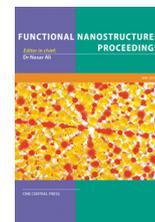


Available online at www.onecentralpress.com

One Central Press

proceedings webpage: www.onecentralpress.com/functional-nanostructures-proceedings

Synthesis of core-shell structures for advanced ceramic nanocomposite fuel cells

Eleonora G. Hochreiner¹, M. Imran Asghar^{1,*} and Peter D. Lund¹

¹New Energy Technologies Group, Department of Applied Physics, School of Science, Aalto University, P. O. Box 15100, FI-00076, Finland.

*corresponding author

ABSTRACT

Ceramic-carbonate nanocomposite fuel cells have been found to show improved ionic conductivity at lower temperatures due to efficient multipolar ion transport. We studied the impact of different doped cerium oxides on the ionic conductivity in nanocomposite electrolytes. Therefore, three doped cerium oxides have been synthesized using different synthesis approaches. They were mixed with a eutectic (NaLiK)₂CO₃-phase (30 wt%), analyzed and their electrochemical performances have been compared to a nanocomposite using Al₂O₃ as skeleton. It has been found that all three cerium oxides showed high ionic conductivity at low temperatures (>0.1 S/cm at 500 °C), whereas Al₂O₃ showed no significant ionic conductivity (0.002 S/cm at 500 °C), despite the carbonate phase. At 600 °C, the single-doped ceria (Sm as dopant) showed the highest conductivity (0.55 S/cm), followed by CaSm-doped ceria (0.28 S/cm).

I. INTRODUCTION

Solid oxide fuel cells (SOFC) are a promising fuel cell technology that still faces several challenges because of their high operating temperatures (about 800-1000 °C). To overcome this issue, new materials are needed that allow lower operating temperatures (400-600 °C) while maintaining the performance. One possible approach are ceramic-carbonate nanocomposite fuel cells (CNFC) that generally consist of doped ceria and an alkali carbonate mixture (mostly eutectic). They allow high ionic conductivity above the eutectic temperature of the carbonate phase due to complex multipolar ionic conduction [1]. In this work, three different doped cerium oxides with promising electrochemical performances (Sm-doped ceria (SDC), CaSm-doped ceria and GdSm-doped ceria) were synthesized using distinct synthesis methods and mixed with a eutectic mixture of (NaLiK)₂CO₃. EIS-measurements determined the ionic conductivity of the materials. As a reference, Al₂O₃ as an insulating support material for the carbonate phase was used.

II. EXPERIMENTAL

Synthesis. Sm-doped ceria (15% dopant) was prepared using the Pechini method [2]. Ce(NO₃)₃·6H₂O and Sm(NO₃)₃·6H₂O were dissolved in de-ionic water. Stirring was continued after adding citric acid and the pH of the reaction mixture was adjusted to 10 using NH₄OH. Finally, an aqueous solution of Na₂CO₃, Li₂CO₃, K₂CO₃ and ethylene glycol was added and stirring was proceeded for 15 min. The solvent was evaporated using a freeze-dryer. After grinding the remaining brown slurry, the obtained powder was sintered at 800 °C for 1.5 h. This resulted in a ceria-carbonate nanocomposite electrolyte (70 w% SDC and 30 w% NLK).

Two co-doped cerium oxides were prepared using a coprecipitation method [3] and a sol gel process [4]. CaSm-CeO₂ (20% dopant) was synthesized by dissolving Ce(NO₃)₃·6H₂O, Ca(NO₃)₂·4H₂O and Sm(NO₃)₃·6H₂O in de-ionic water and adding an aqueous solution of Na₂CO₃ dropwise. The mixture was stirred at room temperature for 30 min, filtrated and dried at 80 °C. After grinding the white powder, it was sintered at 800 °C for 4 h.

GdSm-CeO₂ (15% dopant) was prepared by dissolving Ce(NO₃)₃·6H₂O, Gd(NO₃)₃·6H₂O and Sm(NO₃)₃·6H₂O in de-ionic water. An aqueous solution of citric acid and poly ethylene glycol (CA : PEG = 60) was added slowly. The reaction mixture was stirred at 80 °C until a colorless gel formed. This gel was further dried in the oven at

105 °C, giving a fragile foam that was turned into a fine powder by grinding. Sintering was performed at 700 °C for 4 h.

