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INVESTIGATION OF LONG-TERM HYDROTHERMAL STABILITY OF NANO 3YSZ AT OPERATION TEMPERATURES OF SOFCS

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ABSTRACT

The study of hydrothermal degradation of 3 mol% yttria partially stabilized zirconia was carried out on various grain sizes with the target to prove the long term stability of nano sized 3YSZ applied in solid oxide fuel cells (SOFCs). Samples with grain sizes lower than 100 nm (nano) and higher than 100 nm (submicron) were produced by uniaxial pressing and slip casting. Tests of their mechanical performance such as hardness, however, showed that the way of processing does not have significant impact to the sintered specimen. Therefore are the samples of either process valuable for hydrothermal ageing experiments, which proved so far a complete resistance against water exposure in an autoclave up to 21 days.

INTRODUCTION

SOFCs are oxygen ion conductors and operate at temperatures between 650°C and 1000°C to produce electrical current and heat with water or water vapour as a by-product. The work on SOFCs is of enormous interest since it enables the generation of electric power without any unwanted carbon emissions. This project is focussed on planar SOFCs consisting of a solid, crystalline oxide material, the electrolyte (YSZ¹) sandwiched between two porous electrodes, anode (Ni-YSZ²) and cathode (LSM³). Zirconia was used as the electrolyte for the first time in 1937 and became the focus of research in the 1960's when it was applied for fuel cells in the Gemini rocket.

Furthermore, zirconia stabilised with yttria (YSZ) as the electrolyte is taken into account as it appears to have unique electrical and mechanical properties when doped with 3 mol% of yttrium oxide (Y₂O₃). The reason of moving from the previous application of 8YSZ for SOFCs with distinctive ionic conductivity to 3YSZ was due to the weakness in mechanical strength of the former. By a shift from 8 mol% YSZ with a submicron sized microstructure to 3 mol% nano YSZ, mechanical and electrical properties are predicted to fulfil the conditions required for SOFCs application.

HYDROTHERMAL DEGRADATION

The presence of water at initial starting up and cooling down, between 100°C and 300°C, of the fuel cell involves challenges which can cause Hydrothermal Ageing (HTA) of the zirconia electrolyte. This mechanism of hydrothermal degradation, however, is well explained by Chevalier et al¹. It can affect the phase stability of ZrO₂ and hence the mechanical properties and the ionic conductivity. The aim of the present work is to study the changes in detail.

PROCESSING

The investigation of the mechanical and electrical performance of YSZ was carried out on bulk material produced by two different processing routes with various yttria levels and grain sizes. YSZ green bodies have been formed in dry route by uniaxial pressing of powders at 312 MPa and in wet route by slip casting, where aqueous slurry was used. A debinding heat profile was applied to remove containing organics². The so called brown bodies were then sintered at similar sintering condition of each

¹ Yttria stabilised zirconia

² Cermet of partial reduced Nickel Oxide and YSZ

³ Strontium stabilised Lanthanmanganite

grain size to correlate the influence of applied processes. Nano sizes samples were then heated to a high initial temperature of 1150°C, T1, for 6 s and subsequently dropped to 1050°C, T2, where dwelling of 10 hours was applied³. The submicron 3YSZ green bodies, prepared by both processing routes, were sintered using a conventional sintering cycle at 1500°C with 2 h dwelling and a heating rate of 2°C min⁻¹. It was found that the processing route does not significantly affect the ultimate properties e.g. the hardness of sintered YSZ bodies (see Fig. 1). As a result, samples of both, dry and wet routes were used for the study.

