Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ChemComm

COMMUNICATION

Enhanced stability of Zr-doped Ba(CeTb)O₃₋δ-Ni cermet membrane for hydrogen separation

Yanying Wei [a,b,]*, Jian Xue [a], Wei Fang [a], Yan Chen [b], Haihui Wang [b,c,]*, Jürgen Caro [a]

A mixed protonic and electronic conductor material BaCe₀.₈₅Tb₀.₀₅Zr₀.₁O₃₋δ (BCTZ) is prepared and a Ni-BCTZ cermet membrane is synthesized for hydrogen separation. Stable hydrogen permeation fluxes can be obtained over 100 h through the Ni-BCTZ membrane in both dry and humid conditions, which exhibits an excellent stability compared with Ni-BaCe₀.₉₅Tb₀.₀₅O₃₋δ membrane due to the Zr doping.

High-temperature mixed protonic and electronic conductors (HT-MPECs)[1,2] have attracted increasingly interest due to their wide potential applications as hydrogen sensors, hydrogen pumps, hydrogen permeable membranes for gas separation[3-9] and catalytic membrane reactors,[10] solid oxide fuel cells (SOFCs)[11-14] etc. since Iwahara et al.[15] reported that the ceramics based on strontium cerates show relatively high protonic conductivities. For these applications, the HT-MPECs should not only exhibit high protonic and electronic conductivities but also good chemical stability and phase structure stability under the operation conditions. However, for most doped perovskite oxides, such as BaCeO₃, BaZrO₃, SrCeO₃ and SrZrO₃ etc., their relatively low electronic conductivity is the bottle neck for hydrogen transportation.[16] Therefore, in order to increase the electronic conductivity, a metal phase (usually nickel) can be added to the perovskite oxide to form a cermet (ceramic-metal) composite, which shows much better hydrogen permeability, such as Ni-Ba(Zr₀.₈₋ₓCeₓY₀.₂)O₃₋δ,[17,18,19] Ni-SrCeO₃₋δ,[20] Ni-Ba(Zr₀.₇Pr₀.₁Y₀.₂)O₃₋δ.[21]

Till now, the highest hydrogen permeation flux up to 0.914 ml/min·cm² was obtained at 850 °C through the Ni-BaCe₀.₉₅Tb₀.₀₅O₃₋δ (Ni-BCT) asymmetric cermet membrane with a 90 μm dense layer on a porous substrate reported by Meng et al.[22] Unfortunately, the hydrogen flux through the Ni-BCT membrane declined by about 50% after 75 h operation at 800 °C due to the phase segregation.[22] Therefore, materials with both

high hydrogen permeability and adequate stability are required to be developed. As it is known, the doped BaZrO₃ exhibits a much higher stability compared with the doped BaCeO₃, and the two oxides can form easily a solid solution.[18,19] It is expected that replacing some Ce with Zr in the Ni-BCT system may enhance its phase structure stability due to the constant valence state of Zr⁴⁺. Therefore, in the present study, the hydrogen permeability and the phase structure stability of Ni-BaCe₀.₈₅Tb₀.₀₅Zr₀.₁O₃₋δ (Ni-BCTZ, 50:50 wt %) are investigated. It is found that the Ni-BCTZ cermet membrane can be steadily operated in both dry and humid reducing atmospheres for hydrogen permeation for over 100 h at 800 °C, which demonstrates its excellent stability compared with Ni-BCT.
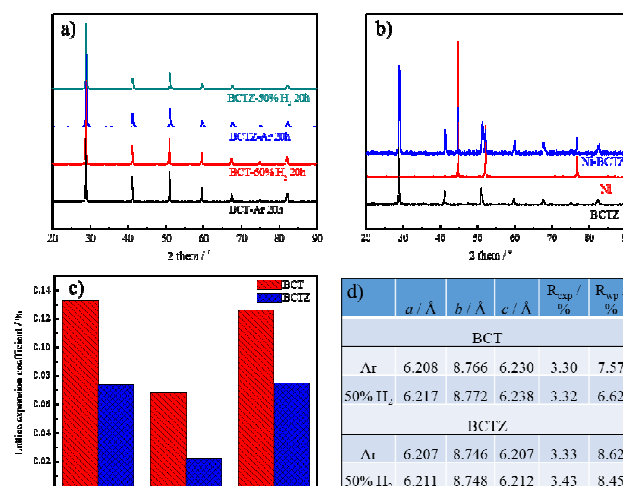

Figure 1. a) XRD patterns of BCT and BCTZ powder after treatment in Ar and 50% H₂-50% Ar atmospheres; b) XRD patterns of the as-calcined Ni-BCTZ cermet membrane; c) Lattice expansion coefficient of BCT and BCTZ; d) Lattice parameters of BCT and BCTZ after treatment in different atmospheres calculated from Rietveld refinements.

