Temperature-Independent Activation Energy for Ionic Conduction of Zirconia Based Solid Electrolytes[*]

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Abstract　　　Previous studies have shown that the temperature dependence of the ionic conductivity of zirconia based solid electrolytes exhibit an unusual non-linear Arrhenius behavior and, as a result, the activation energy for ionic conductivity resulting from the analysis according to the classical Arrhenius equation is temperature-dependent. In this paper, a modified Arrhenius equation was proposed, based on the measurement and analysis of the conductivity for three kinds of Y_2O_3-stablized ZrO_2, to describe the temperature dependence of the ionic conductivity. It was found that the activation energy deduced from the modified Arrhenius equation is a constant independent of temperature. The validity of such a temperature-independent activation energy was further discussed based on the transition-state theory in physical chemistry.

Keywords: 　Ionic conductivity, 　Activation energy, 　Solid electrolyte, 　Zirconia,

Non-linear Arrhenius behavior

Yttria-stabilized zirconia(YSZ)is becoming increasingly important as a solid state electrolyte because of its good electrical and mechanical properties. In the previous studies, it was usually assumed that the temperature dependence of the ionic conductivity of YSZ, can be expressed by an Arrhenius equation[1]:

$$\sigma = \frac{A}{T}\exp\left(-\frac{E}{kT}\right) \qquad (1)$$

where σ is the ionic conductivity, T is the absolute temperature, k is the Boltzmann constant, A is the pre-exponential factor, and E is the activation energy for conductivity. When $\log(\sigma T)$ is plotted against $1/T$, a straight line can be expected with slope $-E/k$ and an intercept on the $\log(\sigma T)$ axis of $\log A$.

However, more and more studies have found that the $\log(\sigma T)$ *vs* $1/T$ plots for YSZ show an unusual non-linear Arrhenius behavior: the absolute values of their slopes are high at low temperature and decrease gradually with increasing temperature [2-4]. Such a phenomenon has been studied by some authors and several particular functions have also been proposed, based on the assumption that the activation energy for conductivity is dependent on temperature, to fit the experimental results [4-6].

This study presents a new function to describe the relationship between σ and T for YSZ, from which a temperature-independent activation energy for conductivity can be deduced.

1　Experimental

Three kinds of yttria-stabilized zirconia, $Y_{0.16}Zr_{0.84}O_{1.92}$ (denoted as 8YZ), $Y_{0.20}Zr_{0.80}O_{1.90}$ (10YZ) and $Y_{0.24}Zr_{0.76}O_{1.88}$ (12YZ), were used in this study. Ultra-fine powders were prepared by the co-precipitation method from the mixtures of $ZrOCl_2$ and $Y(NO_3)_3$ solutions. The samples were prepared by uniaxial pressing following by isostatic pressing at 100 MPa and sintered at 1 600 ℃ for 4 h in air. X-ray diffraction of the sintered specimens showed the presence of a single phase of the cubic fluorite structure.

A direct current (d. c.) four-probe method was employed for the conductivity measurements. The specimens for four-probe conductivity measurements were cut directly from the as-sintered samples and had a shape of rectangle. After being slightly polished, four platinum-paste electrodes were fixed on the specimen as current and voltage probes, respectively. The specimen was then set on an alumina holder and heated in an electric furnace. The conductivity measurements were made over the temperature range 623 to 1 673 K at about 50 K temperature interval during the cooling cycle. About 30 min was given after each temperature change before recording data. At each temperature, at least five conductivity data were recorded and then an average value of these measured data was used for the following analysis. During these measurements, the fluctuation in temperature was controlled to within ±1 ℃. For a given temperature, the potential drop between the central probes was adjusted to give about 1 mA current through the specimen.

