



On Electrochemical Maintaining of the Given Quality of Molten Salt Reactors

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Abstract

A concept for electrochemical maintaining of the given quality of a fuel composition of molten-salt reactor (MSR) is formulated. The correction of molten-salt properties can be carried out with the help of a forced and controllable variation of Reduction–Oxidation (RedOx) potential of any liquid salt mixture by changing its little non-stoichiometry. For this, electronic properties of molten fluorides are studied and optimal managing basic compositions of MSR is offered in using the strong electron influence of molten fluorides on liquidus morphology of these systems which is responsible for ionic and covalent bonds in them. The accent is made on managing the electrochemical potential (Fermi level) in the band-gap of non-stoichiometric molten fluorides by the precise coulomb-metric titration of alkali atoms in a galvanic cell with the solid electrolyte from $A^+ - \beta^- - Al_2O_3$ where A is alkali metal (for example potassium) and liquid-lead working electrode.

Keywords

Electrochemical maintaining; Molten salt reactors; Quality

Introduction

Despite of wide experience in studying molten salts for different applications, their microstructure, atomic dynamics, and electronic properties in the frame of band model have been not enough studied in a little non-stoichiometry of them not to mention an influence of their Reduction – Oxidation (RedOx) potential on structural, thermodynamic, physical, chemical, and corrosion properties of fuel compositions and coolants of molten-salt reactors (MSR) [1,2].

At the same time, studying the electronic properties of molten salts can be useful for providing a high-selective extraction of salt components, for minimizing a corrosion of structural materials in them, i.e. it can prove the reliable operation of molten salts in non-isothermal conditions [3,4].

Instead, the researchers have seen an important task for themselves in searching RedOx pairs suitable for keeping a given quality of fuel compositions and practical inhibiting their corrosion activity [5,6] whereas it is possible to deduce these characteristics from the non-stoichiometric state of salt as a crucial factor of its electrochemical potential as Fermi level in the band gap of salt in the frame of different microscopic models [1,7].

Indeed, the thermodynamic, physical, and chemical similarity of condensed matters takes place for the congruent forms of pair

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Received: July 12, 2016 Accepted: August 08, 2016 Published: August 13, 2016

potentials [8]. Therefore, it is possible to deduce structural and chemical characteristics of any liquid salt as well as its phase diagram from its composition [1] and its non-stoichiometric state as an electrochemical potential [7].

In addition, it is practical to carry out a computation of molten salts as ionic melts by means of molecular dynamics (MD) [8] and quantum-mechanical studying the electron states of the condensed matter [9] to specify the kinds and forms of pair potentials for these MD simulations. Therefore, it is possible to develop a way for effective maintaining the given quality of molten salt from the analysis of its atomic-dynamic and electronic properties.

In accenting the microscopic specificity of molten salts, it is easy to estimate an effect of salts dissociation on component solubility in the melt at changing its composition, to formulate approaches for developing a molten-salt technology.

Materials and Methods

An electronic-band model for molten salts

Usually a RedOx pair is selected as a charged impurity ($M^{k+}/M^{(k-1)+}$) suitable for keeping the given chemical quality of liquid salt by means of electrochemical reaction [6] for the required RedOx potential of molten salt which can be presented by equation.

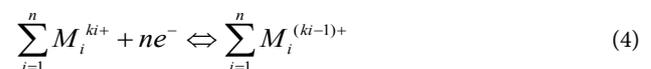


$$E(M^{k+}/M^{(k-1)+}) = E_0(M^{k+}/M^{(k-1)+}) + (RT/F) \ln(c_{M^{k+}}/c_{M^{(k-1)+}}) \quad (2)$$

Or be transformed to the form

$$E(M^{k+}/M^{(k-1)+}) = (RT/F) \ln\left[\frac{c_{M^{k+}}}{c_{M^{(k-1)+}}}\right] \exp\left\{\frac{FE_0(M^{k+}/M^{(k-1)+})}{RT}\right\} \quad (3)$$

Here $E_0(M^{k+}/M^{(k-1)+})$ is the standard potential of cationic pair, $M^{k+}/M^{(k-1)+}$, $c_{M^{k+}}$ and $c_{M^{(k-1)+}}$ are the concentration of oxidizing (M^{k+}) and reducing $M^{(k-1)+}$ ions of the metal impurity, M , of variable valence in the salt, T is Kelvin temperature, R is gaseous constant, and F is Faraday number. For multiple impurities dissolved in the salt, Equation (1) should be presented in the common form:



Where, all the impurities M_{in} should redistribute on their ionic states M_i^{ki+} and $M_i^{(ki-1)+}$ so that their concentrations satisfy to equation [10].

$$E_{tot} = (RT/F) \ln\left[\frac{c_{M_i^{ki+}}}{c_{M_i^{(ki-1)+}}}\right] \exp\left\{\frac{FE_0(M_i^{ki+}/M_i^{(ki-1)+})}{RT}\right\} \quad (5)$$

For each RedOx pair, $M_i^{ki+}/M_i^{(ki-1)+}$

At the same time, it is necessary taking into account a non-stoichiometry of the molten salt itself when its basic metal elements also participate in forming the resulting RedOx potential [10]. Then, the parameter, E_{tot} , becomes an independent electrochemical variable and we can obtain the obvious concentration ratio for each RedOx pair from (5)

$$c_{M_i^{ki+}}/c_{M_i^{(ki-1)+}} = \exp\left[F\left\{\frac{E_{tot}}{RT} - E_0(M_i^{ki+}/M_i^{(ki-1)+})\right\}\right] \quad (6)$$

It is clear that the resulting RedOx potential, E_{tot} , as a unified salt