent for all forms of tungstate ion. The results obtained, in our opinion, offer the prospect of purposeful creation of necessary conditions for controlling the charge transfer upon receipt methods HES materials with desired properties by changing the type and form of electrochemically active particles, provided that the amount of detected micro effects (changing the structure of the reaction products at constant composition of source compounds) would be sufficient to provide a qualitatively new macro characteristics (thermal and electrical conductivity, strength, obtained coatings, etc.)

KEYWORDS

Electrochemical synthesis;
Tungsten carbides;
Cation catalysis;
Ab initio calculations;
Outersphere cations;
Electron transfer.

INTRODUCTION

The theory and development prospect of the kinetics of electron transfer in redox reactions of various types are representing not only theoretical, but also a practical interest. Thus, the statements of Marcus's theory for the homogeneous reactions, which have found experimental confirmation[1], allowed us to explain the characteristic features of many phenomena associated with electron transfer in living organisms (photosynthesis, cell metabolism, tissue respiration, etc.) and in various areas of Applied Physics (electrical conductivity of polymers, corrosion, chemiluminescence, gas separation membrane, etc.). The q*uantum-mechanical* *theory* of electrode reactions for the ionic melts was established by compiling and transferring the results of Marcus's theory on heterogeneous reactions by Levich, Dogonadze and Kuznetsov[1], the methodological principles that allowed to access more adequately the outcomes of various experimental methods for obtaining new materials with desired properties. These methods include high-temperature electrochemical synthesis (HES), carrying out of which is complicated by the lack of clear understanding of the mechanism of multi-electron processes of recovery of different ionic forms of refractory metals and nonmetals in ionic melts, including in tungstate (molybdate) containing[2]

However, while studding electro reduction of various ionic forms of tungsten, was discovered 6-electron reversible transfer[3,4], which was interpreted by authors as flowing in one stage. This assertion was based on the fact that the polarization of such systems, even with a scan rate of potentials up to 20 V/s is not allowed to discover the stages of the total multi-electron process, either because of their implementation in a very narrow, almost insoluble, the potential range and the impossibility of applying for these purposes today chronovoltammetery methods, or indeed such processes flowing in one stage. At the same time the possibility of simultaneous multi-electron transfer has already been discussed in literature, in particular, for biological systems[5-9], despite the popular idea that the electrons are transferred sequentially. Therefore, the evaluation of stages of renewal processes for electrochemically active particles (EAP) is one of the most important issues to justify the implementation of the HES.

Using only traditional criteria for evaluating the characteristics and parameters of the electro reduction of complex structure anion's process in salt melts, involves overcoming considerable difficulties caused by multistep nature of the processes, simultaneous occurrence of individual elementary stages, and very short lifetimes of intermediate products and, therefore, from our point of view, cannot provide a complete and comprehensive information about the thermodynamic and kinetic features of the electrochemical behavior of anions in ionic melts. Therefore, quantum chemistry becomes a very important method, which is an effective way to study none amenable experimental detection of short-lived particles and activated complexes, and to interpret the identified experimental laws on the electronic level. That is why, applying only to the submission for received explanation on the basis of quantum chemical calculations, combined with the experimental data, we can achieve the task.

EXPERIMENTAL

In work[10] within the Self-Consistent Field Molecular Orbital Linear Combination of Atomic Orbital's (SCF MO LCAO) method by analyzing the activation barriers recovery of tungstate-containing melts of the EAP, the priority of simultaneous 6-electrons transfer for cationic particles of $\{M_n^{m+}[WO_4]^{2-}\}^{(mn-2)+}$ kind, was justified. Calculations of the spatial structure and energy characteristics of EAP, and their stepwise and simultaneously reduced forms were carried out within the software package GAMESS in the basis set SBK-31G[11].

Since the simultaneous transfer of electrons occurs in a very short time interval, when the kernel is actually fixed, while the sequential - a product that is formed after the transfer of one electron has enough time to dissociate before the second electron to be moved, finding the differences of energy, chargeable and geometric characteristics of the particles should be essential for physical and chemical properties of the products of electrochemical reactions.

RESULTS AND DISCUSSION

According to the results by Levdin's calculations of atomic charges, when transferring *6*-electrons in the electrode reactions to the "isolated" wolframate-anion the only centre of electron attack is the atom W (tab. 1).

