

On the temperature dependence of oxygen ionic conductivity of 10Sc1CeSZ electrolytes

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The dependency of ionic oxygen conductivity of 10Sc1CeSZ electrolyte made of different nanosized zirconia powders those differ by their impurities and manufacturing technologies, and sintered in air at different temperatures after uniaxial pressing are analyzed in terms of their Arrhenius equations in 250–850 °C temperature range. Deviation from a typical linear dependence of conductivity on temperature that is the most clearly visible in the electrolyte made of the purest powder is observed. The inflection point is determined by powder properties and is practically independent on sintering temperature.

Keywords: oxygen ionic conductivity, DKKK, IPMS, Praxair powders, 10Sc1CeSZ electrolyte, influence of sintering temperature, grain size, activation energy.

Introduction

Cubic zirconia is a typical solid electrolyte for ceramic fuel cells during more than one hundred years since its invention by Walter Nernst [1]. In this solid electrolyte, the charge transport is realized by oxygen ions [2].

Historically, the oxygen conduction was first observed in fluorite structures as John Goodenough has mentioned in his comprehensive review referencing to Michael Faraday who had observed the fast ion conduction in the electronic insulator PbF_2 [3]. This observation is remarkable because all the tetrahedral sites of the face-centered-cubic array of Pb^{2+} ions are fully occupied. The fast F-ion conduction in PbF_2 is due to saddle-point energy between the fully occupied tetrahedral sites that is nearly the same as that of the tetrahedral sites.

The large charge on the O^{2-} ion increases the coulomb repulsion between anions and inhibits the coexistence of O^{2-} ions in both saddle-point and tetrahedral-site position in the MO_2 fluorites, but the energy difference between saddle-point and tetrahedral sites remains small, so the motional enthalpy ΔH_m for an oxide ion to transfer to a neighboring oxygen vacancy is relatively low. Bi_2O_3 has one-quarter of the tetrahedral sites vacant, i. e., $c_0 = 0,75$ and these vacancies are disordered in the high-temperature $\delta\text{-Bi}_2\text{O}_3$ phase. Like Pb^{2+} , the Bi^{3+} ion contains a polarizable $6s^2$ core that reduces the motional enthalpy ΔH_m for an oxide-ion transfer.

However, coulomb repulsions between the O^{2-} ions stabilize long-range ordering of the oxygen vacancies below a first-order order-disorder transition at a temperature T_t . The long-range order creates distinguishable occupied and empty sites separated by an energy ΔH_g . In this situation, thermal excitation of anions into the vacancies introduces a disorder that lowers ΔH_g , which introduces a temperature-dependent feedback:

$$\Delta H_g(T) = \Delta H_g(\text{O}) = c^\delta. \quad (1)$$

The data available show that oxygen ionic conductivity, as some thermo-activated process, may be traditionally described by the typical Arrhenius equation as

$$\sigma T = A \cdot \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

where σ is the ionic conductivity; T — temperature; A — pre-exponential constant, and E_a is the activation energy. In general, some dependencies of the pre-exponential constant and the activation energy on temperature might be expected also.

The activation energy normally includes energies required for formation and migration of oxygen vacancies in a perfect crystal. In the extrinsic regime, the activation energy is dominated by the migration energy. In this case, the activation energy might be represented by the migration energy for doped oxide ionic conductors. If the oxygen vacancies are of a defect association within the oxide, the dissociation energy that is required in order to break this complex at high temperature has to be considered in the activation energy also.

Indeed, following the existing theory, which considers the ionic conduction as ion hopping along defects of the crystal lattice, and according to Van Bueren [4], the hopping frequency may be formally defined as

$$\nu = \nu_0 \cdot \exp\left(-\frac{Q}{kT}\right) \quad (3)$$

where Q is a free activation energy that may depend on temperature too.

By applying an electrical field E , the probability of hopping will become anisotropic. In the simplest case, when positively charged ion has to move between ions in isotropic lattice of distance a , it's hopping in direction of the applying field E is favorable. It means that such the hoppings will occur with higher frequency ν' .

$$\nu' = \nu_0 \cdot \exp\left(-\frac{U - \frac{1}{2}eaE}{kT}\right). \quad (4)$$

Against the field direction, the hopping frequencies ν'' will be lower as

$$\nu'' = \nu_0 \cdot \exp\left(-\frac{U + \frac{1}{2}eaE}{kT}\right). \quad (5)$$

As result, at low electrical field when $eaE \ll kT$, the current density to be determined as a total number of ions running in the field direction through an area unit is

$$j = nea \cdot (\nu' - \nu'') = nea\nu_0 \cdot \left(\exp\left(-\frac{U - \frac{1}{2}eaE}{kT}\right) - \exp\left(-\frac{U + \frac{1}{2}eaE}{kT}\right) \right), \quad (6)$$

where n is a number of ions running through a volume unit.

