Institute of
Technical Thermodynamics

Investigation of Plasma-Sprayed Zirconia Based Electrolytes

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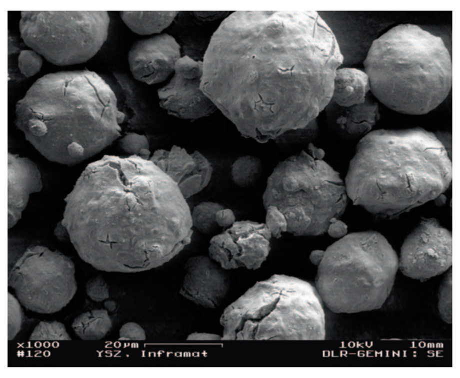
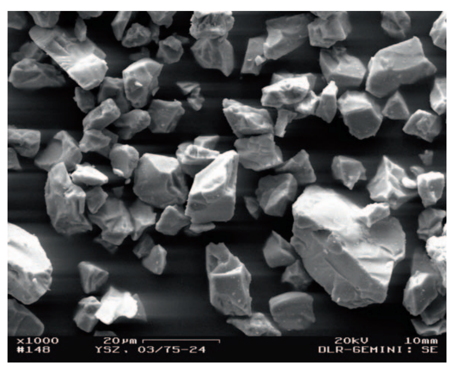
Introduction

Solid oxide fuel cells (SOFC) operating in the temperature range between 800–1000 °C are devices converting directly chemical energy into electrical energy. The SOFC electrolyte layer typically consisting of yttria-stabilized zirconia (YSZ) was prepared using atmospheric plasma spraying technology. Plasma spraying is a cost-effective technique for the production of functional layers in SOFCs and allows the optimisation of the layers' porosity that affects the fuel cell performance (e.g., Life-time).

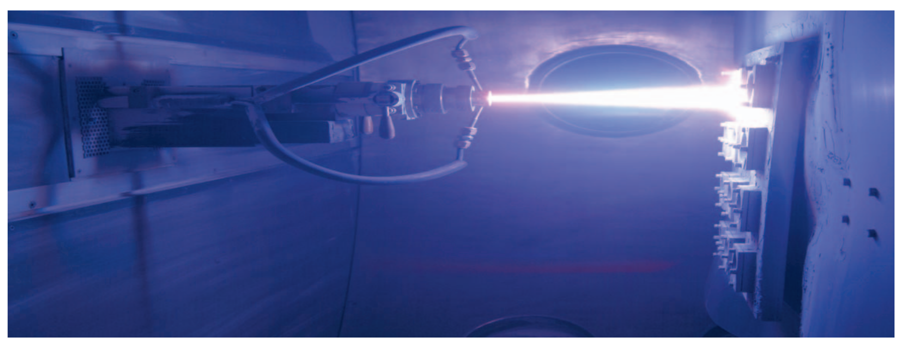
Properties, such as microstructure, conductivity, were investigated by Scanning electron microscopy (SEM), X-ray diffraction (XRD), 4-point dc method and Raman spectroscopy. Raman spectroscopy is a powerful tool for the investigation of structural features, for example, crystallinity, molecular orientation, and phase composition, especially of inorganic thin films. Depending on the preparation conditions (plasma spraying and sintering) charactieristics and behaviour of the plasma-sprayed layers can be influenced significantly.

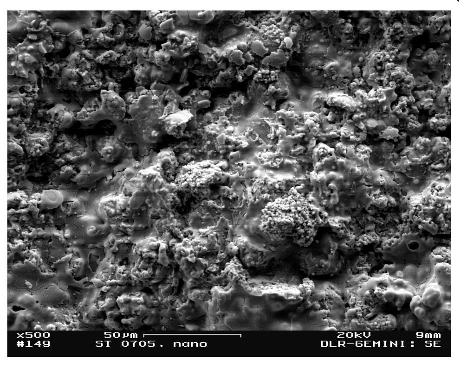
Layer Preparation

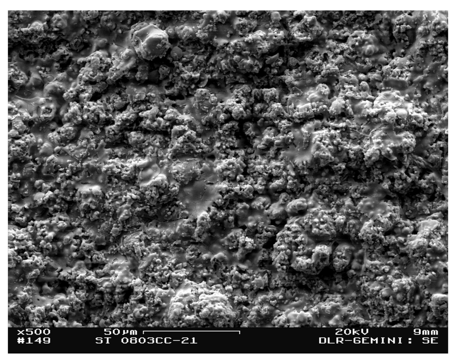




SEM image of conventional (9.5 mol%) and nanostructured (10 mol%) YSZ (ZrO_2-Y_2O_3 85/15) powder and of plasma-sprayed layers (right side)