When electro reduction of the cationized EAP type $\{M_n^{m+}[WO_4]^{2=}\}^{(mn-2)+}$, in contrast, electronic charge is transferred as cations (mainly) and on the tungsten atom (TABLE 1), indicating thereby the presence of two centers of electronic attack. The effect increases with the increase of the specific cation charge and also with increasing coordination number of the cation, while passing through a maximum at n = 4 for $M^{m+} = Li^+$ and 2 - Ca^{2+} and Mg^{2+} (TABLE 1) both at the same time and sequential transfer charge. For example, while transferring 6-electrons in the electrode reactions for the particle $\{Li_4^+[WO_4]^2\}^{2+}$ the charge on atom W reduced by 0.200 au, and each cation Li^+ - to 0.144 au, with sequential transfer - charge on the W reduced by 0.203 au, and each cation Li^+ - to 0.136 au For particle $\{Mg_2^{2+}[WO_4]^{2-}\}^{2+,}$ while acceding - electrons - to 0.344 au and 2.710 au - On the atoms of W and Mg^{2+} -, respectively, in the case of sequential electron transfer, charge on the W reduced by 0.358 au, and the Mg^{2+} - at 2.709 au (TABLE 1).

TABLE 1 : The sampling data of the charge values on the atoms of the EAP (a) and their reconstructed forms at the simultaneous (b) and the sequential (c) charge transfer

EAP	n		W	$O_{(1)}$	$O_{(4)}$	$M_{(1)}$
WO_4^{2-}	0	a)	0,378	-0,595	-0,595	–
		b)	-5,410	-0,630	-0,690	–
$\{Li_n^+[WO_4]^{2-}\}^{(n-2)+}$	1	a)	0,600	-0,623	-0,484	0,613
		b)	0,222	-0,551	-0,592	-4,935
		c)	0,250	-0,610	-0,600	-4,839
	2	a)	0,724	-0,525	-0,525	0,690
		b)	0,529	-0,946	-0,546	-2,172
		c)	0,656	-0,523	-0,629	-2,177
	3	a)	0,928	-0,619	-0,38	0,768
		b)	0,785	-0,454	-0,600	-1,181
		c)	0,155	-0,900	-0,640	-0,766
	4	a)	1,036	-0,560	-0,560	0,800
		b)	0,839	-0,554	-0,554	-0,656
		c)	0,833	-0,552	-0,551	-0,664
$\{Mg_n^{2+}[WO_4]^{2-}\}^{(2n-2)+}$	1	a)	0,706	-0,723	-0,366	1,472
		b)	-0,435	-0,619	-0,554	-3,216
		c)	-0,281	-0,581	-0,688	-3,273
	2	a)	0,875	-0,536	-0,536	1,633
		b)	0,531	-0,669	-0,517	-1,077
		c)	0,517	-0,674	-0,508	-1,076

Despite the slight difference in the values of atomic charges EAP, their complete disregard for the simultaneous and sequential transfer of charge would be a mistake, because even in the most general considerations, the effects of changes in charges should lead to a change in geometric structure. Thus, further analysis of the geometrical characteristics of the intermediates obtained during successive charge transfer showed, that already in the accession stage 2 electrons, a change in their geometrical structure, leading to a change of cation's dentaty (Figure 1). For example, if a sequential electron attachment to the particles $\{Mg_2^{2+}[WO_4]^{2-}\}^{2+}$, cations move from bidentate to monodentate position relative to the anion (a local minimum on the SPE[12]). The change in the coordination spheres of several stages (Figure 1): that is 0 along the axis of a generalized reaction coordinate corresponds to the geometry of the particles before the addition of an electron, which corresponds to the bidentate arrangements of the cations Mg^{2+}, the same arrangement of cations is observed in Volume 1, corresponding this particle is associated with an electron, ie 2 corresponds to the geometric structure of the particles, where one cation Mg^{2+} is in bi-, and second - passed in monodentate position due to successive transfer of 2 electrons. This geometry of the particle is preserved and is 3-5 (Figure 1), corresponding to sequential addition of, respectively, 3, 4 and 5 for EAÐ of the electron, and in v. 6 the geometry of the particle is characterized by a monodentate arrangement has both cations due to successive transfer of 6-electrons. At the same time 6-electron transfer cations do not change their bidentate location (the absolute minimum on the

