Preparation Techniques and Ionic Transport Properties of Ceria-based Electrolytes

Guangshe Li*, R. L. Smith Jr., H. Inomata, K. Arai

Research Center of Supercritical Fluid Technology, Department of Chemical Engineering, Tohoku University, Sendai 980-8579, Japan

INTRODUCTION

Ceria based electrolytes have many potential applications due to their relatively high ionic conductivity, which depends greatly on microstructure and valence characteristics. These characteristics, however, are strongly influenced by the preparation method. This paper reports on the preparation techniques of ceria-based electrolytes $Ce_{1-x}M_xO_{2-\delta}$ (M=Bi, Eu, Tb and Fe) and their ionic transport properties.

EXPERIMENTAL

Samples were loaded into teflon-lined autoclaves (ca. 17 cc) and heated to reaction conditions in a sand bath. Samples treated at supercritical conditions were loaded into smaller (10 cc) non-lined autoclaves. Samples contacted at high temperatures and pressures used a belt-type apparatus.

DISCUSSION

There are many challenges related to the preparation and microstructural/property control for ceria based electrolytes. $Ce_{1-x}Bi_xO_{2-\delta}$ solid solutions with a larger dopant Bi^{3+} cannot be prepared by solid state reactions [1]. For $Ce_{1-x}RE_xO_{2-\delta}$ with rare earth (RE) ions having ionic size close to Ce^{4+}, it is very difficult to stabilize pure trivalent dopants RE^{3+} in lattice [2]. With decreasing ionic size of RE^{3+}, the ionic conductivity decreases gradually [3]. However, from the solid state reaction systems, there is no solution relationship found between CeO_2 and Fe_2O_3 probably due to the much smaller dopants Fe^{3+} [4]. In this work, we used hydrothermal and supercritical water routes as well as high temperatures and pressures to prepare typical solid solutions $Ce_{1-x}M_xO_{2-\delta}$ (M=Bi, Eu, Tb and Fe). The results showed that for solid solutions $Ce_{1-x}Bi_xO_{2-\delta}$, Bi^{3+} ions had an extremely high solubility in ceria by hydrothermal conditions. The cell parameter increased linearly with the dopant content [5]. For $Ce_{1-x}RE_xO_{2-\delta}$ solid solutions, pure trivalent rare earth ions Eu^{3+} and Tb^{3+} could be stabilized in the fluorite lattice at high temperatures and pressures [6], the solid solubility was relatively low and the cell parameter varied non-linearly with dopant content. Solid solutions $Ce_{1-x}Fe_xO_{2-\delta}$ were prepared by supercritical water route. Cell parameter decreased continuously with the dopants Fe^{3+}, as shown in Fig. 1. The impedance spectra of $Ce_{1-x}Fe_xO_{2-\delta}$ solid solutions (Fig. 2) gave distinct grain boundary and bulk conduction. The relationship between lattice parameters and dopant content and the oxide ionic transport properties for these solid solutions can be explained in terms of the chemical nature of dopant ions, cation substitutions as well as the variations of the relative content of oxygen vacancy Vo and defect associations. The defect associations $\{Ce_{Ce}'Vo\}$ are probably a consequence of reduction equilibrium, Ce^{4+}/Ce^{3+} within the solid solutions containing trivalent dopants larger than Ce^{4+}, while the reduction equilibrium was minimized by the smaller dopants Fe^{3+}, as confirmed by EPR measurements.

CONCLUSIONS

Ceria-based electrolytes $Ce_{1-x}M_xO_{2-\delta}$ (M=Bi, Eu, Tb and Fe) could be prepared by hydrothermal, supercritical and high pressure techniques. The doping of trivalent ions with a large ionic size difference provides a method for studying the relationship between microstructure and conduction mechanism of ceria based electrolytes.

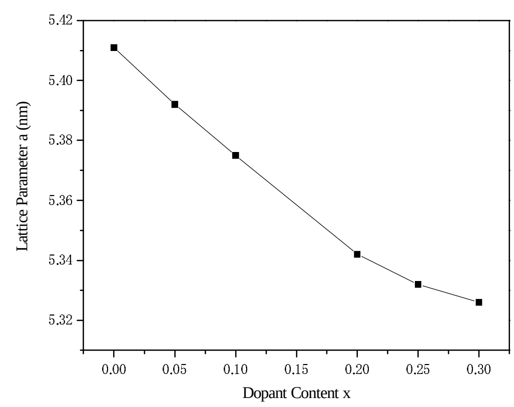

Fig. 1 Relationship between cell parameter and dopant content for $Ce_{1-x}Fe_xO_{2-\delta}$ solid solutions.

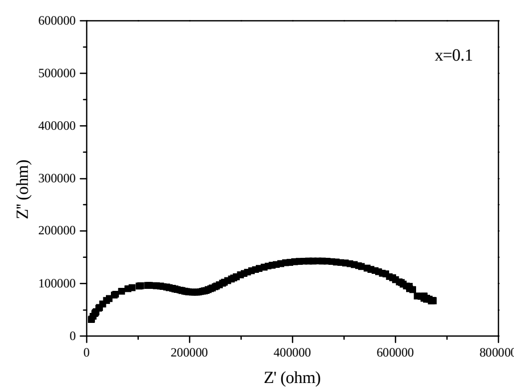

Fig. 2 Impedance spectrum for typical sample of $Ce_{0.9}Fe_{0.1}O_{2-\delta}$ recorded at 450 °C. The distinct grain boundary (low frequency arc) and bulk (high frequency) effects are shown.

REFERENCES

[1] X. L. Chen and W. J. Eysel, J. Solid State Chem., **127**, 128 (1996).
[2] P. Shuk, M. Greenblatt and M. Croft, Chem. Mater., **11**, 473 (1999).
[3] G. B. Balazs and R. S. Glass, Solid State Ionics, **76**, 155 (1995).
[4] M. Hrovat, J. Holc, S. Bernik, et al., Mater. Res. Bull., **33**, 1175 (1998).
[5] G. Li, Y. Mao, L. Li, et al., Chem. Mater., **11**, 1259 (1999).
[6] L. Li, G. Li, Y. Che, et al., Chem. Mater., **12**, 2567 (2000).

----

* corresponding author.
E-mail: guangshe@scf.che.tohoku.ac.jp
Phone: 81-22-217-7282; Fax: 81-22-217-7293.