The Influence of Ultra-dispersion Particles on

Electron Density in SOFC Materials.

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1. Introduction

Further progress in industrial electrochemical generators' designs utilising SOFC considerably depends on problem of obtaining fuel cell materials with predefined properties [1,2]. Due to this fact, considerable efforts of designers are directed on creation of optimum composition «anode-electrolyte-cathode», and on microconstruction of SOFC materials (selection of phase and element composition, defect structure formation, etc.). In the second problem nanocomposite systems having unique properties are of greatest interest [3]. Utilising of such materials as solid electrolyte may allow significantly improve cell's parameters, in particular, increase ionic conductivity [4,5]. However mechanisms leading to this effect were not determined singly.

In this article the influence of nanoparticles ensemble with work of exit that different from the rest of the matrix on the change of electron density in SOFC materials have been examined theoretically. The calculations of concentration distribution of free carriers around single particle and for microparticles ensemble were fulfilled. In conclusion possible directions of forming of nanostructures conformably to SOFC materials discussed.

2. The Electron Density Distribution Around Spherical Particle.

Consider the single spherical particle of radius r_0 in nonmetallic material. In general case the difference of thermodynamic (count from Fermi level) works of exit of the matrix χ_{mat} and of the particle χ_{par} $\varphi_0 = \chi_{par} - \chi_{mat} \neq 0$

If $\varphi_0 > 0$, energetic zones in matrix near the contact "distort up", and around particle the impoverished by carrier's area arise. If $\varphi_0 < 0$, zones "distort down", and the enriched by free carrier's area appear.

Evaluate quantitative parameters that system. Introduce the magnitude $\varphi = - eU$ (e - electronic charge, U - electrostatic potential), which has sense of potential energy of electron in electrostatic field created in matrix by particle. Call the magnitude φ by potential that submit to equation [6]:

$$\Delta\varphi = \frac{4\pi e^2 n_0}{\varepsilon}\left(1 - e^{-\varphi/kT}\right) \qquad (1)$$

with boundary condition:

$$\varphi(r)\big|_S = \varphi_0 \qquad (2)$$

at the boundary S "matrix - particle".

In equations (1, 2) n_0 - the density of carriers far from particle, ε- matrix permittivity.

The density of carriers around particle determines by known expression [6]:

$$n(r) = n_0 e^{-\varphi/kT} \qquad (3)$$

In flat case the analytic solution (1) is known [6] and describe widely used Shottky barrier.

In considering spherical symmetric case the equation (1) has the form:

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} = \frac{4\pi e^2 n_0}{\varepsilon}\left(1 - e^{-\varphi/kT}\right), \qquad (4)$$

and boundary condition (2):

$$\varphi(r)\big|_{r=r_0} = \varphi_0 \qquad (5)$$

For positive and negative φ_0 the solutions of equation (4) will be different. Consider separately these cases.

a) Matrix impoverishment (φ_0 > 0).

As far as all physically interesting cases suppose φ_0 < kT, we can neglect by last term in right part of equation (4).

For determination of second boundary condition in the equation (4) introduce spherical «influence zone» of given particle of radius R. Lets accept that electric field at the boundary «influence zone» equals zero:

$$\left.\frac{d\varphi}{dr}\right|_{r=r_0} = 0 \qquad (6)$$

For numerical estimations of obtained results we need to determine parameters, incoming in equations (4) - (6). Doesn't concretizing material, for calculations we will use middle parameters.

The solution of equation (4) with boundary conditions (5), (6) have the form:

$$\varphi = \frac{1}{6}g\left(r^2 - {r_0}^2\right) + \frac{1}{3}gR^3\left(\frac{1}{r} - \frac{1}{r_0}\right) + \varphi_0, \text{ where}$$

$$g = \frac{4\pi e^2 n_0}{\varepsilon} \qquad (7)$$

Substituting the finding dependence φ = φ(r) in equation (3), we receive the distribution of electron density in space around single particle. For illustration the found dependencies are shown at fig. 1 the calculation n = n(r) were made for value φ_0 = 0,3 eV and different values r_0.

