17th International Conference on Inorganic Membranes
New Frontiers for Inorganic Membranes
July 1 - 5, 2024
Oceania Convention Center - Florianópolis - Brasil

$Ba(Zr,Ce,Y)O_{3-\delta}$ proton-conducting materials: manufacture, performance and stability

W. Zhou[a,*], J. Malzbender[a], J. L. Wolter[a], W. Deibert[a], O. Guillon[a], J. M. Serra[b], C. Segarra[b], , A. Dos Santos[b], L. Almar[b], D. Catalán-Martínez[b], M. Fabuel[b], S. Escolástico[b], W. A. Meulenberg[a,c]
[a] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK), 52425 Jülich, Germany
[b] Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Av. Los Naranjos, s/n, 46022 Valencia, Spain
[c] University of Twente, Faculty of Science and Technology, Inorganic Membranes, P.O. Box 217, 7500 AE, Enschede, the Netherlands

[*] w.zhou@fz-juelich.de

Abstract

Proton-conducting membranes have great potential for applications in proton conducting membrane reactors for the production of commodity chemicals or synthetic fuels as well as for use in solid oxide fuel cells [1-3]. $Ba(Zr,Ce,Y)O_{3-\delta}$ perovskite oxides are of particular interest due to its proven high proton conductivity and good chemical stability [4]. In this work, fabrication of $Ba(Zr,Ce,Y)O_{3-\delta}$ samples, including thick pellet, thin tape-cast and multi-layered half-cell, were studied to prevent the typical challenges like warping, cracking and delaminating [5]. Materials with different stoichiometries were investigated, on their conductivity and chemical stability against NH_3 and H_2O, to select the most promised candidate for future compact membrane reactor. Mechanical behaviors including elastic modulus, hardness, fracture toughness and creep were investigated to warrant long-term structural stability [6-8]. Dual-phase material micro-pillar splitting behavior was for the first time reported and interpreted according to the post-test slice-by-slice FIB milling for in detail microstructure observation (Fig. 1). Thus, a systematic investigation on $Ba(Zr,Ce,Y)O_{3-\delta}$ materials was carried out to pave the road towards widespread application of proton-conducting membranes.