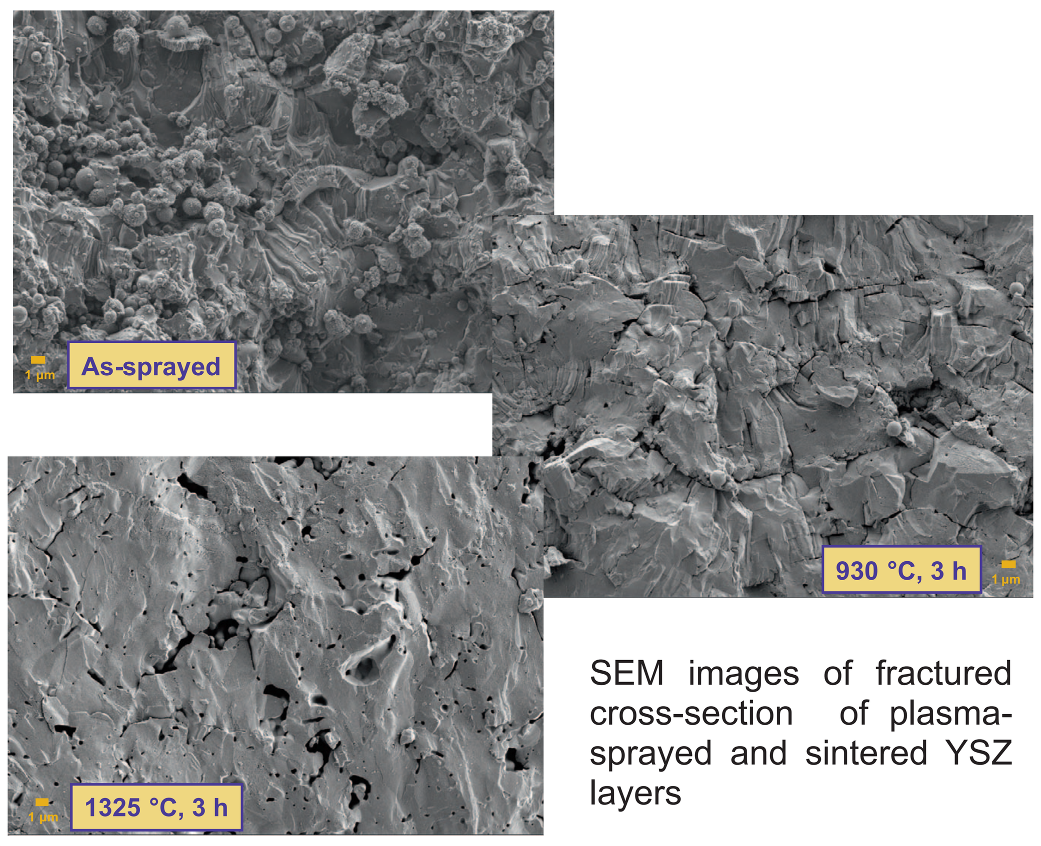




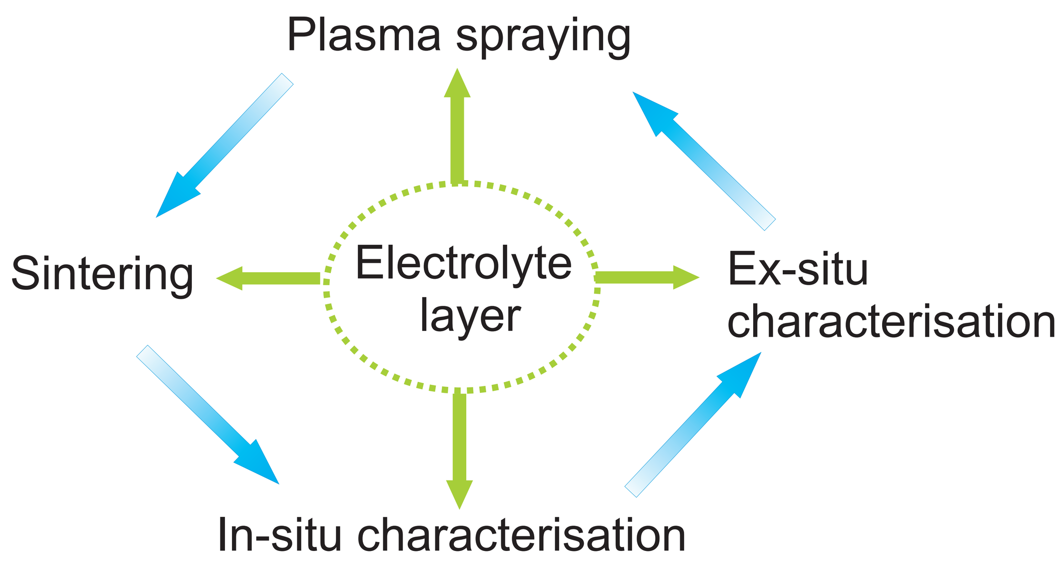


Sintering Experiments

Sintering under different temperatures and holding times (930 to 1325 °C, 3 to 50 h)
- Cracks healing and inter-splat diffusion started at temperatures as low as 930 °C, observed in SEM

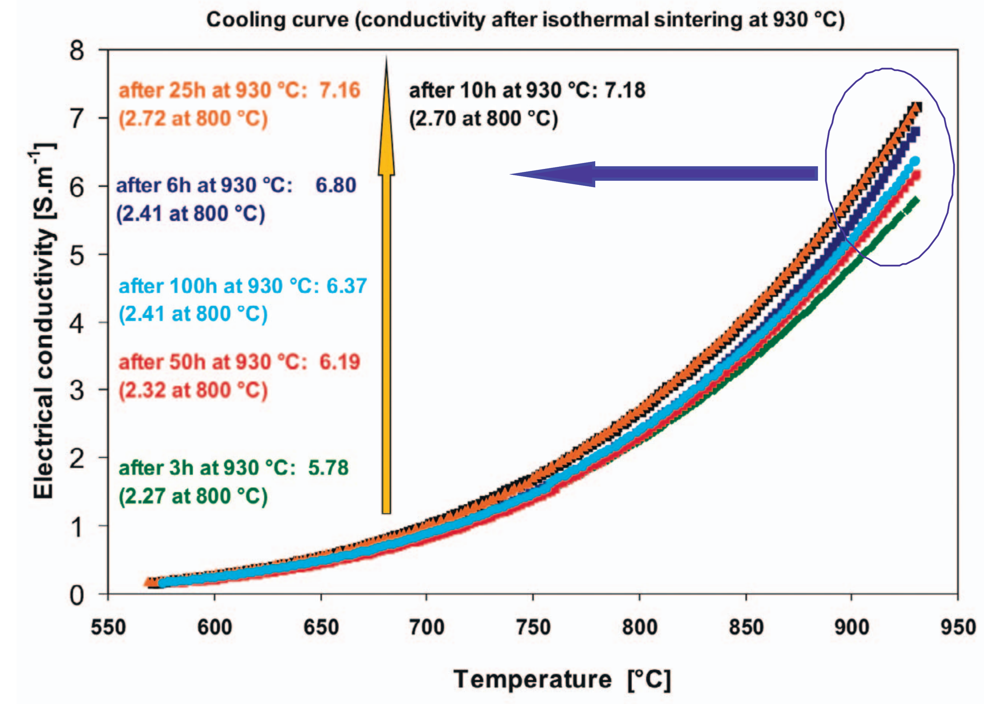


SEM images of fractured cross-section of plasma-sprayed and sintered YSZ layers



In-situ electrical Conductivity Measurements

4-point dc measurement during sintering in temperature range of 930 to 1325 °C, holding times 3 to 50 h
- Lamellar microstructure in as-sprayed samples reduces electrical conductivity of YSZ electrolytes. Sintering of as-sprayed layers lead to higher conductivity at sufficient temperature
- Highest values of electrical conductivity after sintering at 930 to 1000 °C, after 10 h