Firstly, both of the BCT and BCTZ powders were treated in Ar and 50% H_2-50% Ar atmospheres for 20 h at 800 ^{o}C, respectively. Although no obvious change can be found between the fresh and treated powders, and all the powders exhibit an orthorhombic perovskite structure (Figure 1a), the lattice parameters (a, b, c) calculated from the Rietveld refinements (Figure 1d) differ greatly when exposed to different atmospheres which can be mainly attributed to the reduction of Ce^{4+} as well as the formation of oxygen vacancies. The lattice expansion coefficients, α_i, which can be described as follows,

$$\alpha_i = (i_{reducing} - i_{inert}) / i_{inert} * 100\%$$

i stands for the lattice parameters of a, b, c in the three crystallographic directions, the subscript of "reducing" and "inert" stands for the 50% H_2-50% Ar and Ar atmospheres, respectively. As shown in Figure 1c, it is noticed that Zr-doping decreases the lattice expansion coefficient of BCT significantly for all three crystallographic directions. TG and H_2-TPR results (Supporting Information, Figures S1 and S2) also prove that Zr-doping has enhanced the phase structure stability. As shown in Figure 1b for the XRD patterns of the composite Ni-BCTZ membrane, all diffraction peaks can be assigned to either BCTZ or metallic Ni and no new crystalline phases appears, which indicates that no reaction took place between the BCTZ oxide and the metallic nickel during the membrane preparation and the good stability and compatibility between the two phases. BCTZ shows the body-centered orthorhombic phase with space group of Imma (74). The lattice parameters of a, b, c were calculated from the Rietveld refinement to be 6.206 Å, 8.747 Å and 6.208 Å, respectively, with the R_{exp} and R_{wp} of 3.32% and 9.26%.

The microstructures of the Ni-BCTZ membrane, as well as the hydrogen permeation test under different conditions, are shown in Figure S3 to S6. The hydrogen permeation flux increases a little with wet feed gas due to the increase of protonic conductivity. This effect can be ascribed to the hydration of the membrane that allows the formation of two protonated oxygen atoms (lattice or interstitial oxygens), which are the essential charge carriers involved in hydrogen transport.[23,24] The hydrogen flux jumps sharply with wet sweep gas, because in this case some part of the hydrogen comes from the thermal water

Figure 2. a) Hydrogen permeation flux as a function of time with 50% H_2 in feed gas at 800 ^{o}C under dry condition. Ni-BCTZ: 0.5 mm symmetric dense membrane, Ni-BCT: asymmetric membrane with 90 μm dense layer, data of Meng et al.[22] (reproduction permitted with Elsevier License); b) Long term stability test of Ni-BCTZ membrane under humid reducing atmosphere (containing 0.03 atm water steam) at 800 ^{o}C.

splitting.[24]

Much attention has been paid in the long term stability of the Ni-BCTZ membrane for hydrogen separation. The measurement was carried out at 800 ^{o}C using 50% H_2-50% He as the feed gas in both dry and humid conditions. As shown in Figure 2a under dry condition, the hydrogen permeation flux through the Ni-BCTZ membrane with a thickness of 0.5 mm keeps stable around 0.17 ml/min·cm^2 for over 100 h and no decline with time can be found. However, Meng[22] reported that the hydrogen permeation flux through the Ni-BCT membrane decreases from the initial 0.26 ml/min·cm^2 to 0.126 ml/min·cm^2 after 75 h operation. At the beginning of permeation, the hydrogen permeation flux through our Ni-BCTZ membrane is lower than that through the Ni-BCT membrane. There are two reasons for this experimental finding. On the one hand, the substitution of Zr for Ce in the BCT material reduces its protonic conductivity to some extent,[25-27] just like doping Zr into $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ gives lower conductivity, and Zr doping reduces the hydrogen permeation flux.[26] Therefore, we only doped 10 mol % Zr in Ni-BCT aiming to keep its hydrogen permeation flux on a high level. And even so, the hydrogen permeation flux through our Ni-BCTZ membrane is still much higher than that through many other
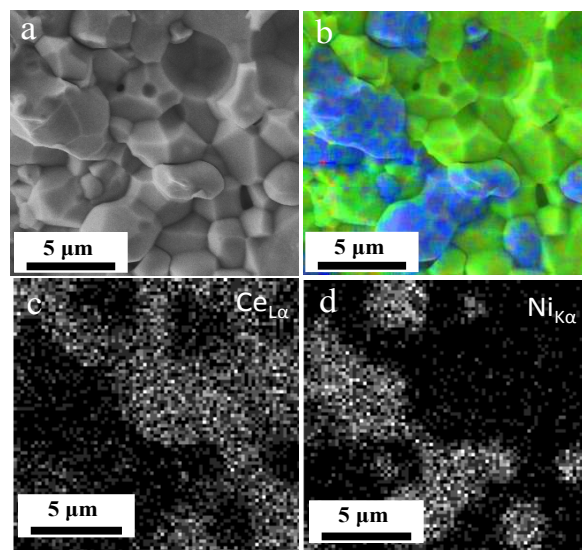