The last equation may be rewriting as

$$j = nea\nu_0 \cdot \exp\left(-\frac{U}{kT}\right) \cdot 2sh\left(\frac{\frac{1}{2}eaE}{kT}\right). \quad (7)$$

The $sh(x)$ may be expanded and limited to the first member:

$$sh(x) = \sum_{n=0}^{\infty} \frac{x^{(2n+1)}}{(2n+1)!} = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots \quad (8)$$

After that procedure, the current density will be determined as follows:

$$j = neav_0 \cdot \exp\left(-\frac{U}{kT}\right) \cdot \left(\frac{eaE}{kT}\right). \quad (9)$$

Proceeding from the first principles, Walter Nernst [5, 6] had determined the ionic conduction, σ , as

$$\sigma = en\mu, \quad (10)$$

where e and n are the charge and the concentration of its carriers, respectively, and μ is the ionic mobility.

The ionic mobility may be defined as

$$\mu = a^2 e v / kT. \quad (11)$$

It is obvious,

$$\sigma = na^2 e^2 v / kT. \quad (12)$$

In this case, finally, the ionic conduction may be determined as

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{U_1}{kT}\right). \quad (13)$$

Typical experimental data on conductivity of solid electrolytes of different classes are shown in fig. 1. Most dependencies are linear. Among zirconia electrolytes, scandia stabilized zirconia (ScSZ) has the highest conductivity.

The latest studies give contradictive data on oxygen ionic conductivity of zirconia electrolytes stabilized with scandia, 10Sc1CeSZ especially, where dependencies, which could be described either one or two lines, are observed (fig. 2) [7, 8].

The purpose of the study was to examine the temperature dependence of electrical conductivity of 10Sc1CeSZ electrolytes to be related to structural features and mechanical behavior of different structure ensuring by different powders and their sintering at different temperatures.

Experimental

10% (mol.) Sc_2O_3 and 1% (mol.) CeO_2 (10Sc1CeSZ) solid electrolyte was made of three different powders produced by IPMS, Ukraine, DKKK, Japan, and Praxair, USA, and compared.

The comprehensive analysis of the powders and their ceramics is given in [9–12]. Here, we remind briefly that the size of initial particles in IPMS's powder was 11 ± 2 nm; DKKK's is 83 ± 20 nm, and Praxair's one is 141 ± 60 nm. The concentration of impurities in the bulk of DKKK is only 0,001% (wt.), which is one order of magnitude lower than the corresponding values for IPMS and Praxair (0,01% (wt.)). IPMS powder contains mainly silica (0,05%) and alumina (<0,025%) while in Praxair's one silica (0,05%) and titania (<0,14%) are present. From the point of surface-bulk distribution revealed with secondary ion mass-spectrometry, in DKKK powder, the surface of particles is enriched with Sc and Al; in Praxair one, Sc and Si are mostly present on the surface. In IPMS powder, the surface is depleted with Sc; Si is localized inside particles.

SEM appearance of 10Sc1CeSZ powders is shown in [9–12]. It is seen that agglomerates of IPMS powders consist of really nano-sized particles. Their commercial analogs consist of much larger particles. DKKK powder is non-agglomerated, but Praxair's agglomerates are as chips of well-sintered polycrystalline ceramics.

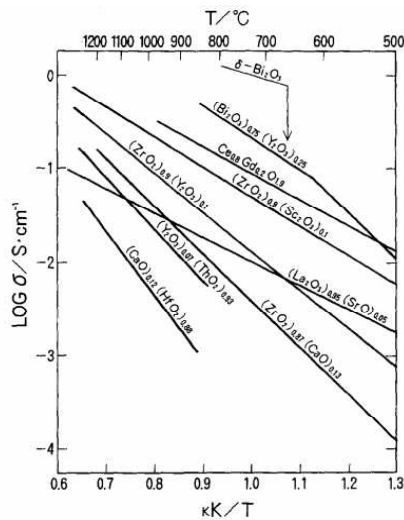


Fig. 1. Typical dependencies of electrical conductivity vs. temperature for ionic solid conductors [2].

