Effects of Redox History on Reducibility, Structural and Electrical Properties of Ce_xZr_{1-x}O₂ for Its Application as SOFC Anode Electrocatalyst

Stefano Desinan, Marta Boaro, Chiara Abate, Matteo Ferluga, Carla de Leitenburg and <u>Alessandro Trovarelli</u>¹* ¹Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, I-33100 Udine (Italy) *trovarelli@uniud.it

Introduction

The well known catalytic properties and the oxygen storage capacity of ceriazirconia mixed oxide ($Ce_xZr_{1-x}O_2$) can be of interest in fuel cell applications, especially in the view of its use as a component of SOFC anodes [1]. Several studies have pointed out the influence of redox history on structural properties of such material, and the correlation between cation sublattice ordering and redox properties [2]. However, the effect of exposure to redox treatments on the electrical conductivity of ceria-zirconia has been seldom studied [3,4], even though it is an important aspect to be considered in the view of its application to SOFCs. The aim of this work is to investigate in parallel how structure, redox properties and conductivity of ceria-zirconia modify upon redox treatments at different temperatures.

Materials and Methods

 $Ce_{0.5}Zr_{0.5}O_2$ was synthesized by a solution-combustion method with citric acid as a fuel and nitrate salts as precursors. Pellet samples of such material were prepared, obtaining either a single phase or the biphasic thermodynamic mixture, depending on the sintering temperature. Their reduction was monitored by TPR (Temperature Programmed Reduction), an approach seldom employed on pellet samples. The samples were reduced at different temperatures (1123-1373 K) in a H₂(5%)/Ar flow, then reoxidized in oxygen flow at 873 K. The reduction-reoxidation cycle was repeated several times for each sample. The conductivity was measured by EIS (electrochemical impedance spectroscopy) in oxidizing and reducing atmospheres. Structural data were collected by XRD (X-ray powder diffraction).

Results and Discussion

 $Ce_{0.5}Zr_{0.5}O_2$ is fully reduced to $Ce_2Zr_2O_7$ ($Ce^{4+}\rightarrow Ce^{3+}$) by the treatment under $H_2(5\%)/Ar$ flow at 1373 K, and the ordered cubic κ -phase [5] is formed on reoxidation (Figure 1); a decrease in the amount of the side phase, when present, is observed upon redox cycling. After the first redox cycle, the TPR reduction peak shifts to lower temperature by more than 400 K and the reduction is completed below 1273 K, while the untreated pellet is fully reduced only above 1373 K. The reduction profiles of both the monophasic and the biphasic materials after the redox cycles show two peaks, which are an indication of the presence of two paths of reduction (Figure 2). A significant reduction enhancement is also observed upon cycling at a temperature as low as 1123 K, despite the absence of evidence of cation sublattice rearrangement.

Such changes in the redox behavior are accompanied by a decrease in the activation energy of the electrical conductivity.



Figure 1. Structural evolution of single-phase $Ce_{0.5}Zr_{0.5}O_2$ upon redox cycling (reduction: 1373 K, reoxidation at 873 K). XRD patterns: A) Starting $Ce_{0.5}Zr_{0.5}O_2$ B) after 1st cycle C) after 2nd cycle D) after 3rd cycle. (\blacksquare) tetragonal $Ce_{0.5}Zr_{0.5}O_2$; (∇) $Ce_2Zr_2O_8$ (κ -phase).



Figure 2. TPR profiles in subsequent redox cycles on single-phase $Ce_{0.5}Zr_{0.5}O_2$ (reduction: 1373 K, reoxidation at 873 K). A) 1st cycle B) 2nd cycle C) 3rd cycle.

Significance

The study compares structural, chemical and electrical properties of ceria-zirconia as they are affected by redox history in a time/temperature screening, providing fundamental data in the view of its application as a fuel cell electrocatalyst.

References

- 1. Ahn, K., He, H., Vohs, J.M., and Gorte, R.J. Electrochem Solid St 8, A414 (2005).
- 2. Yeste, M.P., Hernandez, J.C., Bernal, S., Blanco, G., Calvino, J.J., Perez-Omil, J.A., and Pintado, J.M. *Chem Mater* 18, 2750 (2006).
- 3. Izu, N., Kishimoto, H., Omata, T., and Otsuka-Yao-Matsuo, S. J Solid State Chem 151, 253 (2000).
- 4. Hui, Z., Guillet, N., Valdivieso, F., and Pijolat, M. Solid State Ionics 160, 317 (2003).
- Otsuka-Yao-Matsuo, S., Omata, T., Izu, N., and Kishimoto, H. J Solid State Chem 138, 47 (1998).