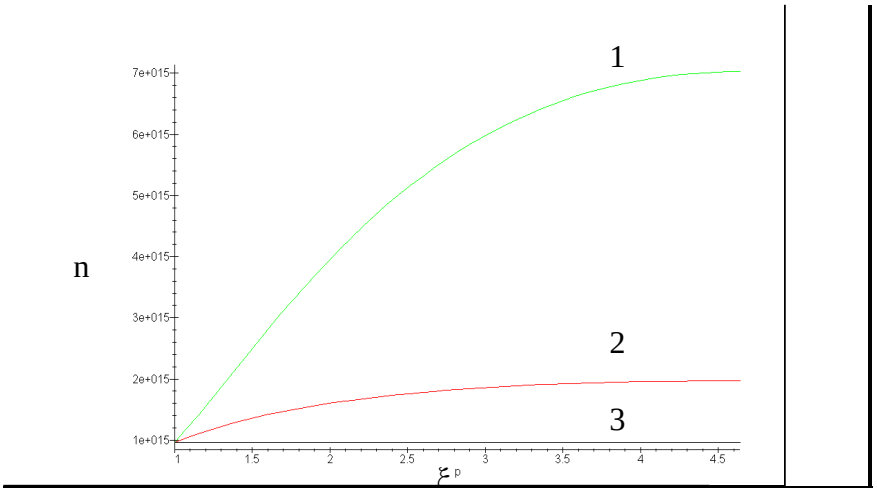

Figure 1. Density of free carriers vs. relative distance for different dispersion particles sizes (T = 1500 K, φ_0 = 0,3 eV, Q = 1 %, ε = 10, $n_0 = 10^{16}$ cm^{-3}).

For comparison the significance n has been given in dependence from relative distance $\xi = \frac{r - r_0}{r_0}$. It is easy to see, that ultradisperse particles are of the greatest influence on concentrations' changes (compare Fig. 1). As was shown by calculations «effect of impoverishment» will increase when φ_0 increases under other equal conditions.

Parameters used for calculations: T = 800,1200,1500 K; $n_0 = 10^{10}...10^{16}$ cm^{-3}; ε = 10; r_0 =10...2500 nm; $-\varphi_0$ (enrichment) =0,2...0,4 eV, φ_0 (impoverishment) =0,1...0,5 eV

For lowering of temperature the efficiency of disperse particles as « snares» for electrons increase. For choosing at fig. 1 parameters the relative impoverishment of matrix $1 - \frac{n(r)}{n_0}$ practically do not depend from ξ and make up for temperatures 800, 1200, 1500 K conformably 76, 62, 54 %.

b) <u>Matrix enrichment ($\varphi_0 < 0$).</u>

The equation (4) for $\varphi_0 < 0$ is essentially nonlinear, so solutions have been done numerical works. The calculative algorithm have been described in detail in [7]. For illustration at fig. 2 we bring calculations the distribution of electron density (the solution of equation (4)).

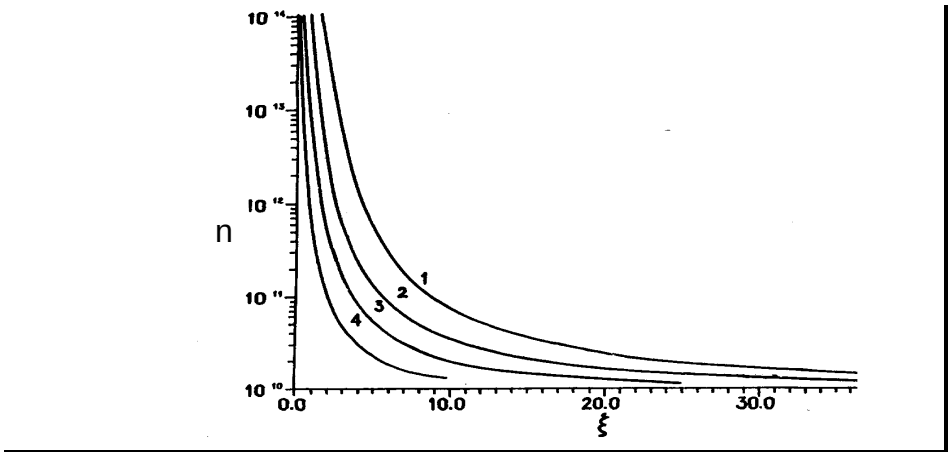

Figure 2. Density of free carriers vs relative distance from boundary «matrix-particle» (Q = 1 %, ε = 10). 1 - 5 nm, 2 - 10 nm, 3 - 20 nm, 4 - 50 nm.

