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Research paper



Modeling the Electronic Structure and Composition Tungsten Adsorbed Metal Complexes of on the Electrode Surface under Conditions of High-Temperature Electrochemical Synthesis

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Abstract

The interest to the physics of nano-dimensional structures, the most urgent and most dynamically developing field of modern solid state physics, is connected both with completely new fundamental scientific problems and physical phenomena, and with the prospects of creating entirely new quantum devices and systems with wide functional opportunities for nano-electronics, measuring equipment, new-generation information technologies, communication equipment, etc.

Keywords: *electrochemical synthesis, tungsten carbides, cation analysis, ab initio-calculations, electron transfer.*

1. Introduction

The result of studies on low-dimensional systems include the discovery of fundamentally new and now well-known phenomena such as the integer and fractional quantum Hall effect in a two-dimensional electron gas, the Wigner crystallization of quasi-two-dimensional electrons and holes, the discovery of new composite quasiparticles and electronic excitations with fractional charges, high-frequency Bloch oscillations, and also much more. Modern semiconductor lasers on heterojunctions are also based on the use of low-dimensional systems (structures with quantum wells, self-organized quantum dots and quantum filaments). The most outstanding achievements in this field are marked by three Nobel Prizes in Physics (in 1985 the quantum Hall effect was discovered, in 1998 the fractional quantum Hall effect was discovered, in 2000 the works were performed that laid the foundations of modern information technology).

Advances in the development and manufacture of nano-structures for various purposes are determined to the greatest extent by the level of development of technologies that allow obtaining with atomic precision nano-structures of the necessary configuration and dimension, as well as methods for complex diagnostics of nano-structure properties, including in-situ manufacturing control and management on its basis by technological processes. According to many forecasts, it is the development of nano-technologies that will determine the appearance of the 21st century, just as the discovery of atomic energy, the invention of a laser and a transistor, determined the development of the 20th century.

In this paper, we propose modeling realization of the production of nano-dimensional high-strength materials by high-temperature electrochemical synthesis (HES), which makes it possible to change the composition and shape of nano-sized particles that determine the physico-chemical properties of nano materials. HES is not possible without carrying out at the current level of study the prospects for the development of the kinetics of electron transport in oxidation-reduction reactions of various types, representing not only purely theoretical, but also practical interest. Thus, the provisions of Marcus theory of homogeneous reactions, which found experimental confirmation [1], made it possible to explain characteristic features of many phenomena associated with electron transfer in a living organism (photosynthesis, cellular metabolism, tissue respiration, etc.) and in various fields of applied physics (electrical conductivity of polymers, corrosion, chemiluminescence, membrane gas separation, etc.). By generalizing and transferring the results of Markus theory to heterogeneous reactions, Levich, Dogonadze and Kuznetsov [1] created a quantum-mechanical theory of electrode reactions for ionic melts, the methodological principles of which allow performing more adequate evaluation of the results of various experimental methods for obtaining new substances with specified properties. Among these methods HES is the implementation of which is complicated by the lack of clear ideas about the mechanism of multi-electron recovery processes for various ionic forms of refractory metals and nonmetals in ion melts, including tungstate (molybdate) [2].

At the same time, in the study of the electro-reduction of various ionic forms of tungsten, six electron reversible transfer was observed [3, 4], which was interpreted by the authors as proceeding in one stage. This assertion was based on the fact that the polarization of such systems, even with potential sweep rates up to 20 V/s, did not allow to detect the stadicity of the total multielectron process either because of its implementation in a very narrow, almost insoluble, range of potentials and the impossibility of applying modern methods of chronovoltametry for these purposes. Or, in fact, such processes take place in one stage. At the same time, the possibility of simultaneous multi-electron transfer has already been discussed in the literature, in particular, for biological sys-

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tems [5-9], despite the generally accepted idea that electrons are transferred sequentially. Therefore, the assessment of the stagedness of the recovery processes of electro-chemically active metal complexes (EAM) is one of the most significant issues in justifying the realization of the HES implementation.