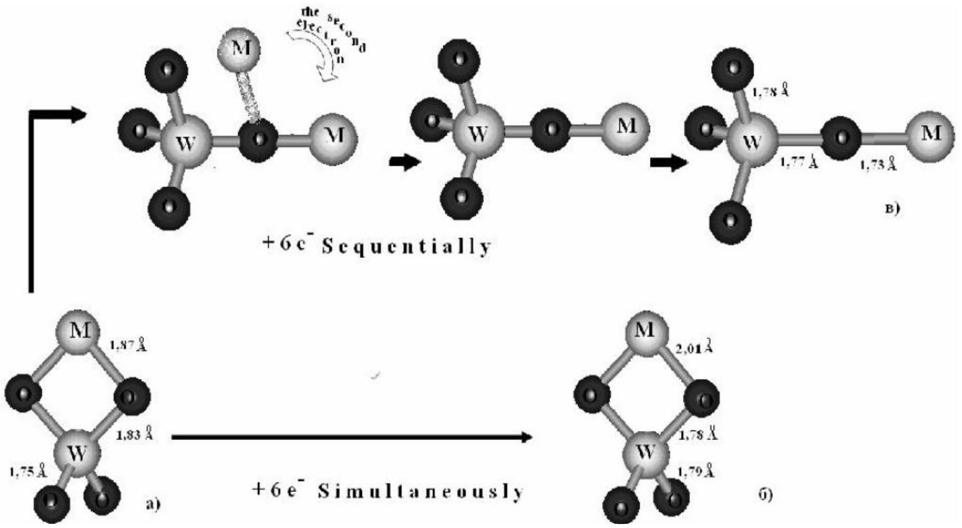

Figure 1: Energy profile of the SPE along the reaction coordinate and generalized) simultaneously and b) the sequential addition of 6-electrons EAP $\{M^{m+}[WO_4]^{2-}\}^{2+}$

PES[12]).

In favor of the foregoing analysis shows the populations of atomic orbitals (AO), which indicates the difference in the distribution of electron density on atoms EAP at the same time and coherent transport 6-electrons. According to Levdin's analysis of the populations of AO, the highest acceptor properties in both cases exhibit s-orbital of the cation (TABLE 2). On the atom W, while the charge transfer acceptor properties are manifested in the active participation of the of $d_{x^2-y^2}$ and d_{z^2} - orbitals, while subject to the implementation of coherent charge transport - with the participation of d_{xy}, d_{xz} and d_{yz} orbitals of atom W (TABLE 2). In the upper occupied molecular orbital (HOMO) EAP, according to calculations, the largest contribution comes from d-orbitals of atom W and s-orbitals of the cation, which indicates the existence of two centers of electronic attack in the process of recovery EAP - tungsten atom and the metal cation. It should be noted that this effect takes place for the entire spectrum of the coordination numbers of the cation.

Conducting energy assessment of preference realization of six-electron charge transfer with no assessment of the lifetime as a whole and the intermediates at each stage of accession, the electron cannot give overall completeness of the justification and understanding of this issue.

TABLE 2 : The sample data of the populations of AO EAP *(a)*, and also their restored forms at 6-electrons simultaneous and sequential (b*)* and (c) accordingly charge transfer

Atom	AO	$\{Li_4^+[WO_4]^{2-}\}^{2+}$			$\{Mg_2^{2+}[WO_4]^{2-}\}^{2+}$		
		a)	*b)*	*c)*	*a)*	*b)*	*c)*
W	$5d_{x^2-y^2}$	0,062	0,044	0,004	0,071	0,066	0,036
	$5d_{z^2}$	0,448	0,455	0,385	0,431	0,507	0,401
	$5d_{xy}$	0,528	0,233	0,529	0,476	0,431	0,492
	$5d_{xz}$	0,526	0,230	0,540	0,465	0,445	0,492
	$5d_{yz}$	0,391	0,236	0,530	0,404	0,391	0,584
$O_{(1)}$	2S	1,115	1,116	1,115	1,109	1,149	1,121
	$2p_x$	1,124	1,119	1,121	1,102	1,079	1,117
	$2p_y$	1,120	1,119	1,117	1,163	1,115	1,111
	$2p_z$	1,125	1,123	1,121	1,149	1,101	1,146
M	s1	0,067	0,210	0,205	0,107	0,744	0,743

[1] **Orbitals of outer shell for cations *Li^+ (L-shell) è Mg^{2+} (Ì-shell)***

According to[13], an estimate of the lifetime of the activated complex for joining both simultaneously and sequentially x electrons in accordance with the expressions:

$$\Delta\tau = \frac{\hbar}{\Delta E} \qquad (1)$$

(where ΔE - activation energy of charge transfer, defined as the difference between the calculated total energies at the moment of accession EAP x electron at the saddle point the potential energy surface ($\mathring{A}_{\tilde{\text{б}}}$) and total energies of EAÐ in the initial state ($\mathring{A}_0$): $\Delta\mathring{A} = |\mathring{A}_{\tilde{\text{б}}} - \mathring{A}_0|$) and

$$\Delta\tau = \frac{1}{|\Delta\omega|} = \frac{1}{2\pi|\Delta\nu|} \qquad (2)$$

where $|\Delta\upsilon|$ - modulus of the difference frequency oscillations in the transition and final states, determined using the harmonic irrational analysis in each stationary point within the capabilities of the program[11], for particles after joining x electrons. With the simultaneous transfer of charge calculation values of the lifetimes of particles in the transition state by (1), (2) does not need further clarification.

