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On Diffusive Confining a Galvanic Crystallization out of Molten Salts

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ABSTRACT

The electron-energy band structure of electric Double Layer (DL) between a molten salt and metal electrode (an anode or cathode) is studied for the electrodepositing crystallization process when the width of DL metal part is less than the one in the molten salt. It is shown that just the molten-salt part of the double layer confines a rate of electrodepositing process. The reason of this is a neutralization of depositing ions into the molten-salt near the electrode and hence their diffusively confined motion in a density gradient field. It is important to minimize the electrodepositing potential for effective component crystallization out of the molten salt and its exchange process including selective extracting of salt components by their crystallization on electrodes of galvanic circuit. It is shown that this can be carried out by means of fine and controllable variation of reduction-oxidation (RedOx) potential of the non-stoichiometric salts. A possible application of a potentiometer for monitoring and managing the salt composition is considered. For this, one uses precise methods of electric-motion-force and coulometer titration by solid electrolyte (for example, M^+-β"-Al_2O_3) of the basic salt metal (M°) as a reduction agent in the molten-salt solution.

Keywords: Molten Salt; Galvanic Crystallization; Metal Electrode; Electric Double Layer; Diffusive Confine

1. Introduction

Despite of wide experience in using molten salts for different technologies [1] including the nuclear reactors, their molecular dynamics has been not enough studied. The thin influence of non-stoichiometric salts or their Reduction-Oxidation (RedOx) potential on physical and chemical properties of multi-component salts are not studied as well as the characteristics of electrodepositing crystallization processes in them [2].

The RedOx potential implies the thermodynamic potential, $-\Delta G_X = -\Delta G_0 + RT\ln a_X$ of the common metalloid, X, for all salts in a mixture, $\sum_{i=1}^{n}\left(\mathrm{M}_i X_{k_i}\right)_{a_i}$ [3,4].

At the same time, the non-stoichiometry of molten salt is varied in the range of $\pm 10^{-6}$ by dissolving atoms of neutral metal, M°, (as a reduction agent) of the salt component less than 1 ppm.

In this connection, it is interesting to study effects of contact between metal electrodes and molten salts when charge exchange in an electric Double Layer (DL), φ_{dl}, strongly varies the band structure of the molten salt in the contact region.

2. The Band Model of Molten Salts

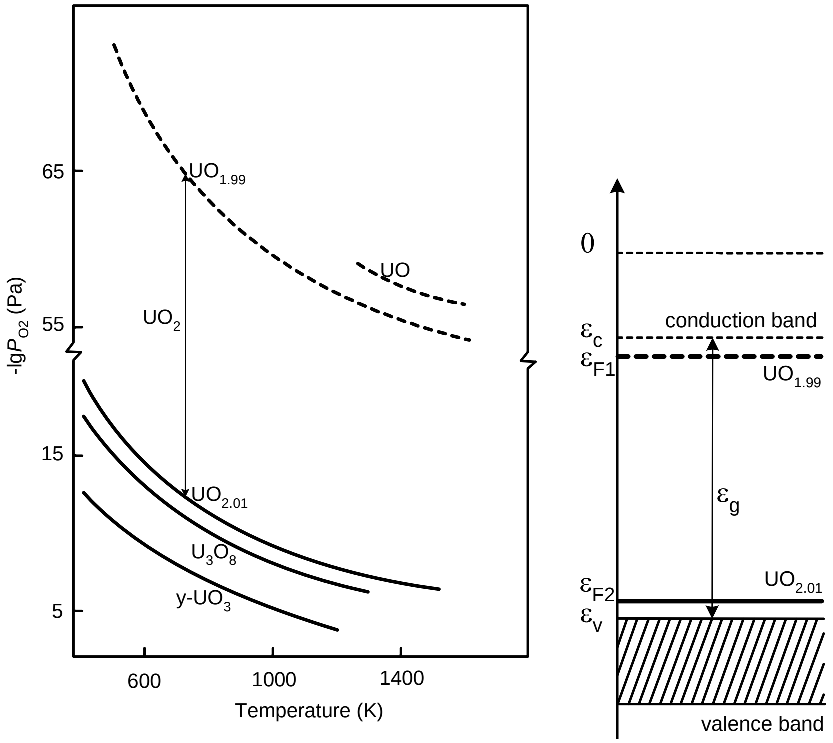
The striking example of non-stoichiometric materials is uranium dioxide, $UO_{2\pm x}$, whose thermodynamic characteristics as the partial oxygen pressure in the function of temperature and electron-energy states in the band model are shown in **Figure 1**.