The use of only traditional criteria for evaluating characteristics and parameters of the process of complex anions electro-reduction in salt melts is associated with the overcoming of significant difficulties caused by the multistage nature of the processes, the synchronous flow of individual elementary stages, and the very short lifetime of the intermediate products. And, therefore, from our point of view, it can not give complete and comprehensive information on the thermodynamic and kinetic features of the electrochemical behavior of anions in ionic melts. In this regard, great importance is attached to the methods of quantum chemistry, which are an effective way of studying directly the short-lived particles that are not amenable to experimental registration and activated metal complexes, and allowing interpreting the revealed experimental patterns at the electronic level. Therefore, applying only the ideas that have been explained on the basis of quantum-chemical calculations, combined with experimental data, it is possible to achieve the solution of the given problems.

2. The theoretical methodology

In [10], within the framework of the SCF MO LCAO by analyzing the values of the activation barriers for the reduction of EAM of tungstate-containing melts, the priority of simultaneous electron transfer for cationized metal complexes of the type is substantiated: $\left\{M_n^{m+}\left[WO_4\right]^{2-}\right\}^{(mn-2)+}$.

Calculations of the spatial structure and energy characteristics of EAM, as well as its forms successively and simultaneously restored, were performed within the framework of the GAMESS software complex in the SBK-31G basic set [11], taking into account the exchange correlation of electrons by the second-order Möller-Plesset procedure (MP2) [12].

3. Results and its discussion

Since simultaneous electron transfer occurs in a very short time interval, when the nuclei are actually stationary, while in the sequential one, the product formed after the transfer of one electron has enough time for dissociation before the second electron is transferred. The finding of differences in the energy, charge, and geometric characteristics of metal complexes should be of considerable importance for physicochemical properties of the products of electrochemical reactions.

According to the results of calculating of charges on atoms in Lovdin, when transferring 6 electrons in electrode reactions to the "isolated" tungstate anion, the only center of the electron attack is the W atom (Table 1).

On the contrary in the electroreduction of cationized EAM species, the electron charge is transferred to both cations (mainly) and to the tungsten atom (Table 1), indicating that there are two centers of electronic attack. It should be noted that the additional taking into account the correlation of electrons with MP2 method at a qualitative level makes it possible to obtain the same result as in the calculation of the basis without taking into account the correlation of the electrons.

The effect is enhanced with an increase in the specific charge of the cation, and also with an increase in the coordination number in the cation, passing through a maximum at n = 4 in the case $M_n^{m+} = Li^+$ and 2 - Ca^{2+} and Mg^{2+} (Table 1) both with simultaneous and consecutive charge transfer.

Table 1: Selected data on charge sizes on EAM atoms (*a*) and their reduced forms while simultaneous (*b*) and consecutive (*c*) charge transfer.

EAM	The mechanism of electron transfer	WO_4^{2-}		$\left\{Li_4^+\left[WO_4\right]^{2-}\right\}^{2+}$		$\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$	
		SBK-31G	MP2*	SBK-31G	MP2	SBK-31G	MP2
W	a)	0,378	0,401	1,036	1,025	0,875	0,870
	b)	-5,410	-5,409	0,830	0,830	0,531	0,530
	c)	-5,410	-5,409	0,825	0,825	0,517	0,570
$O_{(1)}$	a)	-0,595	-0,590	-0,557	-0,557	-0,536	-0,535
	b)	-0,612	-0,612	-0,553	-0,553	-0,517	-0,513
	c)	-0,630	-0,623	-0,551	-0,551	-0,508	-0,494
$M_{(1)}$	a)	-	-	0,801	0,801	1,633	1,632
	b)	-	-	-0,660	-0,660	-1,077	-0,899
	c)	-	-	-0,656	-0,656	-1,079	-1,065

* Calculations were performed in the same basis, taking into account the electronic correlation within Peller-Plesset procedure of the 2-nd order.