Figure 3. SEM and EDXS elemental distributions of Ce and Ni in the bulk of the spent Ni-BCTZ cermet membrane after 100 h hydrogen permeation. Blue: metallic Ni phase; green: perovskite oxide phase.

hydrogen permeable cermet membranes, such as Ni-Ba($Zr_{0.8-x}Ce_xY_{0.2}$)$O_{3-\delta}$,[18] Ni-Ba($Zr_{0.7}Pr_{0.1}Y_{0.2}$)$O_{3-\delta}$[21] etc. On the other hand, the Ni-BCT membrane has an asymmetric structure of 90 μm dense layer supported on a porous substrate which is beneficial for hydrogen transportation while the Ni-BCTZ membrane is a completely dense compact membrane with a thickness of 0.5 mm. On the contrary, our Ni-BCTZ membrane shows excellent stability for the overall process, which is extremely essential for all the applications including hydrogen separation. In the humid reducing atmosphere, Ni-BCTZ membrane also exhibits
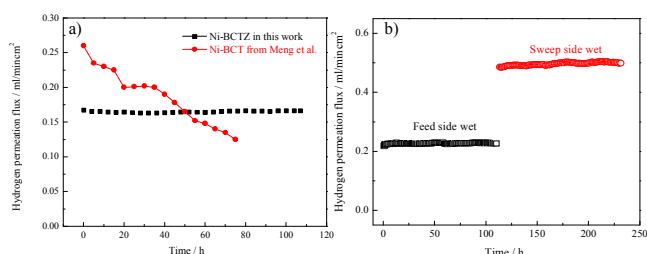
excellent stability and the hydrogen flux keeps steady for over 100 h.

From the XRD, SEM and EDXS results of the spent Ni-BCTZ membrane shown in Figures 3, 4, S7 and Table S1, no big changes of the microstructure can be found in comparison with the fresh cermet membrane (see Figure S4). The spent Ni-BCTZ membrane still keeps its original structure without impurity phases except some residual ceramic sealant. Combined with more EDXS results and compared with Ni-BCT, (Supporting Information, Table S2 and Figures S8-S11), the good phase structure stability of Ni-BCTZ can be evidenced even under reducing atmospheres for a long time. One important thing should be emphasized that among numerous proton conductive oxides for hydrogen separation, there are only a few materials which exhibit both good stability and nice permeation flux (Supporting Information, Figure S12). In consideration of both hydrogen permeability and stability, Ni-BCTZ is really a promising material candidate for hydrogen separation.
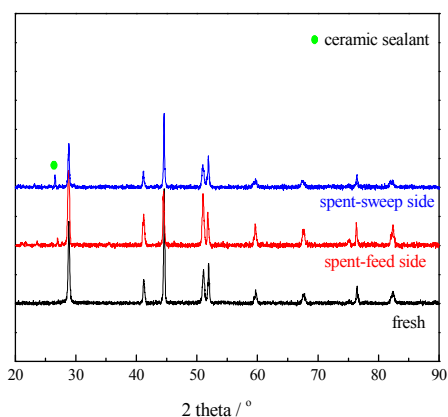

Figure 4. X-ray diffraction patterns of the spent Ni-BCTZ membrane after 100 h hydrogen permeation.

Conclusions

In summary, after doping Zr into the BCT oxide, the phase structure stability of the Ni-BCTZ cermet membrane has been enhanced remarkably. The Ni-BCTZ membrane can be steadily operated under both dry and humid conditions for over 100 h at 800 $^{\circ}$C for hydrogen separation, which shows an extremely enhanced stability compared with Ni-BCT. The XRD and SEM results also prove the outstanding phase structure stability, which promotes the Ni-BCTZ material as a proper candidate of an MPEC material for different potential applications.