One can see that the hypo-stoichiometric uranium dioxide, $UO_{1.99}$, being stable at the low oxygen pressure, $P_{O_2} < 10^{-65}$ Pa, conforms to the shifting of Fermi level, ε_F, up to value of ε_{F1} in the band gap, ε_g, near the bottom, ε_c, of conduction band. For the hyper-stoichiometric uranium dioxide, $UO_{2.01}$, stable at $P_{O_2} > 10^{-15}$ Pa, Fermi level comes to ε_{F2} near the top of valence band, ε_v, according to the equation [3,5]

$$\varepsilon_F = \varepsilon_0(T) - (1/4)k_B T \ln P_{O_2} \tag{1}$$

where $\varepsilon_0(T)$ is the standard chemical potential of uranium dioxide, k_B is Boltzmann constant, and T is the absolute temperature.

The composition of $UO_{2\pm x}$ varies low: $|\Delta x| < 0.01$, but the oxygen pressure varies over fifty orders (see **Figure 1(a)**). As a solid electrolyte with unipolar ionic conductivity [6], $UO_{2\pm x}$ has the high sensitivity of Fermi level,



(a) (b)

Figure 1. Graphs of –lg P_{O_2} as temperature functions for all uranium oxides (a) and the electron-energy band structure of the non-stoichiometric uranium dioxide (b) with variable Fermi level, ε_F.

ε_F, to the variation of the RedOx potential, $-\Delta G_{O2}$, since it is required the minor alteration of the salt composition ($\pm\Delta k_i << 1$) for appreciable displacing ε_F in the band gap.

In comparing lines of –lg P_{O_2} (T) in **Figure 1(a)** with the band structure in **Figure1(b)**, one can see that the bandgap energy corresponds to region of thermodynamic stability of the non-stoichiometric $UO_{2\pm x}$.

At melting salt crystal, its band structure shown in **Figure 2(a)** will be slightly changed (see in **Figure 2(b)**) due to disordering it: local energy states of electrons will be appeared in the band gap decreasing its width (by thin lines in **Figure 2(b)**).

For the solid salt, the position of Fermi level near the midgap is natural because its non-stoichiometric state is possible only on the surface of the crystalline salt. Opposite, its molten state allows changing the composition in the bulk of liquid salt and shifting ε_F in the band gap (see **Figure 2(b)**) by dissociation of the salt compound due to varying the RedOx potential as stated above [3].

Thus, we obtain the band gap as the electrochemical window for electrodepositing crystallization out of the molten salt. It is very important using this window effectively with a minimal polarization of galvanic-circuit electrodes. Therefore, we will consider the properties of the contact between metal electrodes (anode or cathode) and the molten salt.

3. Electric Double Layer

One of the principles recognized is that the direct contact of two phases possesses properties that essentially differentiate from the ones of the free phase surfaces separated macroscopically as it is shown in **Figure 3(a)**.