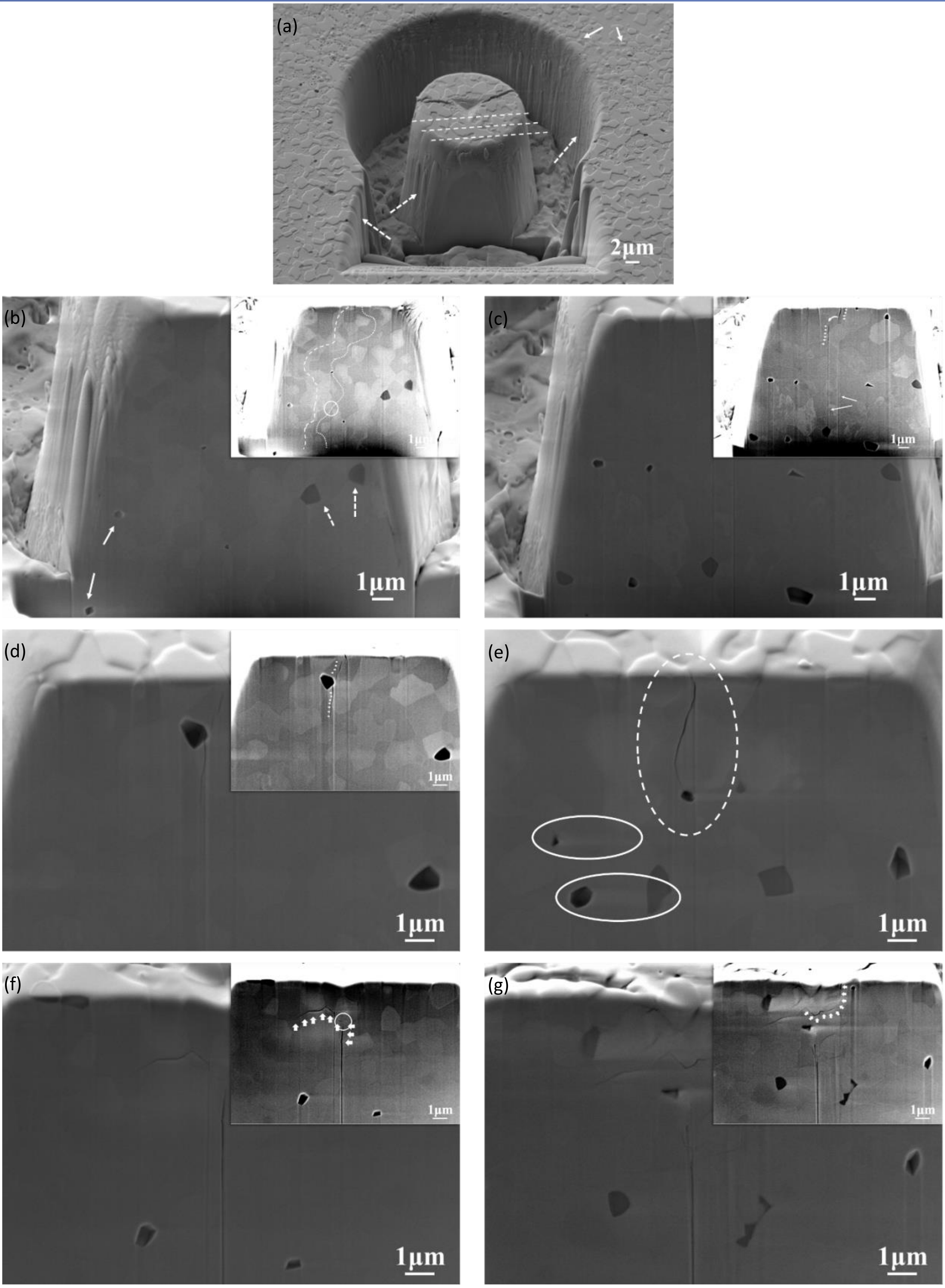

Fig. 1 Slice-by-slice FIB milling of pillar with one kink. (a) Firstly, a window was milled. The solid arrows mark blister-like morphologies. The curtain artifacts, straight down to the pillar bottom, is marked by dashed arrows. Further FIB milling was performed to follow the direction of the 3rd crack, as marked by dashed lines. (b) The solid arrows indicate pores, and the dashed arrows mark Ni exsolution. The dashed and the dotted line mark the individual phases' connections of GDC15 and BCZ20Y15, respectively. The circle marked region in the line demonstrates a path although narrow but indeed connected in spatial. (c) The long arrows mark the FIB curtaining artifact. The short arrows mark that crack propagation stops at GDC15, and then continues to propagate in BCZ20Y15, as

marked by the curved arrow. (d) The crack propagates through BCZ20Y15 towards pores and deflects after encountering the pores (marked by the short arrows). (e) Crack deflection due to pores (dashed circle). Fuzzy bands, marked by the solid circles, due to charging and drift. (f) The median and radial cracks are marked by short arrows. The location of the initial crack nucleation was marked by a circle. (g) The plastic zone, marked by the short arrows.

Acknowledgements: this work was supported by “ALL-IN Zero”, Project No. 101069888 (EU project).

References

[1] K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara, Protonic conduction in Zr-substituted BaCeO3, Solid State Ion. 138(1-2) (2000) 91-98.

[2] N. Radenahmad, A. Afif, P.I. Petra, S.M. Rahman, S.-G. Eriksson, A.K. Azad, Proton-conducting electrolytes for direct methanol and direct urea fuel cells–A state-of-the-art review, Renew. Sustain. Energy Rev. 57 (2016) 1347-1358.

[3] K. Kreuer, Proton-conducting oxides, Annu. Rev. Mater. Res. 33(1) (2003) 333-359.

[4] E. Rebollo, C. Mortalo, S. Escolástico, S. Boldrini, S. Barison, J.M. Serra, M. Fabrizio, Exceptional hydrogen permeation of all-ceramic composite robust membranes based on $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ and Y- or Gd-doped ceria, Energy Environ. 8(12) (2015) 3675-3686.

[5] K. Leonard, W. Deibert, M. E. Ivanova, W. A. Meulenberg, T. Ishihara, H. Matsumoto. Processing ceramic proton conductor membranes for use in steam electrolysis. Membranes, 10(11) (2020), 339.

[6] W. Zhou, J. Malzbender, F. Zeng, W. Deibert, O. Guillon, R. Schwaiger, W.A. Meulenberg, Mechanical properties of $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$ proton-conducting material determined using different nanoindentation methods, J. Eur. Ceram. Soc. 40(15) (2020) 5653-5661.

[7] W. Zhou, J. Malzbender, W. Deibert, O. Guillon, R. Schwaiger, A. Nijmeijer, W.A. Meulenberg, High temperature compressive creep behavior of $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$ in air and 4% H_2/Ar, J. Am. Ceram. Soc. 104(6) (2021) 2730-2740.

[8] W. Zhou, J. Malzbender, F. Zeng, W. Deibert, L. Winnubst, A. Nijmeijer, O. Guillon, R. Schwaiger, W.A. Meulenberg, Mechanical properties of $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$–$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ dual-phase proton-conducting material with emphasis on micro-pillar splitting, J. Eur. Ceram. Soc. 42(9) (2022) 3948-3956.