Thus, for example, with the simultaneous transfer of 6 electrons in the electrode reactions for a metal complex $\left\{Li_4^+\left[WO_4\right]^{2-}\right\}^{2+}$ the charge on the W atom decreases by 0,200 atomic units, and on each Li^+ cation it decreases by 0,144 atomic units. In a sequential transfer, the charge on the W atom decreases by 0,203 atomic units, and on each Li^+ cation, it decreases by 0.136 atomic units. For $\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$ metal complex with the simultaneous attachment of 6 electrons it decreases by 0,344 atomic units and 2,710 atomic units on the W and Mg^{2+} atoms, respectively. In the case of successive electron transfer, the charge on the W atom decreases by 0,358 atomic units and on Mg^{2+} by 2,709 atomic units see (Table 1).

Despite the insignificant difference in charge sizes on EAM atoms, its complete disregard for simultaneous and consecutive charge transfer would be erroneous, since, even for the most general reasons, the effects of charge changes should lead to a change in the geometric structure. Thus, an additional analysis of the geometric characteristics of the intermediates obtained by successive charge transfer showed that even at the stage of addition of 2 electrons, a change in their geometric structure is observed, leading ultimately to a change in the cation dentation (Figures 1, 2). For example, in the case of sequential addition of electrons to a $\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$, metal complex cations pass from bidentate to monodentate positions relative to the anion local minimum on the potential energy surface (PES) [13-19]). In this case, the change in the coordination spheres occurs in several stages (Figure 1).

Point 0 along the axis of the generalized reaction coordinate corresponds to the geometry of the metal complex up to the moment of the electron arrangement, which corresponds to the bidentate arrangement of Mg^{2+} cations. The same arrangement of cations is also observed in Point 1, corresponding to this metal complex with an electron already attached. Point 2 corresponds to the geometric structure of the metal complex, where one Mg^{2+} cation is in the bidentate position, and the second has passed to the monodentate position due to the successive transfer of the 2-nd electron. This geometry of the metal complex is also preserved for points 3-5

(Figure 1), which corresponds to the sequential addition of 3-rd, 4-th and 5-th electrons to EAM, respectively. At point 6, the geometry of the metal complex is characterized by a monodentate arrangement of both cations as a result of the successive transfer of the 6-th electron. With simultaneous 6-electron transfer, cations do not change their bidentate location (absolute minimum by PES [13-19]). A similar analysis also follows from Fig. 2.

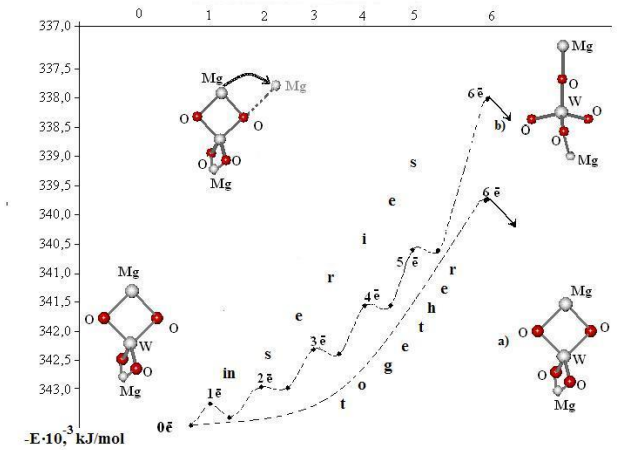


Fig. 1. The energy profile of the PES along the generalized coordinate of the reaction of the a) simultaneous and b) successive addition of 6 (EAP) $\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$.

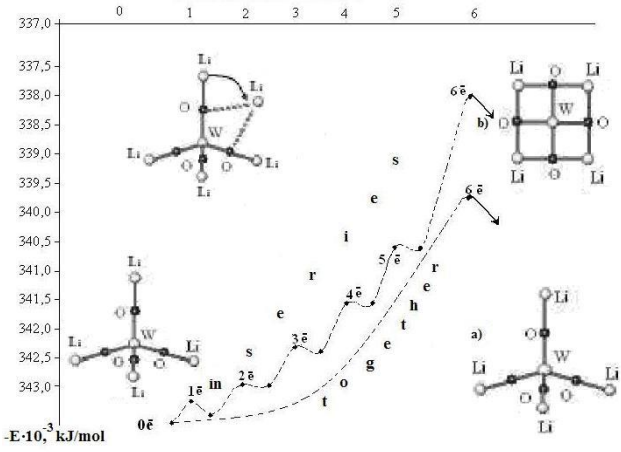


Fig. 2. The energy profile of the PES along the generalized coordinate of the reaction of the a) simultaneous and b) successive addition of 6 EAP $\left\{Li_4^{+}\left[WO_4\right]^{2-}\right\}^{2+}$ electrons.