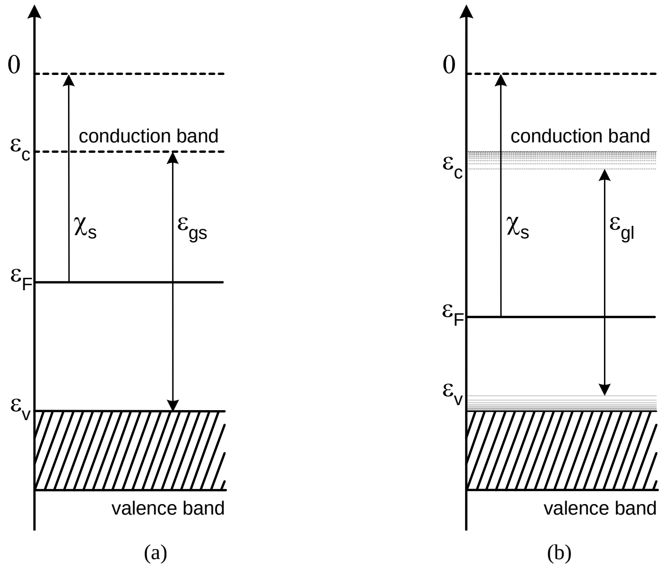
One can see that φ_{dl} is defined strictly by the equation

$$\varphi_{dl} = \chi_s - \chi_m \qquad (2)$$

as a difference of the photoelectric work function, χ_s, of the molten salt and the one, χ_m, of a metal electrode.

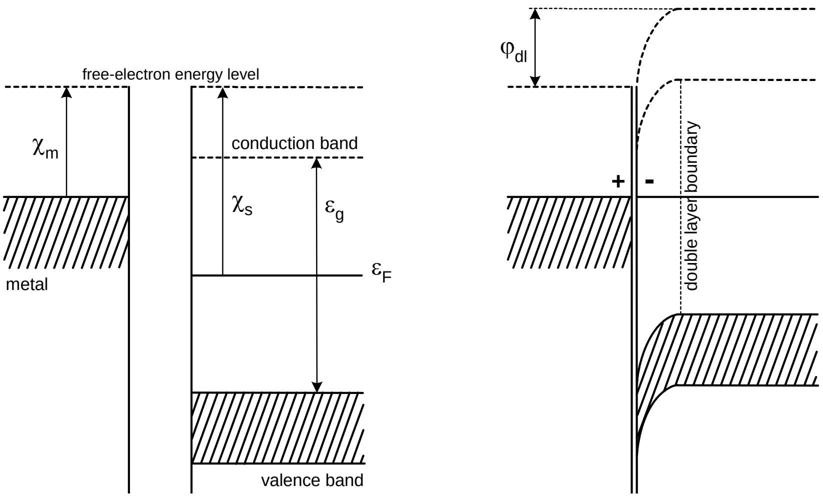
Here $\varphi_{dl} > 0$. The band model of electrical DL allows visualizing correctly the electron energy changes (deforming bands) in the molten salt near the charged electrode. In the specific case of **Figure 3**, the metal electrode is under positive potential and the salt border layer has a negative charge diffusively distributed in the electrical field of Debye length when free electrons are partially neutralizing cations in the salt border layer [7].

The neutral atoms and charged particles will not be uniformly distributed throughout the liquid phase, but will be concentrated near the charged surface. Thus, we have a small finite layer of the liquid phase, which is different from the bulk liquid. The width of border layer is ≤10 nm [7,8]. This concept is a key to understanding the electrochemical reactions in this interfacial boundary that govern external observations of electrodepositing



(a) (b)

Figure 2. Band structure of the stoichiometric solid salt (a): Fermi level is near the midgap, and the non-stoichiometric molten salt (b): Fermi level is not in the midgap and the band gap width is decreased; χ_s is the photoelectric work function of the molten salt.



(a) (b)

Figure 3. Band structures of the separated metal electrode and molten salt (a) and the one in the direct contact of them (b).

