Nano-structured Electrolyte Layers for Solid Oxide Fuel Cells

Mark Kappertz, Research Centre Jülich GmbH, Germany

Increasing pollution of the atmosphere resulting in already noticeable rising average temperature needs an improvement of the efficiency of existing energy production technologies and the development of new retainable strategies for energy conversion. The scientific activities of the Institute of Energy Research in the Research Center Jülich GmbH (FZJ), one of Germany's largest "science factories", are concentrated on the development, testing and characterization of materials for such high temperature applications (solid oxide fuel cells (SOFC), advanced gas and steam power plants, plasma facing materials for future fusion devices).

Mark Kappertz

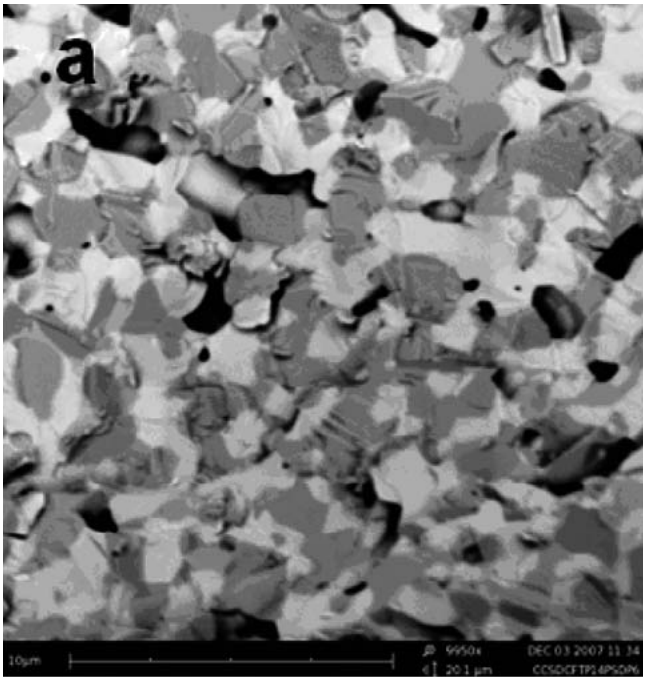
Application

A solid oxide fuel cell (SOFC) which allows converting chemical energy directly into electrical energy is of increasing interest because of its high conversion efficiency, low pollution and fuel flexibility. Recent development is focussed on lowering of the SOFC's operation temperature from above 800 °C down to 600 °C for cost reduction and long term thermal stability. Reduction of the thickness of the electrolyte layer and optimization of its electrochemical properties with respect to higher ionic conductivity at intermediate temperature are the actual fields of research.

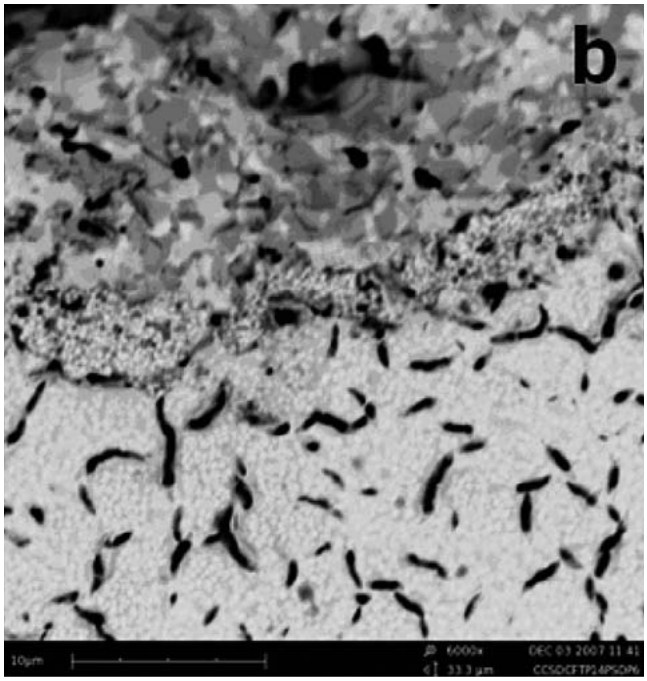
At FZJ a planar anode supported SOFC has been developed. The sandwich structure of the FZJ cell stacks (a) a porous, 0.3 – 1.5 mm thick yttrium stabilized zirconium (YSZ)/NiO anode substrate, (b) a porous YSZ/NiO anode functional layer, (c) a dense, gas-tight 5-10 µm thick 8YSZ electrolyte layer, (d) a porous LSM or LSCF cathode with a thickness of ca. 50 µm. An average power output of 1.4 W/cm^2 at 750 ºC and 0.7 V has been already achieved.

