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Aerosol deposition of thin-film solid electrolyte membranes for anode-supported solid oxide fuel cells

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ABSTRACT

Development of a reliable, easily scalable and economically feasible technology for thin-film solid electrolyte fabrication is critical for the industrial production of solid oxide fuel cells (SOFCs). In the present work, the aerosol deposition (AD) technique has been appraised for this role. The thin-film membranes of 8 mol.% yttria-stabilized zirconia (8YSZ) solid electrolyte were applied onto two-layer anode supports, with subsequent screen-printing of the composite cathodes made of $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ (LSM) and zirconia co-stabilized with 10 mol.% scandia and 1 mol.% ceria (10Sc1CeSZ). High quality of the thin membranes produced by the aerosol deposition was confirmed by scanning electron microscopy and electrochemical measurements, including the measurements of current–voltage dependencies and impedance spectroscopy. At 850 °C, the anode-supported SOFCs with wet hydrogen as fuel and air as an oxidant demonstrated the open-circuit voltage above 1.04 V, whilst the power density was higher than 500 mW/cm^2.

1. Introduction

Solid oxide fuel cell based power plants are highly efficient, environmentally friendly, have no competitors in terms of efficiency especially in a field of distributed generation [1]. However, they still need to be improved to become economically feasible alternative to traditional energy. The main trends in SOFC development are a simultaneous increase in power density and lowering operating temperature. Thin-film electrolyte (<10 μm) deposition technology is a key step in SOFC production, development of new approach is in great need [2].

Despite existence of well-developed techniques, such as chemical vapor/solution deposition (CVD/CSD) [3], electrochemical deposition (ED) [4,5], thermal spray (TS) [6], physical vapor deposition (PVD) [7–9], all of them have a trend in rising deposition temperatures or establishing high vacuum that causes an increase in cost. The aerosol deposition (AD) also known as vacuum kinetic spraying (VKS) is a technique for deposition of thin [10] and thick [11], gas-tight [12] and porous [13] layers. This technology is based on room temperature impact consolidation (RTIC) phenomenon that gives an opportunity to deposit gas-tight films at room temperature and medium vacuum (100–1000 Pa) [14,15], it makes possible to significantly decrease sintering temperatures. Moreover, AD is a very attractive technique in terms of production of fuel cells, because it can deposit composite layers for SOFC electrodes [16]. The AD method does not exploit expensive equipment and has high deposition rate because it deals with micron and submicron particles [17].

The present work was focused on the aerosol deposition and electrochemical characterization of the anode-supported SOFCs with thin-film electrolyte membranes of 8 mol.% yttria-stabilized zirconia (8YSZ).

2. Experimental section

The model SOFCs fabricated in this work were based on the commercial two-layer anode supports from KCeraCell Co. (Korea) with a thickness of 500 μm (NiO/8YSZ composite). The thin-film solid electrolyte was applied by AD using a laboratory setup described elsewhere [2]. The supersonic aerosol jet of ceramic particles was formed using a 0.5 mm^2 Laval nozzle, with working

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pressure of 400 Pa and nitrogen used as a carrier gas. Starting 8YSZ powder (SOFCMAN, China) was milled with zirconia balls (10 mm) at the speed of 400 rpm to destroy agglomerates and increase aerosol homogeneity. The anode support was placed on a PC-controlled platform and moved to form a rectangular raster with a step of 0.2 mm (motion speed of 3 mm/s); afterwards the raster was rotated by 90°. The deposited solid-electrolyte layers were annealed in air at 1000–1400 °C for 2 h.

The composite cathodes made of 60 wt% of $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ synthesized by the glycine-nitrate technique and 40 wt% of commercial 10Sc1YSZ (Qingdao Terio Corporation, China) were prepared in accordance with the route optimized in previous works [18–20]. The cathodes were screen-printed using Ekra E2 (Asys Group, Germany) instrument and annealed in air at 1100 °C for 2 h.