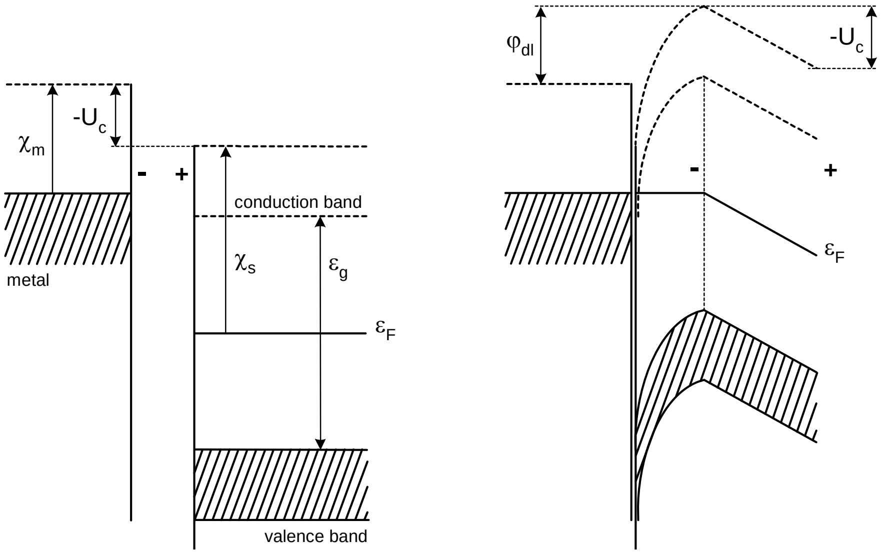
processes.

There are several theoretical presentations of this salt-electrode interface. We will look at a few common ones, not so much from the view of using them in practice, but more from the point of the polarization of galvanic-circuit electrodes.

4. Diffusive Polarization of Galvanic-Circuit Electrodes

Following the Gouy-Chapman-Stern-Grahame (CGSG) model [9] of diffusive DL at the interface between the metal electrode and molten salt, we suggest that applied negative potential at the charged cathode in the broken galvanic circuit can be attributed to the presence of a little excess density of negative ions in the liquid salt for closed circuit due to the constant value of DL potential, φ_{dl} = const, as it is shown in **Figure 4**.

One can see that Fermi level, ε_F, reaches the bottom of conduction band near the cathode and its electrons freely cross the electric double layer and reduce the cations in the molten salt to neutral metal atoms (reducers) supersaturating the salt solution by a metal component. It may be plated on the cathode or/and form colloidal metal particles in the molten salt near the cathode. This opportunity blankets the precipitation of metal particles on the cathode and thereby is diffusively polarizing this electrode in the galvanic crystallization of this metal.



(a) (b)

Figure 4. Band structures of the separated molten salt and cathode under potential $-U_c$ (a) and the ones in direct contact between them in the closed galvanic circuit (b), vertical dotted line is the DL boundary.

It is significant that the molten-salt side of DL itself becomes the cathode of galvanic crystallization process and can extract the metal atoms in the volume of molten salt but not the electrode directly. In this case, the electrodepositing process will be ineffective and the molten salt will change its RedOx potential irreversibly.

It will be the same for the anodic polarization of galvanic metalloid crystallization. One can see it in **Figure 5**. In this case, Fermi level reaches the top of valence band near the anode. The electrons from this band freely cross DL to the anode and oxidize the anions in the molten salt to neutral metalloid atoms (oxidizers) supersaturating the salt solution by this component.

If the neutral metalloid is a gaseous additive in the molten salt, then it forms microscopic bubbles and removes from the melt by flotation. This opportunity decreases the diffusive polarization of the anode but not excludes changing the RedOx potential of salt due to dissolving gaseous impurity in it.

Thus, the forced displacement of the electrodepositing potential into the molten salt near the anode as well as near the cathode is the cause of the diffusive polarization of these electrodes. The other factor of this process is the irreversible change of molten-salt RedOx potential.

5. Discussion of Obtained Results

From the above statements, it is important precisely and online monitoring Fermi level in the molten salt for rigorous controlling its RedOx potential.

At the same time, it is possible to vary this potential thinly ($\pm\Delta k_M < 10^{-6}$) by coulometer titration of one of the metal component [3]. This will allow selectively extracting impurity out of the molten salt with high accuracy.

Thus, the effective galvanic crystallization out of liquid salts needs the precision control and thin managing the molten-salt RedOx potential with small over voltage (~10 MV) due to diffusive polarization of electrodes [3].

The polarization of electrodes and appreciable change of energy of the allowed electron states in the molten salt near the electrodes can be so great that the basic metal components can be extracted from the salt alongside with the additives.