The populations analysis of the atomic orbitals (AO) of is the evidence above findings which indicates a difference in the distribution of the electron density on EAM atoms, of the simultaneous and sequential transfer of 6 electrons. According to the Lovdin AO population analysis, the largest acceptor properties in both cases are the s-orbitals of the cation (Table 2).

On the *W* atom with simultaneous charge transfer, the acceptor properties are manifested with the active participation of d_{x2-y2} and d_{z2} orbitals. At a time when, subject to the realization of successive charge transfer, with the participation of d_{xy}, d_{xz} and d_{yz} orbitals of the *W* atom (Table 2). In the upper filled molecular orbital (UFMO) EAM, according to the calculation, the largest contribution is made by d-orbitals of the *W* atom and the s-orbitals of the cation. This indicates the existence of two centers of electronic attack in the processes of reduction of the tungsten EAM-atom and metal cation. It should be noted that the observed effect occurs for the entire spectrum of coordination numbers over the cation.

PES energy profile created along the coordinate of the successive addition of six electrons have showed (Fig.3) that the largest value of activation barrier is realized at the stage of attachment by a particle of a sixth electron, indicating that it is the stage of the sequential electron accession. Which is limiting.

Table 2: Selected data on the populations of AO EAM (a), as well as their reduced forms at six-electron simultaneous (b) and consecutive (c) charge transfer.

Atom	AO	$\left\{Li_4^{+}\left[WO_4\right]^{2-}\right\}^{2+}$			$\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$		
		a)	b)	c)	a)	b)	c)
W	$5d_{x^2-y^2}$	0,004	0,062	0,054	0,036	0,071	0,066
	$5d_{z^2}$	0,389	0,389	0,367	0,41	0,452	0,384
	$5d_{xy}$	0,487	0,553	0,489	0,482	0,593	0,543
	$5d_{xz}$	0,524	0,525	0,512	0,414	0,593	0,543
	$5d_{yz}$	0,522	0,525	0,47	0,366	0,586	0,319
$O_{(1)}$	$2s$	1,111	1,116	1,129	1,129	1,146	1,117
	$2p_x$	1,121	1,119	1,115	1,081	1,089	1,116
	$2p_y$	1,123	1,119	1,093	1,169	1,174	1,111
	$2p_z$	1,123	1,123	1,111	1,091	1,075	1,159
M	s	0,047	0,216	0,295	0,097	0,471	0,714

* Orbitals of outer shells for Li^+ (L-shell) and Mg^{2+} (M-shell) cations.

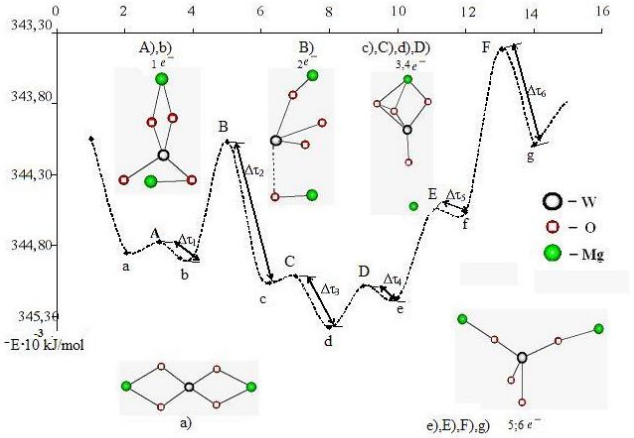


Fig. 3. The PES energy profile along the coordinate of the reaction of successive "addition" of six electrons by a $\left\{Mg_2^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$ particle.

(The configuration of the states before the "joining" of electrons (a), transition states (A-E) and intermediate local minima (b-f) have been shown.)