The thin-film electrolyte layers and model SOFCs were studied using scanning electron microscopy (Supra 50VP, Zeiss, Germany). The electrochemical performance was tested using a computer-controlled setup with isolated fuel and oxidant chambers. Air was used as an oxidant and wet hydrogen (3 vol% H_2O) as a fuel. The range of working temperatures was 650–850 °C. The measurements of current vs. voltage (I-V) curves and impedance spectra were performed using an Autolab PGSTAT302N instrument equipped with FRA32 module (Metrohm, Switzerland). The impedance spectra were collected in a frequency range from 0.1 Hz up to 300 kHz at 20 mV voltage amplitude.

3. Results and discussion

Fig. 1 shows SEM images of the cross-section of thin-film 8YSZ deposited by AD as it is (a) and after sintering at different temperatures (b–f). We found that consolidation of the deposited layer starts at 1000 °C (b). After annealing at temperatures higher than 1200 °C electrolyte layer is gas-tight and shows residual unconnected porosity. The annealing temperature of 1300 °C was chosen as high enough for the formation of a gas-tight electrolyte layer and, thus, optimal. The model SOFCs were fabricated on the anode substrates with the aerosol-deposited electrolyte films sintered at 1300 °C for 2 h.

The model SOFCs were studied by SEM in order to investigate the microstructure and thickness of functional SOFC layers and adhesion at the inner interfaces. SEM images of SOFC cross-sections are shown in Fig. 2. The multilayered structure of SOFCs consists of (from top to bottom) cathode (~15 μm, marked as "C" on Fig. 2), electrolyte (~5 μm, "E"), functional anode layer (~15 μm, "AF") and thick anode support (~0.5 mm, "AS"). At higher magnification (Fig. 2b) it is visible that thin-film electrolyte ("E")

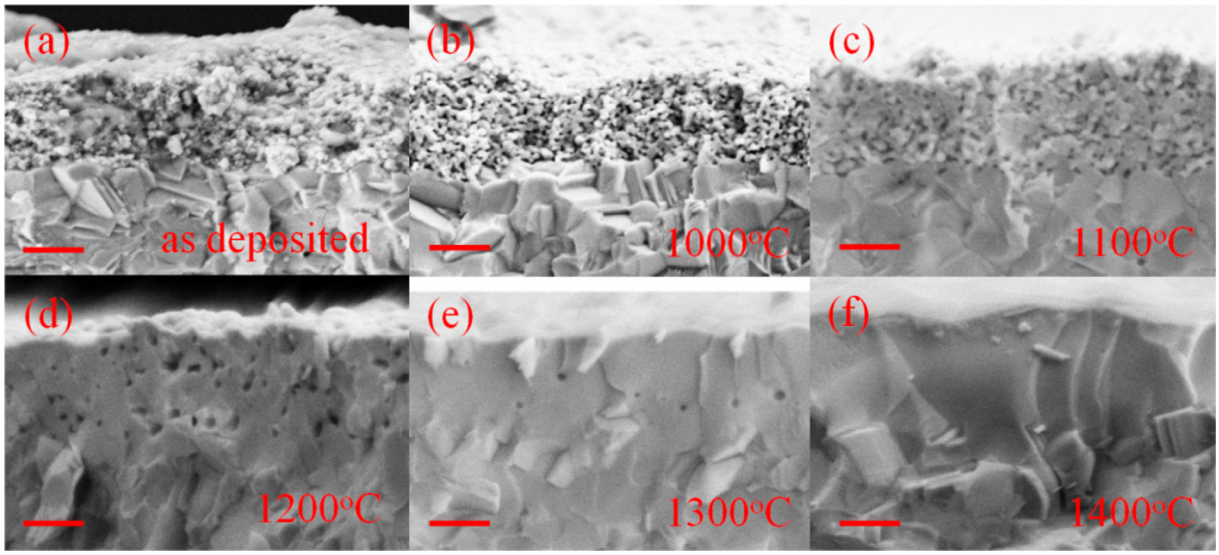

Fig. 1. SEM images of 8YSZ electrolyte film cross-section after deposition (a) and after annealing at 1000 (b), 1100 (c), 1200 (d), 1300 (e) and 1400 °C (f); the bar length corresponds to 1 μm.