It's shown that around metal particle "fur coat" from free carriers is forming which relative size depend essentially from r_0. So if size of enrich zone R with density $n \geq 500\ n_0$ for particles with radius r_0 = 50 nm is R = $1{,}5r_0$, then for ultradisperse particles with r_0 = 5 nm R = $4{,}5r_0$.

3. The Influence Of Particles' Ensemble On Electron Density In SOFC Materials.

Lets go over to ensemble of disperse particles now. Disperse system, consisting from particles' ensemble in a matrix with extent enough areas of enrichment (impoverishment) and high particles' density such to produce area's interlinks, will be possesses heightened (low) density of free carriers in comparison with initial material and so heightened (low) matrix conduction. Properties of such system will be define in first approach by totality of single particle solutions, if define radius R «influence area» of particle as $R = \sqrt[3]{\frac{3}{4\pi N}}$, where N - particles' density in volume unit of matrix. In this case totality of influence areas will exhaust total volume. Selfco-ordinated account of «influence areas», taking into account particles sizes distribution, for equations, similar to (4), given in [8].

Lets introduce Q volume fraction of dispersion particles, $Q = \frac{4\pi r_0^3}{3R^3} = \frac{4\pi r_0^3 N}{3}$. Evidently, Q must be as small as possible to preserve basic matrix properties, for instance, ionic conductivity, mechanical properties etc. We show upper limit Q = 30...40%, which, as well known, correspond to percolation threshold (under such conditions it is possible formation of through bridges from dispersion particles). This limit restricts applicability of examining model with isolated particles. Therefore volume fraction 1-10% was used in the calculations.

Now we use obtained calculation data for prognosis of properties of dispersive compositions conformably to SOFC materials. The values of work of exit of electrons are shown in table 1 [9]. One can see from comparison of values χ for some materials, their difference φ_0 corresponds with calculation data.

Table 1

Values of works of exit of electrons χ some materials[9]

Material	**Work of exit, eV**	**Throw of values, eV**
W	4,54	4,2 - 5,3
Nb	3,99	3,81 - 4,41
Re	5,0	3,98 - 5,43
ZrO_2	3,8	3,12 - 4,57
BaO	1,7	1,0 - 2,4
Al_2O_3	4,0	3,8 - 4,7

Evidently, discussed in section 2a model can be utilised to the materials of solute electrolyte. As follows from table 1, pare parameters ZrO_2-W are corresponding to calculation data (Fig.1). As it is follows from Fig.1 based on the calculation data Q = 1 %. Thus, in accordance with proposed model, introduction 1 % dispersive particles W of size ~10 nm in ZrO_2 can decrease electron density approximately at one order. The second significant consequence of obtained data is effect increasing for low temperatures. This fact gives the possibility to change correlation between ionic and electronic conductivity to the side of ionic for low temperatures and therefore decrease ECG working temperature.

Go over to discussion of case b) - matrix enrichment by free carriers. Using obtained data, one can estimate particle's density N, that required for zone's interlink and their volume fraction Q. When r_0 = 50 nm then Q = 0,3 , when r_0 = 5 nm Q = 0,01.

Thus, when particle's size r_0 = 50 nm one can increase free carriers' density in total volume on approximately one order. If r_0 = 5 nm that density increasing is possible long since Q = 0,01. When Q is a great value we can wait more substantial carrier's density increasing in nanocomposite material. Electron density change in rare-earth elements' cobaltites, manganites, chromites [10] can be related with predicted enrichment of volume by free carriers. At last, using of obtained data allow examine as an envisaging further development electrode materials other class of substances.

4. Irradiation-Plasma Methods Of Forming Nanostructures.

Considering of the real ultradisperse structures conformably to SOFC materials one have to take into account some additional factors that become complicated problem, in particular, dispersion of the dimension particles,

uniformity of their distribution matrix, thermal stability etc. Apparently the state of the boundary «matrix-particle» is imagine factor. The existing defect structure of the interface boundary is determine dispersion of emission data [9] and serves as base of different model of nanostructures [4]. It makes high demands to the technology of nanocomposite's manufactory. Among the most promising methods it is necessary to distinguish processes that are 1) do not introduce (or introduced minimum amount) of impurities and 2) realised the disperse particles forming at high supersaturation of point defects. First of all one must consider vacuum and *in situ* methods.