2　Results and Discussion

Figure 1 shows the original data measured by four-probe method for the three samples on a log (σT) $-1/T$ plot. For the sake of conciseness, all the error bars corresponding to each data point are omitted. The scatter of each data point is typically 2% $-$3% of the conductivity value. As can be seen, a small and gradual
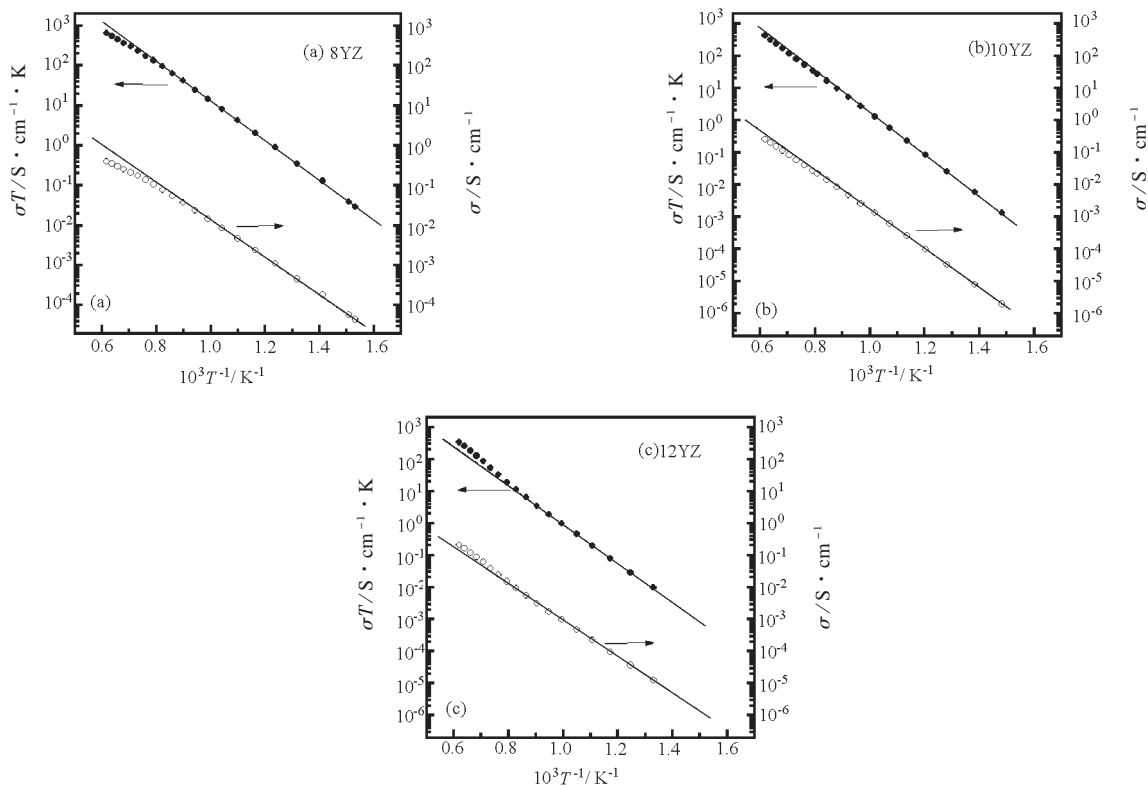

Fig. 1　Arrhenius plots of electrical conductivity of YSZ
(a) 8YZ, (b) 10YZ and (c) 12YZ

decrease in the slopes of the log $(\sigma T) - 1/T$ plots for samples 8YZ and 10YZ are observed as the temperature rises. This behavior is similar to those observed by other authors [2-4]. However, the reverse seems to be true for 12YZ: a small and gradual increase in the slope of log $(\sigma T) - 1/T$ plot is observed, as shown in Figure 1 (c). Such a phenomenon has not been reported previously.

Some authors have also represented the experimental results with an Arrhenius equation of another form [7,8]:

$$\sigma = \frac{A}{T}\exp\left(-\frac{E}{kT}\right) \qquad (2)$$

This expression differs in form from Equation (1) only in the pre-exponential term, which is considered to be temperature-dependent in Equation (1) and temperature-independent in Equation (2). In order to make a brief comparison between these two equations, the $\log \sigma - 1/T$ plots for the present materials are also given in Figure 1, respectively. As can be seen, the slope of the $\log \sigma - 1/T$ plot for each material also varies with temperature. This seems to say that both Equations (1) and (2) are not suitable for describing the temperature dependence of the ionic conductivity for the present materials.