The energy estimate of the preference for implementing the 6-electron charge transfer without estimating the lifetime as a whole and the intermediates at each of the stages of addition of the corresponding electron can not provide a comprehensive completeness in justifying and understanding this question.

According to [20], an estimate of the lifetime of an activated metal complex upon addition of both simultaneously and successively x electrons is performed in accordance with the expressions:

$$\Delta\tau = \hbar / \Delta E \qquad (1)$$

(where ΔE is the activation energy of charge transfer, was determined as the difference between the calculated total EAM energies at the moment of attachment of x electrons at the saddle point of the potential energy surface (E_x) and the total energies of these EAM in the initial state (E_0): $\Delta E = \left|E_x - E_0\right|$) and

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

where $\left|\Delta\nu\right|$ is the modulus of the difference in the frequencies of oscillations in the transition and final states, determined using

harmonic oscillatory analysis at each stationary point within the program's feasibility [11], for metal complexes after attaching x electrons. When the charge is transferred at the same time, the calculation of the life times of the metal complexes in the transition state according to formulas (1), (2) does not require additional explanation. In the case of a sequential 6-electron reduction, the resulting lifetime of the metal complexes in the transition state was determined by means of using the algebraic sum of the lifetime values $\Delta\tau_i$, calculated for all individual elementary stages of successive addition of each of *x* electrons by the metal complex:

$$\Delta\tau_{посл} = \sum_{x=1}^{x} \Delta\tau_i. \quad (3)$$

A comparative analysis of the lifetime values of metal complexes during relaxation from the transition state to the equilibrium state under conditions of invariability of the number of electrons was indicated as the priority of simultaneous charge transfer before the sequential charge for cationized forms of EAM (Table 3), and again confirmed the values established in [13-19] optimal composition and form of EAM: $\left\{Li_4^+\left[WO_4\right]^{2-}\right\}^{2+}$, $\left\{Mg_4^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$, and $\left\{Ca_4^{2+}\left[WO_4\right]^{2-}\right\}^{2+}$.

4. Conclusions

A simulation of the implementation of one of the schemes for obtaining high-strength nano-sized materials by the HES method has been proposed. The possibility of changing the composition and shape of nano-sized particles that determine physico-chemical properties of nano-materials is substantiated by changing the cation composition of solvate shells of metal complexes and predetermining simultaneous or sequential charge transfer.

The results of the calculation of the geometric, energy, charge characteristics of the EAM of tungstate-containing melts and the lifetimes of the intermediates (without taking into account the influence of the adsorption properties of the electrode surface and the values of the overvoltage) make it possible to expand existing ideas about the mechanism of electrode processes, making it possible to conclude that simultaneous electron transfer can be the usual stage in electrode reactions and should always be considered as an alternative when analyzing the mechanisms of such processes.

Thus, based on an analysis of the results of ab initio calculation of the influence of the cationic composition of the tungstate-containing melt on the structural features of the EAM, a difference in the structure of the outer coordination spheres was revealed in the realization of sequential and simultaneous six-electron transfer, and the priority of simultaneous transfer over successive for all cationized forms of the tungstate ion was substantiated. The obtained results, in our opinion, open the prospects of purposeful creation of the conditions necessary for controlling the processes of charge transfer in the production of HES substances with specified properties due to a change in the form and shape of the EAM, provided that the sum of the detected microeffects (change in the structure of reaction products with a constant composition of the initial compounds) will be sufficient to provide qualitatively new macro characteristics (thermal and electrical conductivity, strength of the coatings obtained, etc.).

Table 3: EAM lifetime ($\Delta\tau \cdot 10^{15}$,) for: a) sequential and b) simultaneous processes of 6 electrons transfer (sample data).

EAM	*n*	$\Delta\tau = \frac{h}{\Delta E}$		$\Delta\tau = \frac{1}{2\pi\Delta\nu}$	
		a)	b)	a)	b)
$\left\{Li_n^+\left[WO_4\right]^{2-}\right\}^{(n-2)+}$	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
$\left\{Mg_n^{2+}\left[WO_4\right]^{2-}\right\}^{(2n-2)+}$	5	3,801	1,049	0,342	0,019
	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

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