Density of sintered samples was measured with the Archimed's method. Grains size was measured with ImageJ and Image Lab programs of SEM images of sample cross-sections.

Samples of ceramic electrolytes were tested for their mechanical behavior studying their fracture

micromechanisms with SEM and strength at biaxial three points bend at room temperature.

The electrical properties of ceramic pellets (15 mm diameter) was performed using AC impedance Solartron 1260 frequency response analyzer in air in the temperature range 250—850 °C in the range of 6MHz—0,1Hz. Platinum ink (Engelhard) was used for the electrodes coating on each side of pellets, followed by annealing at 900 °C for 1 hour.

To determine the inflection point (point of intersection) of two lines, we have developed an algorithm based on the method of least squares. Thus an array of input points, a[N] crashed into two halves containing a different number of elements b[M1], c[M2], but the total number of elements coincides with the total number of elements in the input array $M1 + M2 = N$. On the next step, was conducted in each area approximating straight to the method of least squares. Next, calculated amount root mean square (rms) deviations of two lines. Dynamically changing the number of elements in the arrays b , from 2—N-2, and repeat iteration of the standard deviation obtained

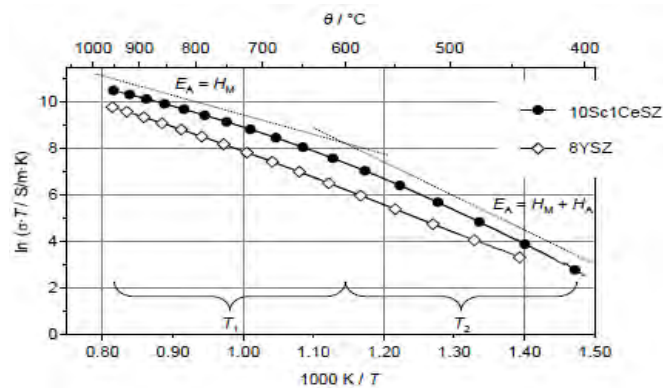


Fig. 2. Typical dependencies of electrical conductivity vs. temperature for 10Sc1CeSZ and 8YSZ electrolytes usually used in SOFC [3, 4].

K[N-2] averages. Next, using the bubble sort method were the least value of total deviation K[i]. That factor is clearly displays all essential factors of both lines. Thus, analytically find the point of intersection of two lines and that will determine the point of inflection.

$$\begin{aligned} y_1 &= k_1x + b_1; \\ y_2 &= k_2x + b_2; \\ t_k &= \frac{b_1 - b_2}{k_1 - k_2}, \end{aligned} \quad (14)$$

where t_k is the x-coordinate of the point of intersection.

Results and discussion

The powders had different ability to sintering [12]. Being sintered, e. g., at 1500 °C for 1,5 hour, DKKK samples had practically zero porosity, ~0,95 for Praxair one and ~0,80 only for IPMS one. Fig. 3 demonstrates data on porosity, grain size and biaxial strength of electrolyte samples sintered at different temperatures as well as their structures revealed with fracture at room temperature.

Uniaxially pressed 10Sc1CeScSZ—IPMS samples demonstrated less sensitivity to the grain growth at high temperatures than 10Sc1CeScSZ—Praxair and DKKK ones where the grain growth from 0,3 to 4 μm was detected instead of 0,8—2,2 μm observed in IPMS electrolyte.

The highest biaxial strength (375 MPa) was obtained for 10Sc1CeSZ—DKKK ceramics sintered at 1350 °C. The second highest value was obtained for co-deposited 10Sc1CeScSZ—IPMS samples (250 MPa) sintered at 1500 °C. The lowest biaxial strength was detected for 10Sc1CeScSZ—Praxair (220 MPa) sintered at 1450 °C.

Sintered at 1500 °C and higher the 10Sc1CeScSZ—IPMS and Praxair samples demonstrated the similar biaxial strength around 250 MPa while the value of biaxial strength for 10Sc1CeScSZ—DKKK was only 150 MPa.

The cleavage fracture mechanism was detected for porous 10Sc1CeScSZ—IPMS samples with no any changes with sintering temperature while DKKK samples fail with mixed mode (cleavage and intergranular) and Praxair ones fail with intergranular mechanism mainly.

