Raman Spectroscopic Investigation of Plasma-Sprayed Zirconia-Based Electrolytes

A. Haug,[a] C. Christenn,[a] B.-E. Schuster,[a] G. Schiller,[a] T. Chassé,[b] K. A. Friedrich[a]

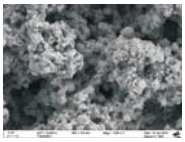
[a] German Aerospace Center, Institute of Technical Thermodynamics, Pfaffenwaldring 38–40, 70569 Stuttgart, Germany
[b] University of Tübingen, Institute of Physical and Theoretical Chemistry, Auf der Morgenstelle 18, 72076 Tübingen, Germany

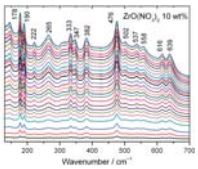
Introduction

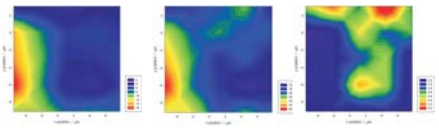
Solid oxide fuel cells (SOFC) operating in the temperature range between 800–1000 °C are devices converting directly chemical energy into electrical energy. The SOFC electrolyte layer typically consisting of yttria-stabilized zirconia (YSZ) was prepared using atmospheric plasma spraying technology. Plasma spraying is a cost-effective technique for the production of functional layers in SOFCs and allows the optimization of the layers' porosity that affects the fuel cell performance (e.g., life-time). 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. In order to get further information concerning the thin-film properties of plasma-sprayed zirconia-based electrolytes X-ray diffraction (XRD) as well as scanning electron microscopy (SEM) were applied. In this study we show that depending on the preparation conditions the crystal growth and the density of the plasma-sprayed thin films can be influenced significantly. Therefore Raman spectra as well as XRD and SEM pictures show subtle differences concerning the crystallinity of various samples.

Method A

ZrO_2 layer prepared from $ZrO(NO_3)_2$ 10 wt% before sintering

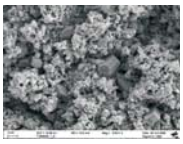


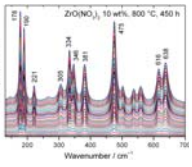


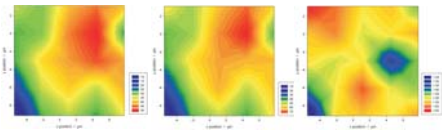


Contour plots (top and bottom):
Left: tetragonal phase (616 and 639 cm^{-1})
Middle: monoclinic phase (178 and 190 cm^{-1})
Right: ratio of monoclinic and tetragonal phase (peak intensities)

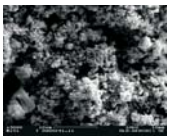
ZrO_2 layer prepared from $ZrO(NO_3)_2$ 10 wt% after sintering at 850 °C for 450 h

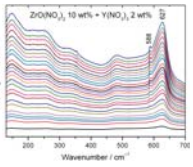




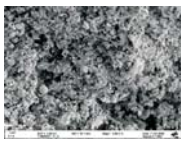


YSZ layer prepared from $ZrO(NO_3)_2$ 10 wt% + $Y(NO_3)_3$ 2 wt% before sintering





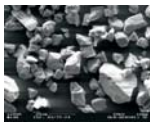
YSZ after sintering



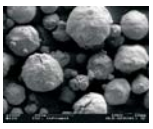
- Layers with ZrO_2 and YSZ were prepared by solution precursor plasma spraying.
- A solution of 10 wt% of $ZrO(NO_3)_2$ + 90% H_2O and 10 wt% $ZrO(NO_3)_2$ + 2 wt% $Y(NO_3)_3$, respectively, was used.
- The coated samples were sintered at 850 °C for 450 h.
- After sintering the thickness of the coated layer decreases caused by the formation of ZrO_2 and less porous layer was formed.

- Due to sintering of the ZrO_2 layers prepared from $ZrO(NO_3)_2$ 10 wt% a change in the morphology – formation of caskets – can be observed.
- In contrast, the sintered layers prepared from $ZrO(NO_3)_2$ 10 wt% + $Y(NO_3)_3$ 2 wt% did not show this effect after 450 h at 850 °C.
- For each sample 25 spectra (mapping) were recorded (12 x 12 µm). A high variation of the signal intensities was observed, which can be related to the surface roughness.
- The main peaks in the obtained spectra from the resulting ZrO_2 before and after sintering can be assigned as following: monoclinic phase: 178, 190 and 476 cm^{-1}; tetragonal phase: 616 and 639 cm^{-1}.
- The main peak in the formed YSZ layer (reaction of $ZrO(NO_3)_2$ 10 wt% + $Y(NO_3)_3$ 2 wt%) at 627 cm^{-1} is assigned to cubic YSZ.
- The ratio between both ZrO_2 phases becomes more homogeneous due to sintering.
- The reflectivity seems to be related to the ratio of both phases, at higher monoclinic quotient lower intensities of the spectra were recorded.

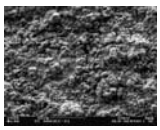
Method B

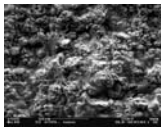


SEM image of conventional powder 9.5 mol% YSZ (ZrO_2-Y_2O_3 85/15)

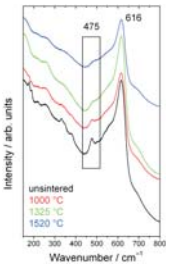


SEM image of YSZ (10 mol%) nanostructured powder

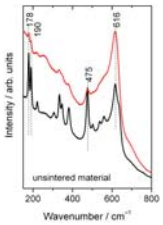




- The second way to prepare YSZ layers is to use atmospheric plasma spraying.
- For receiving free-standing electrolytes, the powder was sprayed on steel substrates, which were treated with HCl to remove the steel substrate.
- Due to the spraying process the morphology of the powder changes significantly, typically plasma-sprayed layers with not or not fully melted particles, and the material recrystallizes.



- The spectra on the left 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).
- Comparison of two different spectra from the same surface (unsintered): ZrO_2 as well as cubic YSZ can be detected on the surface [penetration depth of the laser (λ = 442 nm) approx. 10 nm].
- 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 on the left were measured at two different positions of the unsintered layer prepared from conventional powder.
- The band structure from 150–800 cm^{-1} is characteristic of the cubic YSZ phonon modes.
- Dominant peak at 616 cm^{-1} is characteristic fort he 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.

Experimental Set-up

Raman and SEM

The Raman spectra were performed on a confocal Raman microscope LabRAM HR800 (Horiba Jobin-Yvon). The samples were irradiated with a He-Cd laser (λ = 442 nm). The spectra were obtained with a laser power of 80 mW, a hole of 1000 µm, and a resolution of 0.4 cm^{-1}. The 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 [7]. 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 and 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.

Acknowledgment

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References

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