The sequential 6-electron reduction resulting value of the lifetime of the particles in the transition state determined by the algebraic sum of the lifetimes $\Delta\tau_i$, calculated for all individual elementary stages of the sequential addition of particles of each of the x electrons:

$$\Delta\tau_{\text{siquential}} = \sum_{i=1}^{x} \Delta\tau_i \qquad (3)$$

Comparative analysis of the values of the lifetimes of the particles during the relaxation from the transition state to equilibrium at constant number of electrons have as a priority of simultaneous charge transfer to serial to cationized forms EAÐ (TABLE 3) and also was allowed to reaffirm established in[14], the optimal composition and shape of EAÐ : $\{Li_4^{+}[WO_4]^{2-}\}^{2+}$, $\{Mg_2^{2+}[WO_4]^{2-}\}^{2+}$ and $\{Ca_2^{2+}[WO_4]^{2-}\}$

TABLE 3 : The lifetime (“τ ’” 10^{15}) EAP when: a) stepwise and b) a simultaneous transfer process 6-electrons (sample data)

EAP	n	$\Delta\tau = \frac{\hbar}{\Delta E}$		$\Delta\tau = \frac{1}{2\pi\Delta\nu}$	
		a)	b)	a)	b)
$\{Li_n^{+}[WO_4]^{2-}\}^{(n-2)+}$	0	0,128	2,278	0,010	0,540
	1	109,392	2,192	0,523	0,040
	2	32,933	0,317	0,497	0,007
	3	52,062	8,039	0,314	0,011
	4	4,875	4,824	0,311	0,005
	5	3,801	1,049	0,342	0,019
$\{Mg_n^{2+}[WO_4]^{2-}\}^{(2n-2)+}$	1	29,032	0,965	0,565	0,098
	2	27,864	0,254	0,238	0,209
	3	6,847	1,855	0,184	0,276

CONCLUSIONS

Overall results that are obtained in the calculation of geometric, energy, charge characteristics EAP tungstate-containing melts and the lifetimes of intermediates (excluding the effect of the adsorption properties of the surface of the electrode and the overvoltage) make it possible to extend existing ideas about the mechanism of electrode processes, allowing to conclude that the simultaneous transfer of electrons can be a normal step in electrode reactions, and always be considered as an alternative to analyze the mechanisms of such processes.

Thus, based on the analysis of *ab initio*-calculation of the effect of cation composition tungstate-containing melt structural characteristics EAP detect a difference in the structure of the outer coordination spheres in the implementation of sequential and simultaneous 6-electrons transfer, and justified the priority of simultaneous transport of cationized consistent for all forms of tungstate ion. The results obtained, in our opinion, offer the prospect of purposeful creation of necessary conditions for controlling the charge transfer upon receipt methods HES materials with desired properties by changing the type and form of EAP, provided that the amount of detected micro effects (changing the structure of the reaction products at constant composition of source compounds) would be sufficient to provide a qualitatively new macro characteristics (thermal and electrical conductivity, strength, obtained coatings, etc.).

Additional analysis of the Upper Occupied Molecular Orbital (UOMO) EAP confirmed the above conclusions about the existence of two centers of electronic attack in the process of recovery EAP - tungsten atom and the metal cation with the largest contribution comes from atom W's d-orbital and s-orbital's cation, and also showed that the sequential charge transfer tungsten atom do not contribute significantly to the UOMO in the background of cations, while the same charge transfer, in contrast, the tungsten atom makes a major contribution to the UOMO

Overall, the results obtained in the calculation of geometric, energy and charge characteristics EAP wolframate-anion melts (excluding the effect of the adsorption properties of the surface of the electrode and the overvoltage) make it possible to extend existing ideas about the mechanism of electrode processes, allowing to conclude that the simultaneous transfer of electrons can be a normal stage in electrode reactions, and always be considered as an alternative to analyze the mechanisms of such processes.

Thus, based on the analysis of *ab* initio-calculations of the effect of cation composition wolframate-anion melt structural characteristics EAP discovered that the priority center of electronic attack, while electron transfer is an atom W, and sequential transfer of electrons - EAP cations. Priority simultaneous transfer over serial justified for all forms of cationized tungstate ion and due priority contribution of d-orbitals of the central atom EAP - W atom in the UOMO. The results obtained, in our opinion, offer the prospect of purposeful creation of necessary conditions for controlling the charge transfer upon receipt methods HES materials with desired properties by changing the type and form of UACH, provided that the amount of detected micro effects (changing the structure of the reaction products at constant composition of source compounds) would be sufficient to provide a qualitatively new macro characteristics (thermal and electrical conductivity, strength, obtained coatings, etc.).

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