So, ceramic electrolyte samples made of 10Sc1CeScSZ—IPMS powder are less inclined to high temperature recrystallization than Praxair's and DKKK's ones. Moreover, it was reported also [4, 7] that ceramics made of IPMS and Praxair's powders are practically insensitive to cold isostatic pressure (CIP) applied to powder at formation of green ceramic bodies in comparison with DKKK's powder where increasing CIP pressure from 20 to 80 MPa results in grain growth from 3—7 to 20—30 μ, and pores (up to 20 μ) and final dramatic decrease of biaxial strength less 50 MPa.

As to the general conductivity, 10Sc1CeSZ electrolyte itself as well as its temperature dependence demonstrate their strong dependencies on both type of powders and sintering temperature resulting from presence and redistribution of stabilizing additives and dopants, density/porosity, grain size and other structural features (fig. 4). It is seen that samples sintered at 1300—1400 °C are more sensitive to testing temperature than samples sintered at higher temperatures, 1450—1550 °C.

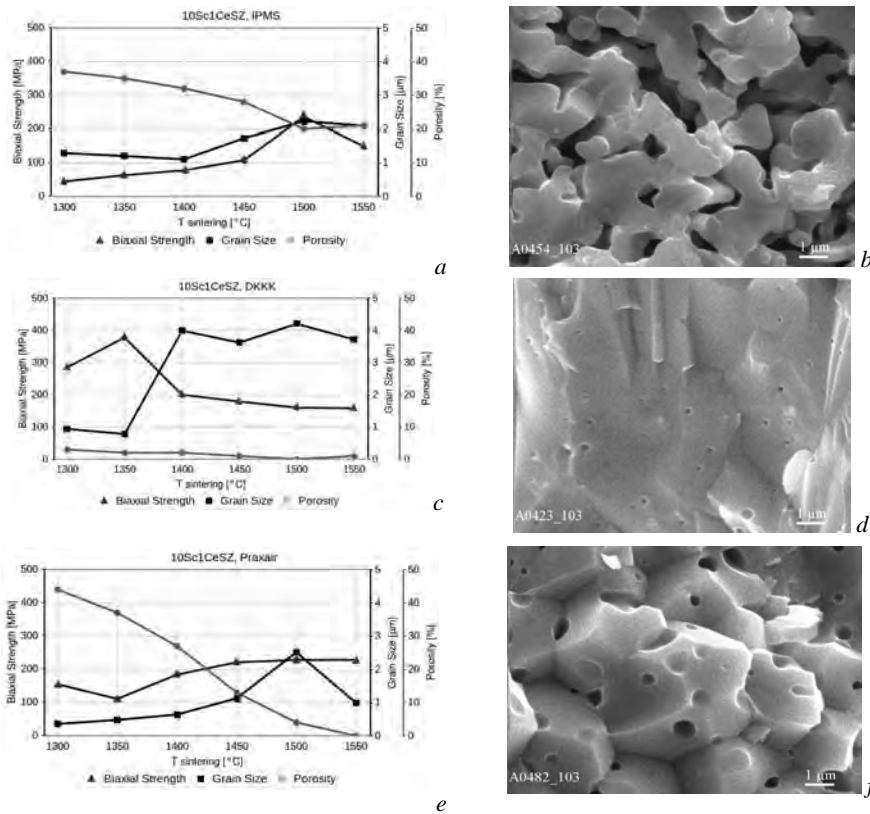


Fig. 3. Bi-axial strength, grain size, porosity (*a, c, e*) and structure of fracture surfaces (*b, d, f*) respectively of the uniaxially pressed samples of 10Sc1CeSZ electrolytes made of IPMS (*a, b*), DKKK (*c, d*) and Praxair (*e, f*) powders sintered at different temperatures in air.