It can be seen from Figure 1 that the deviation of the $\sigma - T$ relation predicted with the Arrhenius equation from the experimental results depends on the pre-determined form of the pre-exponential factor. For samples 8YZ and 10YZ, Equation (2) seems to fit the experimental data better than Equation (1), while Equation (1) seems to be better for sample 12YZ. Thus, it is reasonable to assume that the temperature dependence of ionic conductivity should be described with an Arrhenius equation of a general form

$$\sigma = A_0 T^m \exp\left(-\frac{E_0}{kT}\right) \qquad (3)$$

where A_0 and E_0 are temperature-independent constants, m is an adjustable parameter.

The corresponding best-fit values of parameters in Equation (3), A_0, E_0 and m, obtained by iterative regression minimizing total variance, are listed in Table

Table 1   Best-fit values of parameters in Equation (3) for 8YZ, 10YZ and 12YZ

Sample	$A_0/\text{S} \cdot \text{cm}^{-1} \cdot \text{K}^{-m}$	E_0/eV	m
8YZ	3.55×10^{15}	1.19	-3.8
10YZ	2.17×10^{8}	1.33	-1.8
12YZ	1.03×10^{-12}	0.79	4.3

1. The experimental results are then re-plotted in Figure 2, where the ordinate is $\log(\sigma T^{-m})$. Clearly, Equation (3) gives good fits to the experimental data.

Note that a modified Arrhenius equation with the same form of Equation (3) has been frequently employed in the field of physical chemistry to describe the temperature dependence of the reaction rate for some complex chemical reactions exhibiting non-linear Arrhenius behavior [9]. On the other hand, the ionic conduction in YSZ can also be considered as a complex chemistry reaction and the ionic conductivity, σ, which is proportional to the migration rate of the charge carrier, oxygen vacancies, can be treated as the reaction rate. Thus the physical meanings of the parameters included in Equation (3) can be analyzed based on a physical chemistry consideration.

According to the transition-state theory in physical chemistry, E_0 in the modified Arrhenius equation is considered to be a potential energy barrier for a given
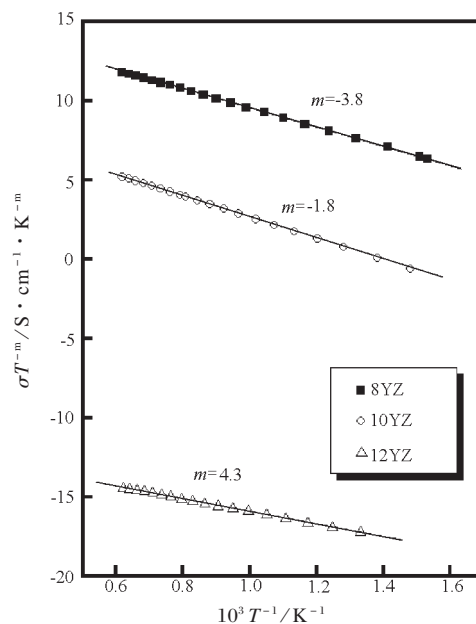

Fig. 2   Modified Arrhenius plot of electrical conductivity of the three samples

chemical reaction at standard states [9]. Similarly, we can define E_0 as a potential energy barrier for ionic conduction at 0 K.

It has been confirmed that the ionic conduction in ZrO_2-Y_2O_3 system is due to the migration of oxygen ions through the oxygen vacancy [1]. In general, there are at least two forms of oxygen vacancies in the ZrO_2 lattice, one being free and the other being associated. The potential energy barrier for the anionic jump through the associated-vacancy can be determined approximately as the sum of the disassociation energy, E_a, and the migration energy, E_m, of oxygen vacancy at 0 K; while the potential energy barrier for the anionic jump through free-vacancy is determined roughly only as E_m. For a given material, if we denote x as the ratio of associated-vacancy number to the total number of vacancy in the lattice, the potential energy barrier for ionic conduction can be calculated as

$$E_0 = x(E_a + E_m) + (1-x)E_m \qquad (4)$$

In a series of theoretical studies [10, 11] on the lattice defects in cubic zirconia, the migration energy of oxygen vacancy in YSZ was calculated to be 0.8 eV and the disassociation energies for the defect clusters $[Y_{Zr} - V_O]^{\cdot}$ and $[Y_{Zr} - V_O - Y_{Zr}]^{\times}$ were calculated to be 0.28 eV and 0.63 eV, respectively.