Notes and references

[a] Institute of Physical Chemistry and Electrochemistry, Leibniz University of Hannover, Callinstrasse 22, 30167 Hannover, Germany

[b] School of Chemistry and Chemical Engineering, South China University of Technology, 510640 Guangzhou, China

[c] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

*E-mail: yanying.wei@pci.uni-hannover.de (Y. W.); hhwang@scut.edu.cn (H. W.)

1 M. S. Islam, R. A. Daviesa and J. D. Gale, *Chem. Commun.*, 2001, 661–662.
2 S. Li, F. Schönberger and P. Slater, *Chem. Commun.*, 2003, 2694.
3 M. Amsif, A. Magraso, D. Marrero-Lopez, J. C. Ruiz-Morales, J. Canales-Vazquez and P. Nunez, *Chem. Mater.*, 2012, **24**, 3868.
4 S. Escolastico, S. Somacescu and J. M. Serra, *Chem. Mater.*, 2014, **26**, 982.
5 S. Escolastico, V. B. Vert and J. M. Serra, *Chem. Mater.*, 2009, **21**, 3079.
6 S. Escolastico, C. Solis, C. Kjølseth and J. M. Serra, *Energy Environ. Sci.*, 2014, **7**, 3736.
7 S. Escolastico, J. Seeger, S. Roitsch, M. Ivanova, W. A. Meulenberg and J. M. Serra, *Chemsuschem*, 2013, **6**, 1523.
8 J. Seeger, M. E. Ivanova, W. A. Meulenberg, D. Sebold, D. Stover, T. Scherb, G. Schumacher, S. Escolastico, C. Solís and J. M. Serra, *Inorg. Chem.*, 2013, **52**, 10375.
9 D. Holt, E. Forster, M. E. Ivanova, W. A. Meulenberg, M. Müller, S. Baumann and R. J. Vaßen, *Eur. Ceram. Soc.*, 2014, **34**, 2381.
10 G. Marnellos and M. Stoukiddes, *Science*, 1998, **282**, 98.
11 D. Pergolesi, E. Fabbri, A. D'Epifanio, E. Di Bartolomeo, A. Tebano, S. Sanna, S. Licoccia, G. Balestrino and E. Traversa, *Nature Mater.*, 2010, **9**, 846.
12 L. Yang, S. Wang, K. Blinn, M. Liu, Z. Liu, Z. Cheng and M. Liu, *Science*, 2009, **326**, 126.
13 A. Aguadero, D. Perez-Coll, J. A. Alonso, S. J. Skinner and J. Kilner, *Chem. Mater.*, 2012, **24**, 2655.
14 F. Bozza, W. Schafbauer, W. A. Meulenberg and N. Bonanos, *Int. J. Hydrogen Energy*, 2012, **37**, 8027.
15 H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics*, 1981, **3/4**, 359.
16 S. J. Song, E. D. Wachsman, J. Rhodes, S. E. Dorris and U. Balachandran, *Solid State Ionics*, 2004, **99**, 167.
17 C. Zuo, T. H. Lee, S. J. Song, L. Chen, S. E. Dorris, U. Balachandran and M. Liu, *Electrochem. Solid-State Lett.*, 2005, **8**, J35.
18 C. Zuo, S. E. Dorris, U. Balachandran and M. Liu, *Chem. Mater.*, 2006, **18**, 4647.
19 C. Zuo, T. H. Lee, S. E Dorris, U. Balachandran and M. Liu, *J. Power Sources,* 2006, **159**, 1291.
20 S. J. Song, T. H. Lee, E. D. Wachsman, L. Chen, S. E. Dorris and U. Balachandran, *J. Electrochem. Soc.*, 2005, **152**, J125.
21 Z. Zhu, W. Sun, Y. Dong, Z. Wang, Z. Shi, Q. Zhang and W. Liu, *Int. J. Hydrogen Energy*, 2014, **39**, 11683.
22 X. Meng, J. Song, N. Yang, B. Meng, X. Tan, Z. Ma and K. Li, *J. Membr. Sci.*, 2012, **401-402**, 300.
23 R. Haugsrud and C. Kjølseth, *J. Phys. Chem. Solids*, 2008, **69**, 1758.
24 S. Escolastico, C. Solis, T. Scherb, G. Schumacher and J. M. Serra, *J. Membr. Sci.*, 2013, **444**, 276.
25 T. Oh, J. Li, H. Yoon and E. D. Wachsman, *Ionics*, 2009, **15**, 525.
26 Z. Zhong, *Solid State Ionics*, 2007, **178**, 213.
27 K. Katahira, Y. Kohchi, T. Shimura and H. Iwahara, *Solid State Ionics*, 2000, **138**, 91.