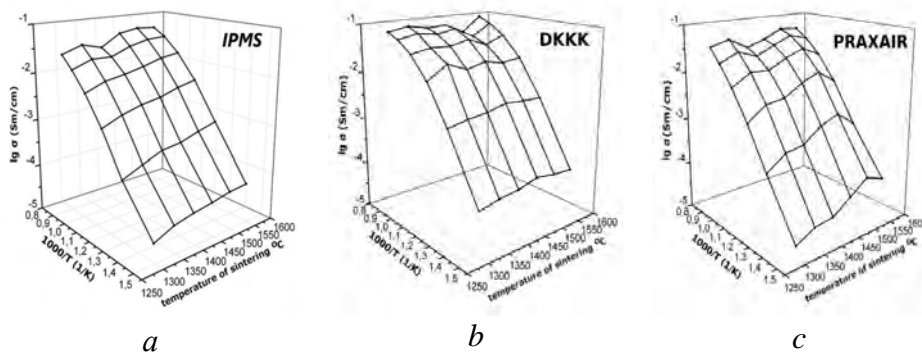


Fig. 4. The ionic conductivity of 10Sc1CeSZ electrolytes made of IPMS (*a*) powder sintered at 1250—1550 °C for 1,5 hour in air vs. temperature, the ionic conductivity of 10Sc1CeSZ electrolytes made of DKKK (*b*) and Praxair (*c*) powder sintered at 1250—1550 °C for 1,5 hour in air vs. temperature.

Fig. 5 summarizes the temperature dependency of the ionic conductivity of 10Sc1CeSZ electrolyte made of different powders. It is seen that testing temperature has different influence on low and high temperature parts of the dependencies, and different activation energies E_a , respectively.

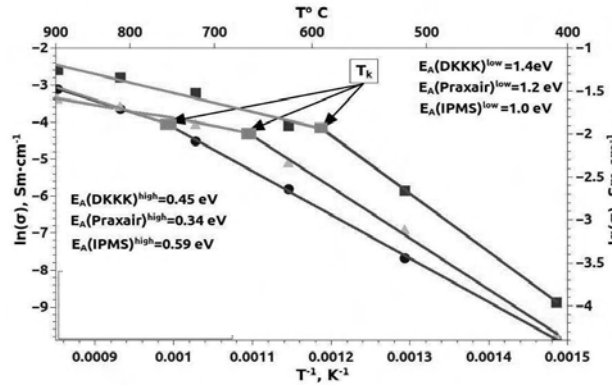


Fig. 5. The temperature dependencies of oxygen ionic conductivity of 10Sc1CeSZ electrolytes made of IPMS, DKKK and Praxair powders sintered at 1450 °C for 1,5 h in air: ■ — DKKK; ● — IPMS; Δ — Praxair.

dependency has own an inflection point, position of which on the temperature axis depends mainly on impurities: the purer 10Sc1CeSZ electrolyte the lower temperature of inflection and clearer the inflection.

It is obvious that the temperature dependencies of electrical conductivity of the 10Sc1CeSZ electrolyte cannot be described by the one linear dependency in terms of the Arrhenius equation. Any corrections by taking into account, e. g., temperature dependence of the A coefficient, porosity and/or grain size were not able "to straighten" the dependencies.

The temperature dependencies could be easily described by two Arrhenius equations differing by their activation energies for low and high temperature ranges separately. The inflection points, T_k , has been determined as the point of intersection of its approximating straight lines, which might be defined by minimizing the mean square deviation of experimental points from their approximating lines in each low and high temperature intervals separately, i. e., before and after the inflection point.

In the two term description, the inflection point T_k might be determined from two the Arrhenius equations:

$$\sigma_1 = \sigma_{0,1} \cdot \exp\left(-\frac{U_1}{kT}\right) \quad (15)$$

and

$$\sigma_2 = \sigma_{0,2} \cdot \exp\left(-\frac{U_2}{kT}\right). \quad (16)$$

Finally, the inflection point T_k is defined as the function

$$T_k = \frac{U_2 - U_1}{k \cdot \ln\left(\frac{\sigma_{0,1}}{\sigma_{0,2}}\right)}. \quad (17)$$

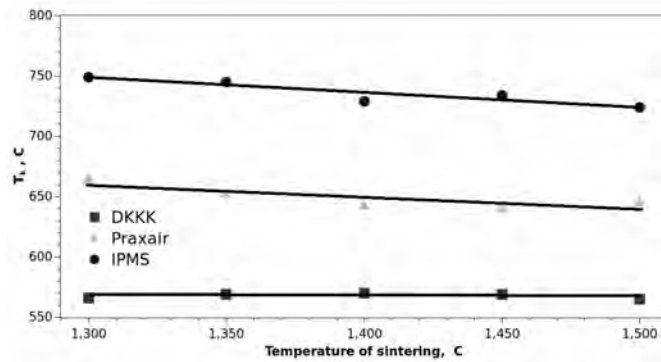


Fig. 6. The dependencies of the inflection points T_k on temperature dependencies of the ionic conductivity of 10Sc1CeSZ electrolytes made of IPMS, DKKK and Praxair powders sintered at 1450 °C for 1,5 h in air on sintering temperature: ■ — DKKK; Δ — Praxair; ● — IPMS.