To obtain co-doped ceria-carbonate nanocomposite electrolytes, Na_2CO_3 , Li_2CO_3 and K_2CO_3 were mixed in their eutectic composition ($\text{Na}_2\text{CO}_3 : \text{Li}_2\text{CO}_3 : \text{K}_2\text{CO}_3 = 33.4\% : 32.1\% : 34.5\%$) and added to the cerium oxides in a ratio of oxide : NLK-carbonate = 70 wt% : 30 wt%. Each mixture was homogenized by ball milling at 200 rpm for 1 h and ground before analysis. This procedure was also performed with Al_2O_3 (<50 nm powder) to get the reference sample.

Material Characterization. The crystal structures of the materials were analyzed using an X-ray diffraction unit (PANalytical X'Pert PRO MPD). A scanning electron microscope (SEM, Zeiss Sigma VP) was utilized to examine the morphological properties of the electrolytes.

EIS-Measurements. For the electrochemical measurements, pellets have been prepared by filling 0.7 g powder in a 13-mm-dye and applying 250 MPa for 2 min using a press machine (Carver Inc.). These pellets were sintered at 590 °C for 4 h. To provide a current collector, gold paste (terpineol as solvent) was applied on one side of the pellets and sintering was repeated (500 °C for 20 min). The procedure was conducted likewise for the other side of the pellets. The ionic conductivity of the electrolyte materials was determined by using a Probostat fuel cell setup (NorECs).

III. RESULTS AND DISCUSSION

Powder-XRD measurements of the powders before and after the final sintering step confirmed a successful formation of cerium oxide. SEM images show the nanostructure of the synthesized materials (Figure 2). The nanocomposite structure is built up by nanosized grains (ceria) and the homogeneous sand-like structure of the carbonate-phase as in the case of CaSm-doped ceria. However, the nanocomposite materials using SDC and GdSm-doped ceria showed besides the ceria nanoparticles more crystalline, needle-like structures that might be the carbonate phase.

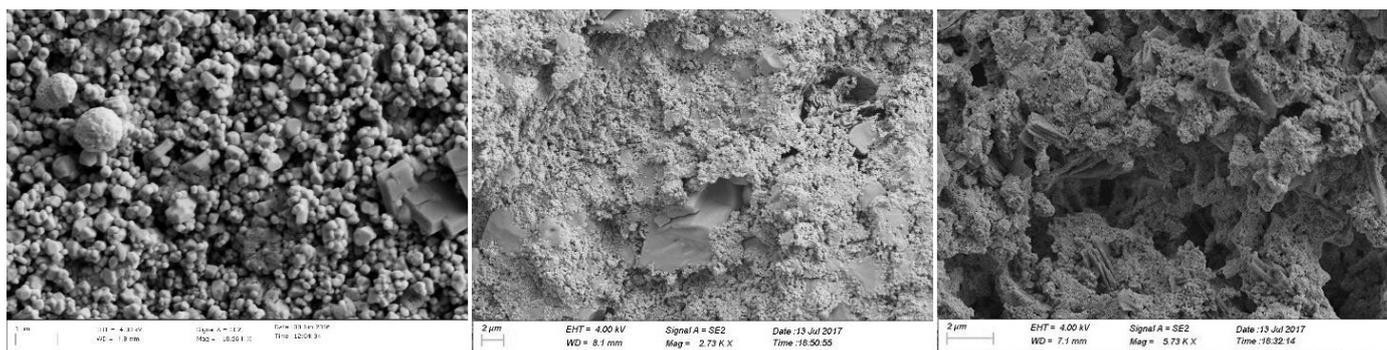


Figure 1 SEM images of ceria-carbonate nanocomposite electrolyte materials (left: SDC, middle: CaSm-doped ceria, right: GdSm-doped ceria).

