Nanocrystalline CGO thin films for Micro-Solid Oxide Fuel Cells

J.L.M. Rupp and L.J. Gauckler
Nonmetallic Inorganic Materials
Swiss Federal Institute of Technology
Wolfgang-Pauli-Str. 10,
CH-8093 Zurich, Switzerland

The power density of a Solid Oxide Fuel Cell can be increased by decreasing the thickness of the electrolyte, and therefore its ohmic resistance, or by using cerium gadolinium oxide (CGO) which has a higher ionic conductivity than state-of-the-art YSZ. Up to now, it is unclear how the defect distribution, and thus conductivity mechanisms, of mixed ionic/electronic conducting CGO electrolytes are affected when grain size is decreased below 100 nm [1, 2]. Spray pyrolysis offers the advantage to deposit amorphous and dense thin films, which can be converted to nanocrystalline microstructures by annealing [3].

In the present work amorphous, dense and crack-free $Ce_{0.78}Gd_{0.22}O_{1.9-x}$ thin films with a typical thickness of 100 – 600 nm were deposited on sapphire substrates by spray pyrolysis. Grain growth, stability and conductivity of those thin films were investigated as a function of temperature, oxygen partial pressure and average grain size.

The thermal stability of those thin films as a function of annealing temperature (600-1200°C) and dwell time (0-30h) was investigated by in-situ XRD and SEM experiments and the grain growth was characterized. We observe two regimes of grain growth: at less elevated temperatures grain growth is smooth and moderate up to limiting size values between 50 and 100 nm, depending on temperature. The grain growth ceases and a stable microstructure is reached after five to ten hours isothermal annealing for temperatures lower than 1100°C. E. g. an average grain size of 20 nm can be obtained after 10 hrs at 800°C. Grain growth in this nano-material does not obey the parabolic grain growth behavior typical for microcrystalline ceramics with grains in the μm range. Moreover, the grains in these films show low grain boundary mobilities $4.0*10^{-22}$ - $3.1*10^{-19}$ m^3/Ns and a low activation energy 3.35 eV compared to CGO with e.g. grain size of 0.65-3.32 μm, for which an activation energy of 9.46 eV was found [4].

Electrical conductivity has been studied as a function of temperature (600-900°C), oxygen partial pressure (0.21-10^{-25}atm) and grain size. The ionic conductivity is dominant in the high and intermediate partial pressure range for CGO with stable grain size of 80 nm. At low oxygen partial pressures n-type semi-conductivity is observed. However, at temperatures as low as 600°C the material is an ionductor at O_2 partial pressures as low as $1.07*10^{-20}$ atm. An ionic conductivity of 3.66 S/m was measured at 700°C being comparable to the conductivity for microcrystalline CGO[5].

The final goal of this study is the integration of such low-cost spray pyrolysis CGO electrolytes in micro-SOFC operating in the low temperature regime.

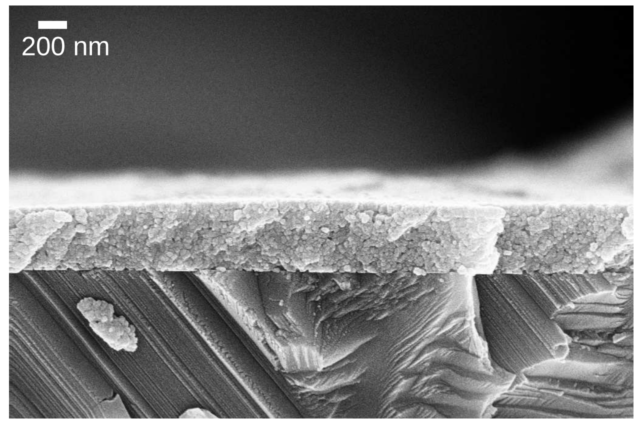

Figure 1: Nanocrystalline CGO film on sapphire substrate

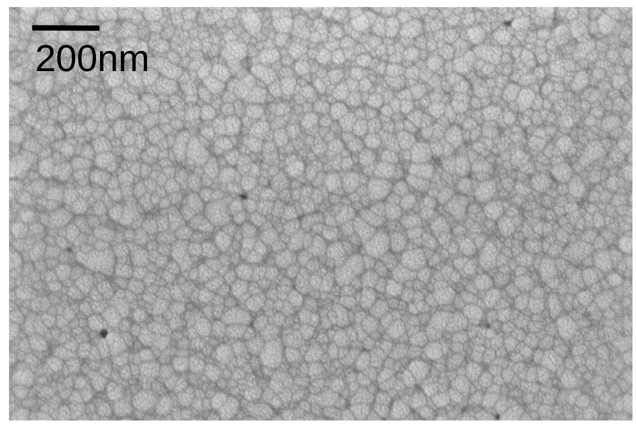

Figure 2: Annealed for 0h at 1100°C (3°C/min.)

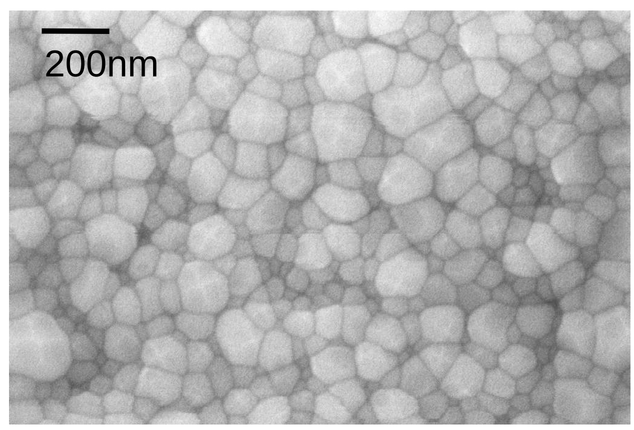

Figure 3: Annealed for 24h at 1100°C (3°C/min.)

1. Chiang, J.-M.-., Lavik, E.B., Kosacki, I. and Tuller, H.L:, *Nonstoichioentry and electrical conductivity of nanocrystalline CeO2-x.* Journal of Electroceramics, 1997. **1:1**: p. 7-14.
2. Suzuki, T., I. Kosacki, and H.U. Anderson, *Microstructure-electrical conductivity relationships in nanocrystalline ceria thin films.* Solid State Ionics, 2002. **151**(1-4): p. 111-121.
3. Perednis, D. and L.J. Gauckler, *Solid oxide fuel cells with electrolytes prepared via spray pyrolysis.* Solid State Ionics, 2004. **166**(3-4): p. 229-239.
4. Lewis, G.S., *Low Temperature Sintering of Solid Oxide Fuel Cell Electrolytes.* pHD, Department of Materials, Imperial College of Science, Technology and Medecine, London, 2002.
5. Kleinlogel, C. and L.J. Gauckler, *Sintering and properties of nanosized ceria solid solutions.* Solid State Ionics, 2000. **135**(1-4): p. 567-573.