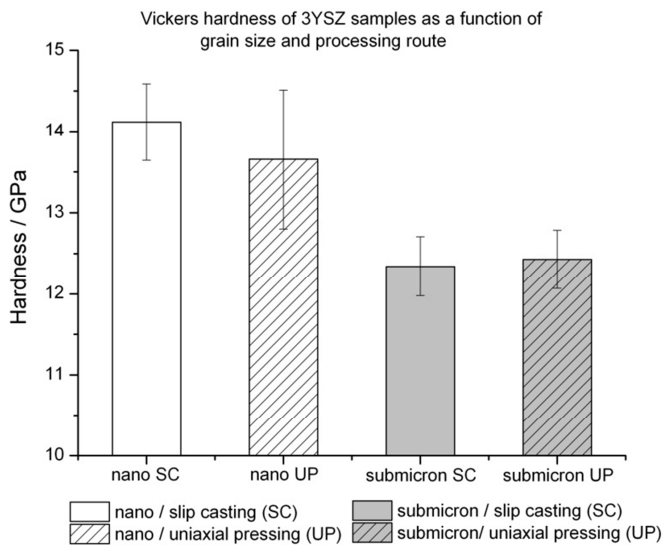


Fig. 1. Vickers hardness of unaged 3YSZ samples in correlation to their grain size and their way of processing.

EXPERIMENTAL

To understand the cause of formed water and water vapour as a by-product of the electrochemical reaction at the cathode-electrolyte interface in SOFCs, the effect of the presence of water at elevated temperatures is required to be explored. For this, fully dense specimens were hydrothermally aged at temperatures up to 245°C in a pressure vessel containing deionised water. While submicron grain sized 3YSZ disks turned into powder in as little as 1 h of hydrothermal treatment, nano 3YSZ showed no effect at all at mentioned conditions even after 21 days (= 504 h). The disintegration is due to a phase transformation from tetragonal phase to the stable monoclinic phase. Hydrothermally aged samples were characterized using X-ray diffraction and Raman to determine existing crystalline phases. It was proved that 3 mol% yttria stabilized zirconia with grain sizes below 180 nm was resistant to HTA. The critical grain size range was found to exist between 180 nm and 230 nm (see Fig. 2).

HTA was established to be dependent on grain size, density, porosity, yttria content and yttria distribution.

According to the long operating time of SOFCs, the mechanical strength of the YSZ electrolyte material was a crucial property to look at. Vickers hardness, fracture toughness and flexural strength of the samples have been tested after hydrothermal treatment. Thus Vickers hardness as an indicator for mechanical strength remains unaffected for nano 3YSZ (<100 nm) with 13.6 GPa, whereas submicron 3YSZ (>100 nm) decreased in terms of the resistance to plastic deformation of the material significantly after 10 h of HTA and ending with 8.5 GPa after 180 h HTA. Hence the fracture toughness is very low, whereas the flexural strength is comparable for both grain sizes.

Ionic conductivity measured by AC impedance spectroscopy on sintered samples from 20°C to 900°C proved that submicron 3YSZ and nano 3YSZ give matching results of about 0.035 S cm⁻¹.

CONCLUSION AND FUTURE WORK

The hydrothermal ageing of nano 3YSZ was primarily investigated on bulk material and is going to be extended for thin layer electrolyte material applied in an actual fuel cell rig. Mechanical and electric properties of nano sized zirconia with 3 mol% yttria content in the zirconia microstructure was proved to achieve distinctive results. According to the latter results, experiments have been done up to 245°C for 504 h to prove the hydrothermal ageing resistance and are going to be tested at higher temperatures for longer periods of time to simulate SOFCs conditions.

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REFERENCES

- Chevalier, J., Gremillard, L., Virkar, A. V. & Clarke, D. R. The Tetragonal-Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends. *JOURNAL-AMERICAN CERAMIC SOCIETY* **92**, 1901-1920 (2009).
- Paul, A., Vaidhyanathan, B. & Binner, J. G. P. Hydrothermal Aging Behavior of Nanocrystalline Y-TZP Ceramics. *J Am Ceram Soc* **94**, 2146-2152 (2011).
- Binner, J., Annapoorani, K., Paul, A., Santacruz, I. & Vaidhyanathan, B. Dense nanostructured zirconia by two stage conventional/hybrid microwave sintering. *Journal of the European Ceramic Society* **28**, 973-977 (2008).