

THERMODYNAMIC CORRELATION AMONG DEFECTS IN CERIA-ZIRCONIA SOLID SOLUTIONS

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The oxide ionic, electron and hole conductivity as well as the surface reaction rate in yttria stabilized zirconia, yttria doped ceria and their solid solutions $(Zr_{1-x}Ce_x)Y_{0.2}O_{1.9}$ ($x = 0.0 - 1.0$) have been discussed in terms of the thermodynamic properties and the observed physicochemical properties. Focus will be placed on the comparison between the macroscopic thermodynamic description and the microscopic defect chemical description. The microscopic thermodynamic properties have been derived from the phase diagram information together with emf and other thermodynamic properties. The microscopic properties were based on the ionic configuration of oxide vacancies reported in literatures. Fig. 1 indicates that the small deviation from the linearity can be interpreted in terms of the difference in the location of vacancy. From the macroscopic properties, the electron and the hole conductivity has been correlated with the chemical potential and its related concentration of cerium trivalent ions and the concentration of the hypothetical species, YOO, which is determined from the chemical potential of $YO_{1.5}$. The proton solubility has been correlated with the chemical potential of $YO_{1.5}$ in a similar manner as the hole conductivity, that is, chemical species, YOOH, was used to represent the protons in solid solutions. Fig. 2 compares the composition dependence of the proton solubility and hole conductivity together with the activity of $YO_{1.5}$ which was derived from the phase diagram calculation. The excellent agreement is obtained. The chemical potential of $YO_{1.5}$ was discussed in terms of the ionic configuration, that is, the oxide ion vacancy formation in the location of the nearest neighbor (NN) or the next nearest neighbor (NNN). In YSZ, the vacancy is formed around Zr^{4+} and is located at the NNN position from the dopant, Y^{3+} . In yttria doped ceria (YDC), the vacancy is formed around Ce^{4+} . This makes it possible to correlate among the proton solubility and the hole conductivity from the microscopic point of view. As shown in Fig. 3, proton solubility is small when the vacancy is formed in the NNN position and large when the vacancy is formed in the NN position. This is reasonable from the chemical considerations that water has strong affinity with the basic oxide, $YO_{1.5}$. The change in the ionic configuration of the oxide ion vacancies gives the explanation for the decrease in the ionic conductivity in the middle of the concentration. On the other hand, the maximum value in the surface reaction rate for the oxygen isotope exchange reaction in the middle can be ascribed partly to the electron behavior even in the oxidative atmosphere, although to understand fully the behavior of the surface reaction rate, more experimental data will be required on the effect of water vapor etc.

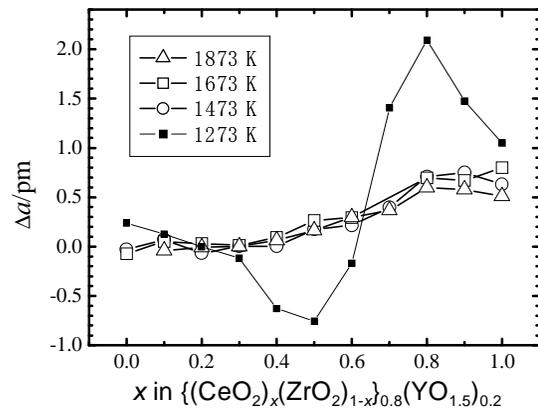


Fig. 1 The deviation of lattice constant from the linearity obtained in the ZrO_2 -rich region indicates that the lattice constant is related with the difference in the ionic configuration, that is, the location of vacancy around Y^{3+} or Zr^{4+} (or Ce^{4+}).

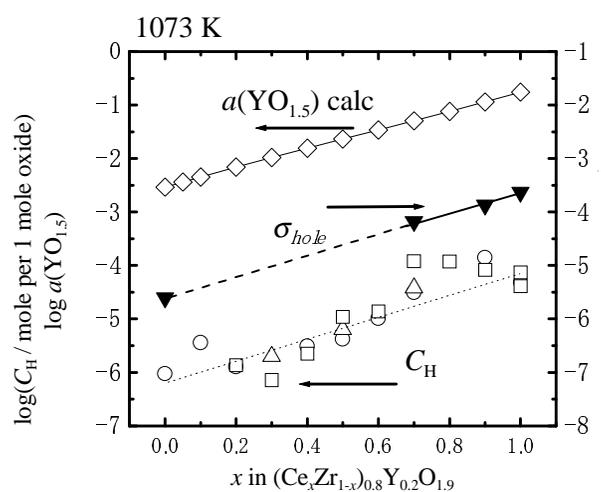


Fig. 2 Comparison of composition dependence among the observed proton solubility, hole conductivity and calculated activity of $YO_{1.5}$.

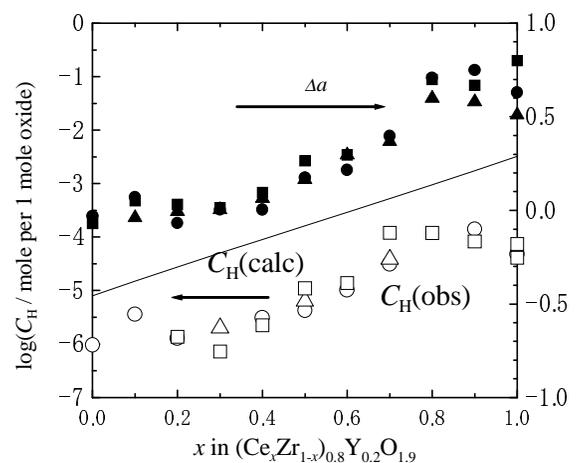


Fig. 3 The proton solubility in solid solutions and its comparison with the deviation of lattice constants from the linearity in the ZrO_2 -rich region (see Fig. 1). The solid line is evaluated from the calculated $\mu(YO_{1.5})$ together with $\mu^q(YOOH)$ in the Raoult approximation.