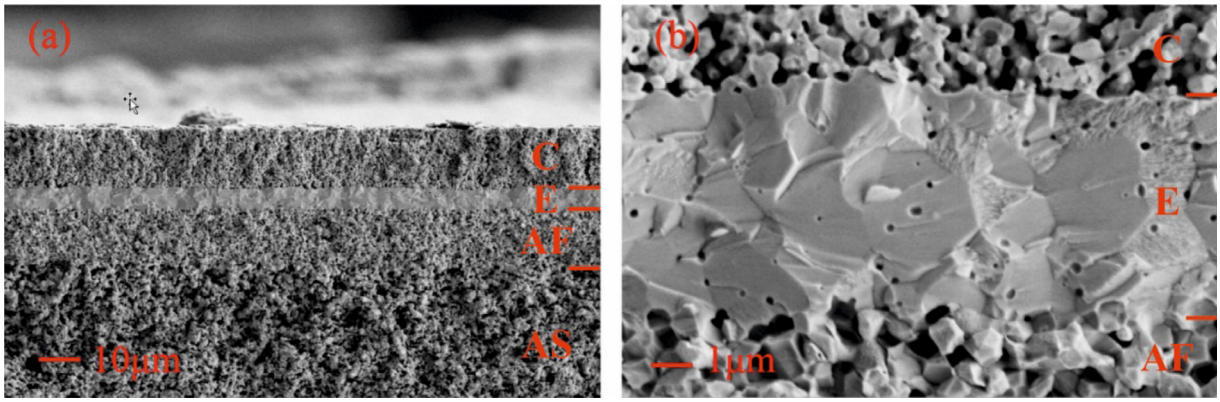

Fig. 2. SEM images of model cell cross-section.