EIS-measurements provided information about the ionic conductivity of the materials at different temperatures. The ionic conductivities are shown in an Arrhenius plot in Figure 2. Except for Al_2O_3 , all electrolyte materials show the same sudden jump at around 400 °C. This is due to the melting of the eutectic carbonate phase that results in a drastic increase of the ionic conductivity. At the requested operating temperature (600 °C), all three cerium oxides show good ionic conductivities (SDC: 0.55 S/cm, CaSm- CeO_2 : 0.28 S/cm, GdSm- CeO_2 : 0.18 S/cm). The required ionic conductivity of > 0.1 S/cm is also still achieved at 500 °C (SDC: 0.34 S/cm, CaSm- CeO_2 : 0.20 S/cm, GdSm- CeO_2 : 0.12 S/cm). However, the nanocomposite using Al_2O_3 as skeleton showed only little ionic conductivity (0.002 S/cm at 500 °C, 0.005 S/cm at 600 °C), suggesting that the multipolar ionic conduction only works in combination with an ionic conductive material such as ceria. Furthermore, the activation energy of the materials at high temperatures (> 400 °C) was calculated. The nanocomposite with CaSm- CeO_2 showed the smallest activation energy (21.51 kJ/mol), followed by GdSm- CeO_2 (27.61 kJ/mol) and SDC (34.41 kJ/mol). The nanocomposite with Al_2O_3 showed a significant higher activation energy (51.09 kJ/mol).

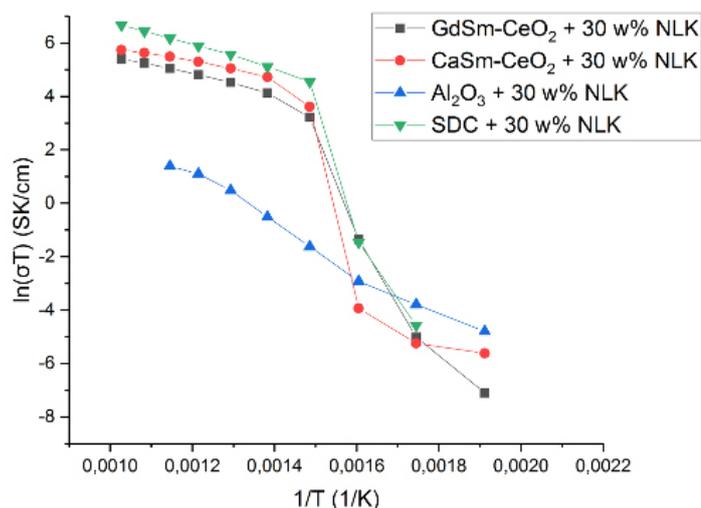


Figure 2 Arrhenius plot showing the temperature dependence (T) of the ionic conductivities (σ).

IV. CONCLUSIONS

The preparation of nanostructured electrolyte materials by different synthesis methods was successful. All the prepared ceramic-carbonate nanocomposites (except Al_2O_3) showed high ionic conductivity at low temperature (> 0.1 S/cm at 500 °C). The reference sample with Al_2O_3 showed that an ionic conductor such as ceria is needed in combination with the carbonate phase to get high ionic conductivity due to multipolar ionic conduction. Further work is needed to study the impact of the difference in the addition of the carbonate phase to the cerium oxide. It might be a reason for the high ionic conductivity of the SDC (preparation by the Pechini method) and could have potential to further increase the ionic conductivity in co-doped ceria.

This work made use of the premises from Aalto University Nanomicroscopy Center (Aalto-NMC). We thank the Academy of Finland (Grant No. 13282962 and 13279204), the Aalto Science Institute internship program (ASCI) and Erasmus+ for their financial support.

V. REFERENCES

- [1] J. Patakangas, Y. Jing, M. I. Asghar, P. D. Lund, Investigation of LiNiCuZn-oxide electrodes prepared by different methods: Synthesis, characterization and properties for ceramic carbonate composite fuel cells, *Int. J. Hydrogen Energy*. 41 (2016) 7609–7613.
- [2] M. I. Asghar, M. Heikkilä, P. D. Lund, Advanced low-temperature ceramic nanocomposite fuel cells using ultra high ionic conductivity electrolytes synthesized through freeze-dried method and solid-route, *Material Today Energy*, 2017.
- [3] Raza, R., Wang, X., Ma, Y., Zhu, B., Study on calcium and samarium co-doped ceria based nanocomposite electrolytes, *Journal of Power Sources* 195(19) (2010) 6491-6495.
- [4] Wang, F. Y., Chen, S., Cheng, S., Gd^{3+} and Sm^{3+} co-doped ceria based electrolytes for intermediate temperature solid oxide fuel cells, *Electrochemistry communications*, 6(8) (2004) 743-746.