Novel method in synthesis of YSZ microtubes and their application as ALD substrates

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Materials with microtubular geometry have attracted considerable attention during the past few decades due to their broad range of applications. One interesting field of these applications are microfluidic devices used for energy storage and production, like SOFC, where microtubular geometry could possess better thermo-mechanical properties and sealing simplicity compared to other geometries [1]. Another possible application of microtubes is to use these as miniature plasma chambers. There exists many different methods for preparation of ceramic microtubes applied for these purposes, including chemical vapor deposition (CVD), electrophoretic deposition, extrusion of slurries, different template methods etc. However, all the known methods have significant disadvantages, which set restrictions to use of the materials. In most of cases obtained tubes have lack in their mechanical properties, materials are highly porous also and cannot be applied to seal the gasses into tubes. Moreover, there seems to be no methods, suggested for preparation of gas-tight ceramic microtubes with diameter in the range from 10-100 microns. Therefore, it is important to elaborate the methods for preparation of microtubes in the mentioned range range.

In the present work we introduce a method for preparation of metal oxide microtubes in mentioned range. Obtained materials have superior physical and chemical properties due to their nanohomogeneous structure based on crystallites with size up to some tens of nanometers [Fig. 1, 2]. The method is based on sol-gel technology, known as a versatile preparation route to ceramics from corresponding metal alkoxides. Its main advantages are generally related to relatively low processing temperatures, flexibility of method in order to prepare materials in desired geometries etc [2]. In order to obtain the materials in desired shape, the processing should be combined with some kind of mechanical manipulations like use of templates or molds and their subsequent removal, dip coating procedure, extrusion etc. Our studies focus on yttria stabilized zirconia (YSZ), that is widely used as solid electrolyte and material in engineering of SOFC and for other technical solutions [3].

The proposed method is based on direct drawing of microtubes from metal alkoxide-based precursors. The hollowing is achieved as a result of rearrangement of jet material during the solidification, which for the content is saturated on the outer surface of the jet, while released alcohol remains into tube [2]. Obtained gel structures are post-treated by aging and thermal annealing to achieve removal of alcohol and to achieve dense nanocrystalline structure. Doping of the materials with yttria results in 100% transition of tube material into tetragonal structure. Obtained tubes exhibit tensile strength around 1 GPa, the value that is close to same of stainless steel, while Young modulus remains into very high 100-200 GPa range at the same. Ionic conductivity of tubes remain into 0,002-0,05 S/cm range that that is comparable to YSZ materials obtained by conventional methods [Fig. 3]. Pressurizing of the tubes by applying gasses or oil inside enabled to show resistance up to 1000 atm pressure. The tubes are thermally stable at least up to 1000℃.

With these properties, the tubes we have synthesized met all requirements for SOFC and plasma chamber applications. For use in these applications the tubes should be functionalized by different coatings. We have demonstrated that $LaSrMnO_2$ films as cathode of SOFC can be deposited on the inner side of the tubes by using sol-gel dip coating process [Fig. 4]. For real testing, the tubes can be sealed by using commercial high temperatural ceramic pastes. To favor emission of electrons form the inner surface of the tubes, required for plasma chamber applications, atomic layer deposition (ALD) of

MgO [Fig. 5] has been carried out on tubes. The films were deposited from magnesium *beta*-diketonate by using ozone as oxygen precursor [4]. Controlled growth of films enable to achieve ultrathin and dense films both on the inner and outer surface. Due to homogeneity of nanocrystalline structure, the tubes could also be applied as optical waveguides or miniature light sources in photonics [Fig 6].

References

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Figures

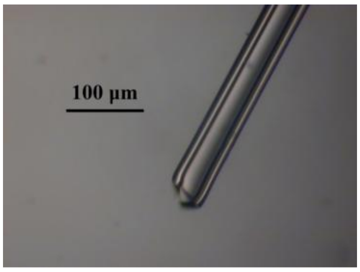

Figure 1: YSZ microtubes appeared to be transparent. Optical microscope was used to evaluate the productivity of tubes and their primary parameters.

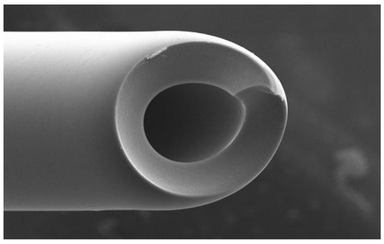

Figure 2: SEM was used to mesure diameters and wall thickness of microtubes.

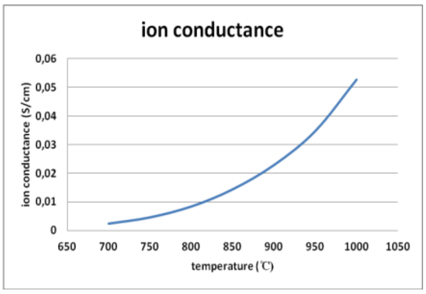

Figure 3: Ion conductance of YSZ microtube as a function of temperature.

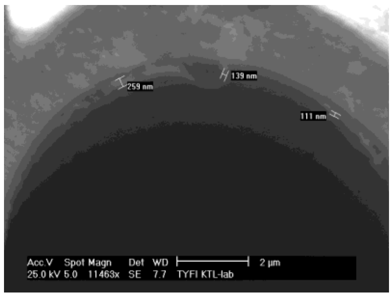

Figure 4: SEM image of $LaSrMnO_2$ layer on inner surface of YSZ microtube.

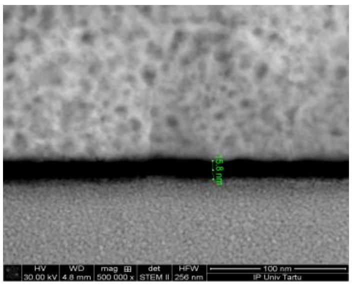

Figure 5: Deposited MgO film on the inner surface of YSZ microtube.

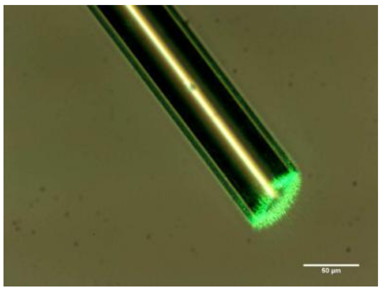

Figure 6: Very good light emittance of YSZ microtubes indicates to their good nanocrystalline properties.