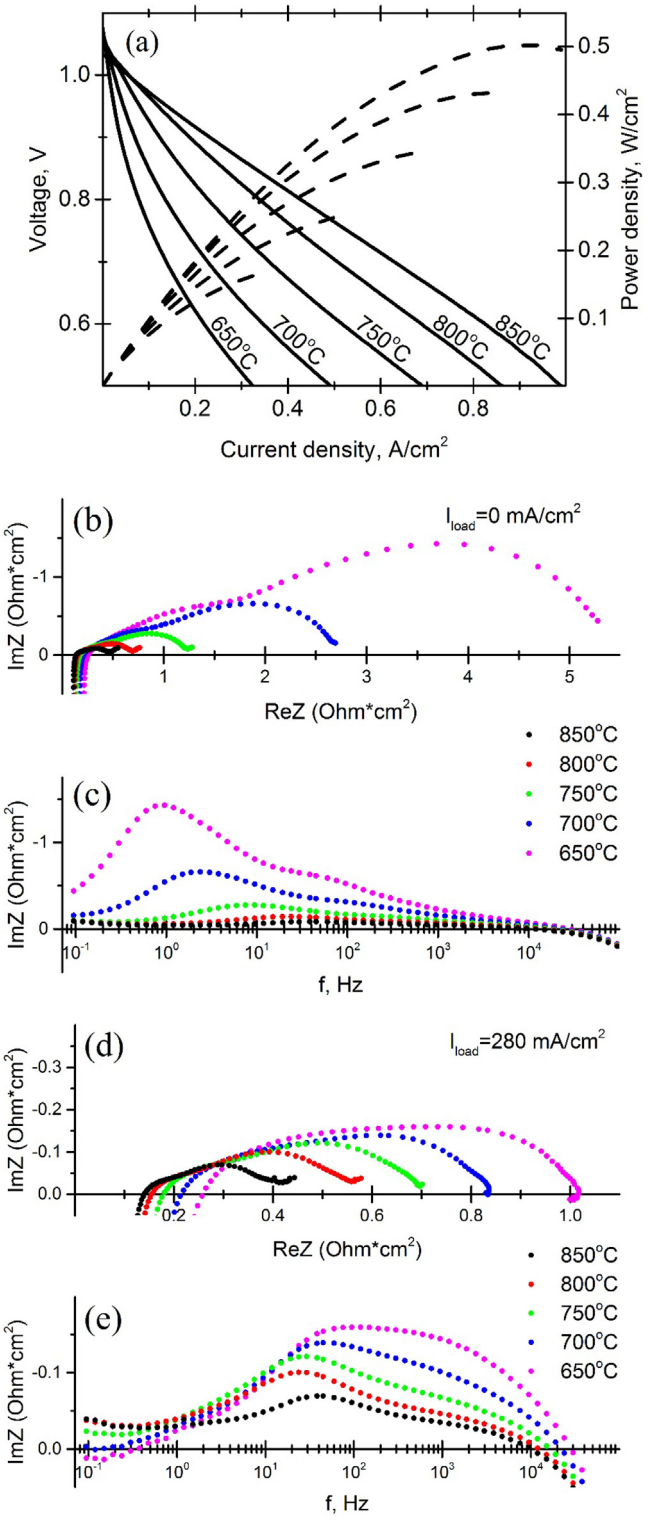

Fig. 3. (a) I-V and power curves of model SOFCs measured for different working temperatures from 650 to 850 °C. (b–e) Impedance spectra and ImZ over frequency dependencies for OCV conditions (b, c) and under 280 mA/cm^2 current load (d, e) for different temperatures.

has a coarse-grained structure (grain size is higher than 1 μm) and high density with isolated pores (<100 nm). A good adhesion at the anode | electrolyte and electrolyte | cathode interfaces should be mentioned as well.

The I-V and power vs. current density curves of the model SOFCs for different working temperatures are presented in Fig. 3a. The open circuit voltage (OCV) is higher than 1 V for all working conditions: it increases at lower temperatures and exceeds the level of 1.08 V at 650 °C. Such OCVs provide a direct evidence of the absence of gas and electronic leaks between the anodic and cathodic chambers of the cell, which indicates the high quality of dense uniform thin-film electrolyte without electron-conducting impurities.

The power density rapidly decreases with decreasing of operating temperature (from 0.5 W/cm^2 at 850 °C to <0.2 W/cm^2 at 650 °C). This behavior is explained by grows of the nonlinear section of the I-V curves (I_{load} < 0.5 A/cm^2). Internal resistance grows mainly due to the polarization part of the impedance (Fig. 3b, d) with a prevailing contribution of low-frequency (0.1–10 Hz) processes (Fig. 3c), which is explained by low ionic conductivity of manganite-based cathodes at OCV conditions [21]. Under current load (Fig. 3e) low-frequency part associated with surface transport phenomenon is eliminated but the contribution of the ohmic losses is steel not dominating as for electrolyte-supported SOFCs [18–20].

4. Conclusions

Fabrication routine and electrochemical performance of planar anode-supported SOFCs with thin-film AD-applied solid electrolyte were described. Electrochemical tests and microstructure investigation showed that deposited layer after annealing at 1300 °C exhibits dense structure with no gas leaks or conductive impurities. Current-voltage curves and impedance spectra showed electrochemical performance to be limited by the polarization of the electrodes, application of more electrochemically active cathode is needed. AD was shown to be suitable for the deposition of dense uniform pore-free anion conductor membrane on anode support. This approach due to high deposition rate in combination with flexibility and cheap equipment is believed to significantly increase the competitiveness of SOFC technologies.

CRediT authorship contribution statement

I.S. Erilin: Investigation, Writing - original draft. **D.A. Agarkov:** Writing - original draft, Writing - review & editing. **I.N. Burmistrov:** Investigation, Visualization, Writing - original draft. **V.E. Pukha:** Investigation, Resources. **D.V. Yalovenko:** Investigation. **N.V. Lyskov:** Investigation, Writing - review & editing. **M.N. Levin:** Funding acquisition, Resources. **S.I. Bredikhin:** Project administration, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: **I.S. Erilin** (Institute of Solid State Physics RAS, Moscow Institute of Physics and Technology), **D.A. Agarkov** (Institute of Solid State Physics RAS, Moscow Institute of Physics and Technology), **I.N. Burmistrov** (Institute of Solid State Physics RAS, Moscow Institute of Physics and Technology), **V.E. Pukha** (Institute of Problems of Chemical Physics RAS), **D.V. Yalovenko** (Institute of Solid State Physics RAS), **N.V. Lyskov** (Institute of Problems of Chemical Physics RAS), **M.N. Levin** (EFKO Group, Biruch Innovation Center), **S.I. Bredikhin** (Institute of Solid State Physics RAS, Moscow Institute of Physics and Technology).

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