For the manufacturing of the electrolyte layer normally vacuum slip-casting or screen-printing is used. Thinning of this layer needs another deposition technique like the sol-gel process. In a liquid solution of an organometallic precursor a new phase – the sol – is formed by hydrolysis and condensation. This sol is a stable mixture of a solid phase dispersed in a liquid, in which the dispersed phase is much smaller than a micrometer, so that gravitational force is negligible and particle interactions are dominated by short-range forces. The dispersed particles in the sol can condense in a gel, in which the solid is still immersed like in a liquid. Drying and firing of the gel during a subsequent low temperature thermal treatment, it is possible to obtain solid matrices with a tailored microstructure. A fundamental property of the sol-gel process is the generation of a ceramic material at rather low temperature compared to traditional routes.

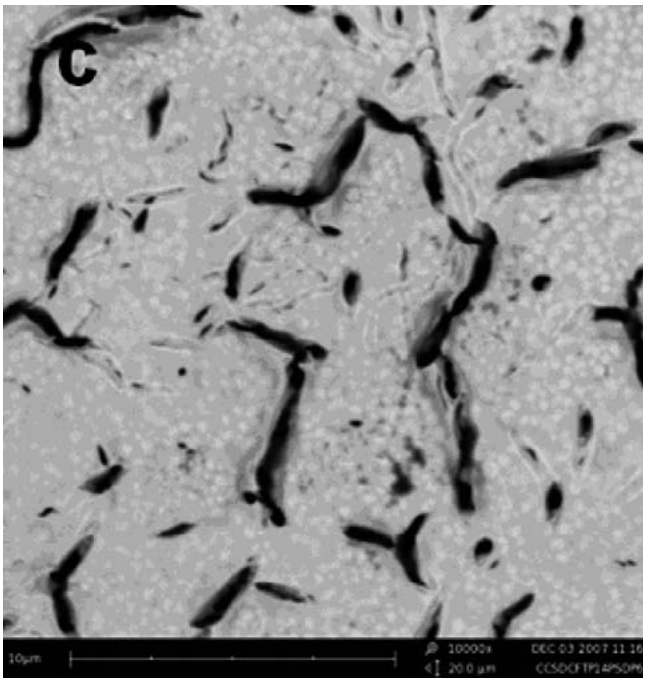
Nano-structured Electrolyte Layers



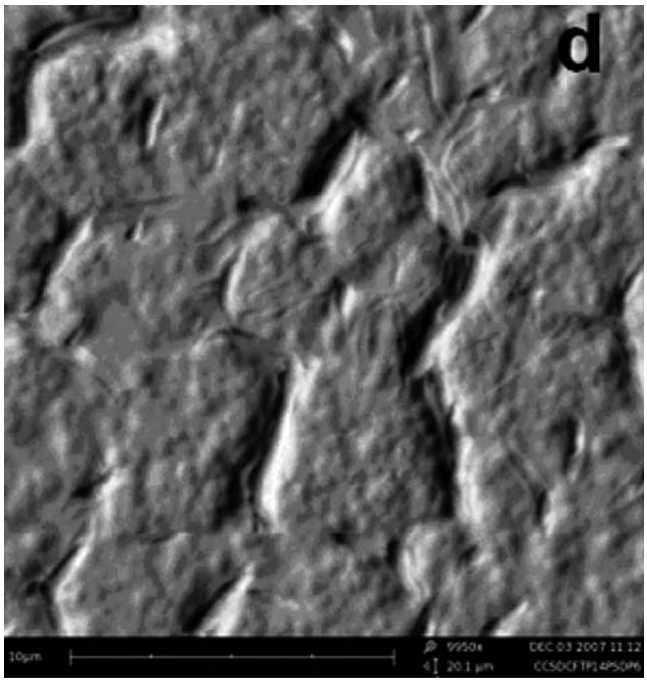
Naked surface of the substrate (compo, bar = 10 µm)



Once dip-coated with a colloidal sol (compo, bar = 10 µm)



Additionally once dip-coated with polymeric sol (compo, bar = 10 µm)



Additionally twice dip-coated with polymeric sol (topo, bar = 10 µm)

SEM images of a layer from a colloidal sol deposited onto a tape-casted substrate sintered at 1400 ºC (Figure 1).