As discussed by Kilner and Steele [1], at low temperatures and low dopant concentrations, all the oxygen vacancies in YSZ may form clusters with dopant cations. So the potential energy barrier, E_0, for samples with lower dopant concentrations can be predicted theoretically to be between 1.08 (in case that all the vacancies are in the form of $[Y_{Zr} - V_O]^{\cdot}$) and 1.43 eV (in case that all the vacancies are in the form of $[Y_{Zr} - V_O - Y_{Zr}]^{\times}$) according to Equation (4). The regression analysis of the experimental results for the sample with lower dopant concentration studied here, 8YZ, gives $E_0 = 1.19$ eV, being in good agreement with the theoretically predicted results and providing a

sound support for the above analysis. Similar explanation may also be suitable for experimental result of the sample 10YZ. The larger E_0 for sample 10YZ compared with sample 8YZ can be attributed to the fact that higher dopant concentration would result in more associated oxygen vacancies in the form of $[Y_{Zr} - V_O - Y_{Zr}]^{\times}$.

The association and disassociation between oxygen vacancies and the dopant cations are in fact a dynamic equilibrium. Thus, for samples with much higher dopant concentrations such as 12YZ, some free oxygen vacancies may be expected to exist. The experimentally determined value of E_0 for sample 12YZ, 0.79 eV, is very close to the theoretically estimated value of defect migration energy, 0.8 eV, implying that no disassociation of associated defects occurs in this sample and the conductivity is mainly due to the migration of the free anion vacancies.

In continuation of the above analysis, a possible explanation for experimentally determined m-values listed in Table I can also be provided. In the transition-state theory [9], the parameter m in Equation (3) is considered as a measure of the complexity of the reactants. For sample 8YZ, the reactants are $[Y_{Zr} - V_O]^{\cdot}$ and $[Y_{Zr} - V_O - Y_{Zr}]^{\times}$. For sample 12YZ, the reactant is only free oxygen vacancy. So it seems not to be surprising that sample 8YZ has a large m while sample 12YZ has a small m.

Finally, a short comment should be made on the pre-exponential factor A_0. A difference of more than several ten orders was observed between the A_0-values obtained for the three samples examined here. At present, we are unable to propose a quantitative explanation for such a large difference and it is reasonable to believe that this difference may be attributed to several complex factors including the concentration of charge carriers, the jump attempt frequency and the association state of defects, etc.

3　　Concluding Remarks

In the present study, it was found that the modified Arrhenius equation, Equation（3）, may give a satisfactory description for the temperature-dependence of the measured ionic conductivity of YSZ. The activation energy for ionic conduction deduced from this equation is temperature independent and in good agreement with the theoretically predicted values. However, it should be pointed out that this analysis is still somewhat phenomenological. A further theoretical analysis, combined with detailed experimental observations, should be conducted in future.

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氧化锆基固体电解质材料与温度无关的离子电导活化能*

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摘要　　氧化锆（ZrO_2）基固体电解质材料的离子电导率随温度的变化关系呈现非线性 Arrhenius 特征;相应地,由经典的 Arrhenius 公式计算得到的电导活化能是一个与温度有关的参数. 本文通过对实验获得的几种 Y_2O_3 稳定立方 ZrO_2（YSZ）材料的电导率 – 温度关系的分析,对经典的 Arrhenius 公式进行了修正. 由修正后的 Arrhenius 公式计算得到的电导活化能是一个与温度无关的常数. 此外,还进一步借助于物理化学中的过渡状态理论,从材料离子导电机制出发对这一与温度无关的电导活化能的合理性进行了讨论,发现这一活化能在数值上与理论计算结果吻合得很好.

关键词:　离子电导率,　活化能,　固体电解质,　氧化锆,　非线性 Arrhenius 行为