The structure properties of the two-phase materials Me - ZrO_2 (Me = Ta,W,Re,Nb,Mo etc.) which received by vacuum CVD and PECVD methods have been investigated [11-13]. As electron microscopy showed the structure these materials represent two-phase system: matrix with uniformly distributed 5-10 nm. The implantation methods are very interesting to manufacturing of nanostructures *in situ*. The effect of forming of ultradisperse fraction under low temperature irradiation in multicomponent systems has been predicted [14]. The theoretical model has been experimentally checked [15]: the original particles have been solved under ionic bombardment of the nimonic PE-16 as new fine particles with the sizes 10 nm yielded.

5. Conclusions

5.1. Theoretical analysis was performed of electron density distribution n = n(r) around single particle with work of exit of electron differ from matrix. The dependencies n(r) are obtained at different values of parameters: temperature, φ_0 etc. The concentration of electrons in matrix near particles are a) decrease for $\varphi_0 > 0$ and b) increase for $\varphi_0 < 0$.

5.2. The influence of particles' ensemble on the changes in electron density in solid electrolytes has been studied. It is shown that addition of ~ 1% ultradisperse (~ 10 nm) particles with $\varphi_0 = 0{,}3$ eV decrease electron concentration in matrix at 1500 K approximately to one order. The effect becomes intensive at lower temperatures. It is possible to suggest such nanocomposite materials for solid electrolytes with lower working temperature.

5.3. The distribution of electron density *n* in nanocomposites with $\varphi_0 < 0$ have been considered numerically. As calculations shown, addition 1 % fine particles with radius 5 nm increased *n* more those two orders. This effect gives opportunity to expanse the types of materials for electrodes (first of all, air electrode) SOFC.

5.4. The irradiation-plasma methods for nanocomposites manufacturing have been examined.

6. References

1. Proc. of 3d Int. Symp. on SOFC, Hawaii, May,1993.

2. Proc. of 4th Grove Fuel Cell Symp., London, sept., 1995.

3. И.Д. Морохов, Л.И. Трусов, В.Н. Лаповок. Физические явления в ультрадисперсных средах .- М.: Энергоатомиздат .1984 . 224 с.

4. N.J. Dudney. Composite electrolytes.- Ann.Rev.Mater.Sci., 1989, v.19, p. 103-120.

5. M.I. Osendi, J.R. Jurado. Duplex Y_2O_3 - ZrO_2/Al_2O_3 nanocomposites as solid electrolytes.- in [1], p. 82-91.

6. В.Л. Бонч - Бруевич, С.Г. Калашников. Физика полупроводников .- М .: Наука . 1990 .

7. Н.М. Кирюхин, А.В. Коропов, В.В. Сагалович и др. О возможности увеличения плотности носителей в нанокомпозитных материалах. Препринт ХФТИ 92-37., Харьков, 1992, 10 с.

8. V.V. Slezov, V.V. Sagalovich. Theory Of Diffusive Decomposition Of Supersaturated Multicomponent Systems. J. Phys. Chem. Solids., 1977, v.38, p. 943-948.

9. В.С. Фоменко. Эмиссионные свойства материалов . Справочник .- Киев .: Наукова думка . 1970 . 148 с.

10. С.Ф. Пальгуев, В.К. Гильдерман, В.И. Земцов. Высокотемпературные оксидные электронные проводники для электрохимических устройств.- М .: Наука .1990 .197 с.

11. В.Е. Иванов, В.М. Криворучко, В.В. Сагалович и др. Кристаллизация тугоплавких металлов из газовой фазы. - М.: Атомиздат. 1974. 220 с.

12. Н.С. Полтавцев, В.В. Сагалович, В.В. Слезов и др. Всесторонние упругие деформации в двухфазных сплавах. - ФТТ, 1974, т.16, с. 1890-1894

13. Е.П. Нечипоренко, В.В. Слезов, В.В. Сагалович и др. Коалесценция в двухфазных сплавах. - ФТТ, 1972, т.14, с. 1469-1474. (Coalescence in two-phase alloys. Soviet Physics - Solid State, 1972, v. 14, p. 1259-1264).

14. А.С. Бакай, Н.М. Кирюхин. Об эволюции выделений в состаренных сплавах под облучением.- ВАНТ, серия ФРПРМ, 1983г., вып.5(28), с. 33-40

15. В.Н. Воеводин, Н.М. Кирюхин, И.М. Неклюдов и др. Изменение распределения выделений по размерам при облучении сплава типа нимоник тяжелыми ионами.- ФММ, 1988, т.66, вып.3, стр 619-621