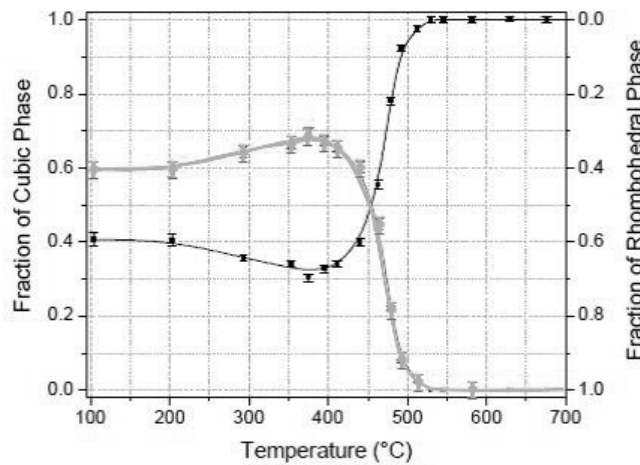


Fig. 7. Phase content of the electrolyte sample made of DKKK 10Sc1CeSZ powder and sintered at 1200 °C determined with XRD (Rietveld multiphase analysis) [6].

The surprising independence, or very weak dependence, of temperature of the inflection T_k on sintering temperature is obvious (fig. 6). The position of T_k is determined mainly by the type of zirconia powder, and the amounts of its alloying and doping elements.

As the most likely cause of such the behavior of the oxygen ionic conductivity of 10Sc1CeSZ electrolyte is the phase transition between its cubic and rhombohedral states that takes place in the temperature interval studied. The inflection point, T_k , is, probably, the upper temperature limit of the cubic-rhombohedral transition [6, 13], after which the structure becomes cubic totally.

Conclusions

The temperature dependencies of oxygen conductivity of 10Sc1CeSZ electrolyte might be described by two Arrhenius equations with different

activation energies. It has no any visible correlation with their structural parameters like grain size or porosity and mechanical behaviors. The inflection point on the entire temperature dependency is mainly determined by type of zirconia powder and is practically independent on sintering temperature. The probable cause of such the behavior of electrolyte conductivity is its cubic-rhombohedral phase transition.

Acknowledgements

The author gratefully thanks all members of the IPMS SOFC team for fruitful discussions and financial supports from the National Academy of Science of Ukraine, NATO "Science for Peace" Program, project N980878 "Solid oxide fuel cells for energy security" and EU FP6 project N020089 "Demonstration of SOFC stack technology for operation at 600 °C".

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Температурна залежність йонної електропровідності цирконієвих електролітів 10Sc1CeSZ

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Йонна провідність електроліту 10Sc1CeSZ залежить від багатьох факторів, зокрема від способу виробництва порошку, анізотропного пресування нанорозмірних порошків в зразок і температури спікання зразків. Так, після спікання у повітрі при різних температурах порошку 10Sc1CeSZ різних виробників залежність його йонної провідності від температури 250—900 °С виражається через рівняння Арреніуса. Опис та аналіз відхилення від прямолінійного ходу залежності електропровідності є важливим аспектом розуміння і покращення властивостей електроліту. Так, точка перегину визначається властивостями порошку і практично не залежить від його температури спікання, тобто є важливою характеристикою матеріалу.

Ключові слова: киснева йонна провідність, порошки DKKK, IPMS, Praxair, електроліти 10Sc1CeSZ, вплив температури спікання, розмір зерна, енергія активації.

Температурная зависимость ионной проводимости циркониевых электролитов 10Sc1CeSZ

О. Кирпа

Ионная проводимость электролита 10Sc1CeSZ зависит от многих факторов, в частности от способа производства порошка, анизотропного прессования наноразмерных порошков в образец и температуры спекания образцов. Так, после спекания на воздухе при различных температурах порошка 10Sc1CeSZ разных производителей зависимость его ионной проводимости от температуры 250—900 °С выражается через уравнение Аррениуса. Описание и анализ отклонения от прямолинейного хода зависимости электропроводности является важным аспектом понимания и улучшения свойств электролита. Так, точка перегиба определяется свойствами порошка и практически не зависит от температуры спекания, то есть, является важной характеристикой материала.

Ключевые слова: ионная проводимость кислорода, порошки DKKK, IPMS, Praxair, электролиты 10Sc1CeSZ, влияние температуры спекания, размер зерна, энергия активации.