Nano-structured Electrolyte Layers

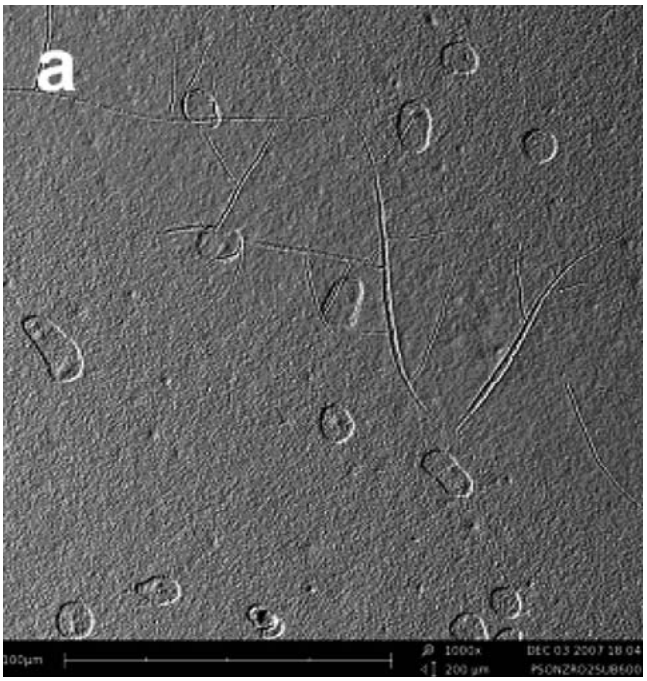
By tuning hydrolysis and condensation reactions the desired nano-sized ceramic particles are obtained for making advanced layers. Such thin layers can be deposited by spraying, spin coating, dip coating or even painting. The asdeposited gel layers contain still a large solvent amount. Drying (evaporation of the solvent) creates the final amorphous or crystalline layer, which is further processed by calcination (decomposition of starting materials and formation of reaction products) and sintering (densification).

Table top SEM

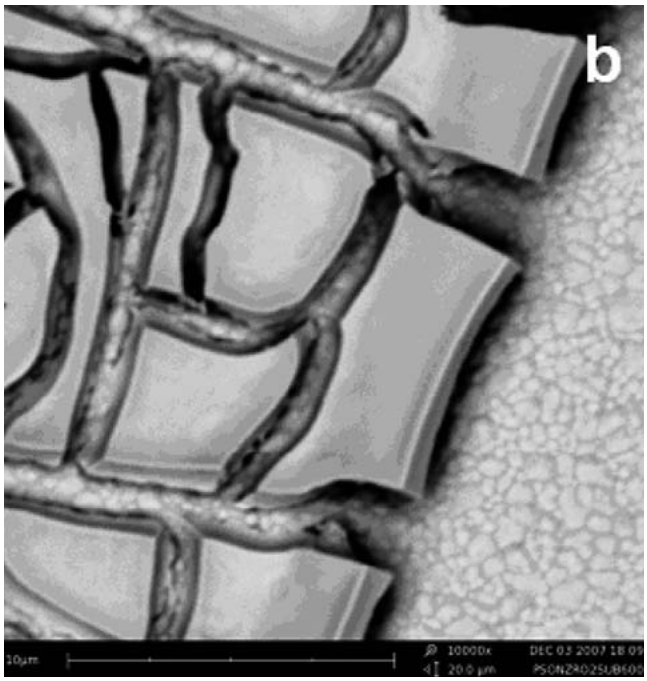
Homogeneity of multi-layers by repeated coating, soaking of the sol into the substrate grain assembly due to capillary tension, crack formation and their growth are problems under investigation in the sol-gel layer route.

The laboratory uses a high end SEM microscope and several optical microscopes for studying the layer formation. The information retrieved from optical microscopy was not sufficient with respect to detail resolution. The high end SEM can overcome this problem, but the workload on it results in a long sample throughput. The way-out offers a microscope which imaging capabilities exceed those of an optical one and which allows quick access to shorten cycle time between coating manufacturing and microstructure evaluation.

For this, the table top scanning electron microscope “Phenom” has been utilized and is being used for studying (i) improvement of the substrate surface quality, (ii) optimization of coating process, and (iii) evaluation of layer quality.



Survey of the coating (topo, bar = 100 µm)



Cracked coating after firing (compo, bar = 10 µm)

Polymeric sol dip-coated and fired at 600 ºC on tape-casted 3YSZ substrate with a well finished surface (Figure 2).

Nano-structured Electrolyte Layers

The table top SEM has been utilized for imaging of surface topography, cross sections and fractured sandwiches since a magnification of 5000-10000x was sufficient, the low accelerating voltage of 5 kV together with the high-sensitive backscattered electron detector generate detailed surface-enhanced images, and its simple operation shortens the already mentioned cycle time.

The table top SEM has been operated in its two imaging modes; compositional (compo) and topographical (topo) contrast mode. In compo contrast mode differences in the average atomic number of different phases and early stages in grain formation can be seen (Figure 1).

Topo contrast mode shows that topographic features of the substrate prevent from getting an even and homogenous layer. This leads to the conclusion that high quality thin electrolyte layers can be made only on well finished substrate surfaces and with a particle size of the solid constituent in the gel slightly larger than the size of remaining defects.

Conclusion

The application of the table top SEM instead of an optical microscope allowed to extent the magnification range beyond the typical light-optical limit of 1000x, to collect more information about the sample due to the backscattered electron signal (topo and compositional information) and to maintain simple device operation supporting a quick micro structural sample characterization at reasonable costs.

CT00201WW v1.0

Phenom-World BV, Dillenburgstraat 9E, 5652 AM Eindhoven, The Netherlands, www.phenom-world.com

PHENOMWORLD