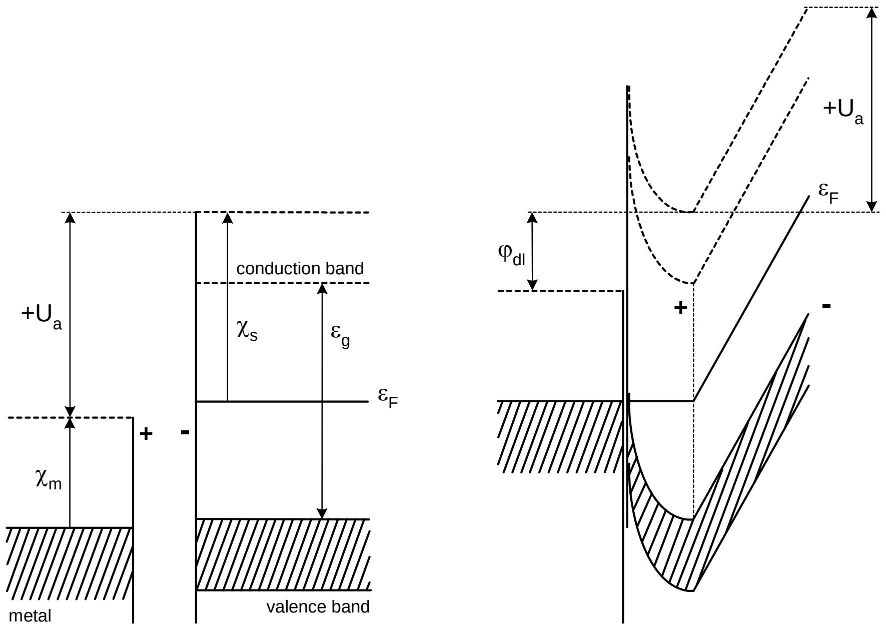
In this case obviously, monitoring the RedOx potential cannot precise due to impossible eliminating indefinite polarization effects on electrodes in the galvanic circuit with the molten salts [10]. Therefore, the RedOx potential of molten salt is to measure without current by using an electrochemical sensor of thermodynamic activity of the metal reducer in molten salt on base of solid electrolyte, for example, of M^+-β''-Al_2O_3 in the electrochemical cell:

$$\mathrm{M}\,|\,\mathrm{Mo}\,||\,\mathrm{M}^+\text{-}\beta''\text{-}\mathrm{Al_2O_3}\,||\,\mathrm{Pb}\,|\,\mathrm{salt}\,[\mathrm{M}] \qquad (3)$$

The action principle of such the gauge is based on the method of electric-motion-force (EMF) when the reference and measuring (lead/salt) electrodes are located on both sides of the solid electrolyte. EMF, *E*, of the sensor is defined by the thermodynamic activity, a_M, of metal, M, as a reduction agent in the molten salt [10].

$$E = \left(RT/F\right)\ln a_{\mathrm{M}} \qquad (4)$$

Using the potentiometer method, it is possible to organize continuous and precision monitoring the ReDOx(Fermi level) of the molten salt in any cases.



(a) (b)

Figure 5. Band structures of the separated molten salt and anode under potential +U_a (a) and the ones in direct contact between themin the closed galvanic circuit (b), vertical dotted line is the DL boundary.

For selecting the salt composition, it is useful to carry out the molecular-dynamic simulation of multicomponent systems and to test their microstructure and atomic dynamics by diffraction scattering of neutrons and synchrotron radiation. On the base of these data, it is possible to classify impurities in salt solutions.

6. Conclusions

The accent is done in the possible application of the potentiometer for monitoring and managing properties of MSR fuel compositions. For this, one can use the precise methods of EMF and coulometer titration of basic metal of the molten salt in the galvanic cell with solid electrolyte, for example, $Na^+(Li^+)$-β''-Al_2O_3.

The potentiometer is offered for solving the problem for optimal choosing the basic salt solutions of uranium and actinides in order to provide the given properties of fuel compositions by impurity correcting or forced changing the RedOx potential of non-stoichiometric salts.

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