Experimental Set-up

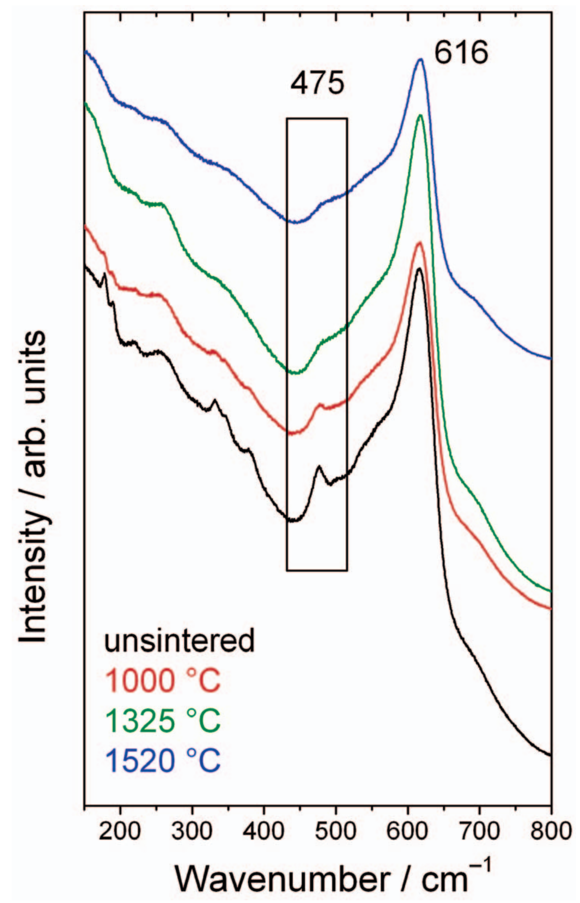
Raman and SEM

Raman spectra were performed on a confocal Raman microscope LabRAM HR800 (Horiba Jobin-Yvon). Samples were irradiated with a He-Cd laser (λ = 442 nm). Spectra were obtained with a laser power of 80 mW, a hole of 1000 μm, and a resolution of 0.4 cm^{-1}. SEM images were recorded on a Gemini Ultra Plus (Zeiss) and Gemini LEO 982 (Zeiss).

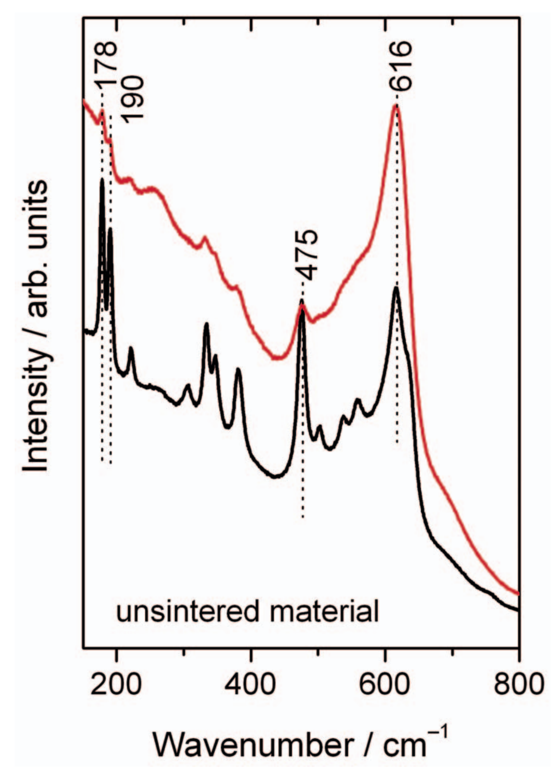
Materials for Plasma Spraying

Two commercial yttria-stabilized zirconia were used as raw powder for preparing electrolyte layers by the direct current (DC) plasma spray process. A conventional 9.5 mol % YSZ (ZrO_2-Y_2O_3 85/15; fused and crushed; H.C. Starck, 03/75-24) with a mean particle size between 5 -22 µm and a 10 mol% YSZ nanostructured powder (NanoxTM S4017, MCD293YSZ10; Inframat Advanced Technology), with a particle size range of 60–90 nm, agglomerated to 5–20 µm particles, were used.

Raman Spectroscopy



The spectra were measured after sintering of the layers prepared from conventional powder at various temperatures.
- ZrO_2: the absolute intensity of the 475 cm^{-1} band decreases with sintering temperature. The sintering temperature influences the homogeneity of the surface (ZrO_2/YSZ).
- ZrO_2 possesses a low ion conductivity, YSZ possesses a better ion conductivity. With lower content of ZrO_2 (peak at 475 cm^{-1} decreases) in the sample the ion conductivity increases.



The spectra were measured at two different positions of the unsintered layer prepared from conventional powder.
- ZrO_2 as well as cubic YSZ can be detected on the surface [penetration depth of the laser (λ = 442 nm) approx. 10 nm].
- The band structure from 150–800 cm^{-1} is characteristic of the cubic YSZ phonon modes.
- Dominant peak at 616 cm^{-1} is characteristic for the F_{2g} phase of the cubic YSZ structure. This band corresponds to the out-of-phase stretching of the oxygen bound to zirconium.

- ZrO_2: the monoclinic ZrO_2 presents very well defined peaks, the more intense of which are located at 177, 190, 475 cm^{-1}. That means that mainly the monoclinic phase is present. The presence of the tetragonal phase can be excluded.
- The unsintered layer prepared from the conventional powder shows an inhomogeneous composition related to complete different Raman spectra.

Acknowledgment

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