DEVELOPMENT OF NANO-STRUCTURED SOLID OXIDE FUEL CELL ELECTRODES

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Introduction

Solid oxide fuel cells (SOFC) are considered as highly efficient and environmentally friendly energy converters for future energy supply systems. They convert directly chemical energy from fuel gases such as hydrogen, natural gas or other hydrocarbons (gasoline, kerosene, biogas) into electrical energy and heat. The basic components of a SOFC cell are the porous electrodes, an anode for fuel supply and a cathode for air supply, which are separated by a gastight but oxygen ion conductive electrolyte layer. This electrolyte usually consists of ionic conductive ceramics such as doped zirconia or ceria whereas a cermet consisting of yttria-stabilized zirconia (YSZ) and nickel is mostly used for the anode and perovskite-type oxides such as doped lanthanum manganite (LSM), lanthanum cobaltite and ferrite (LSF, LSCF) for the cathode.
The electrodes have to provide the reaction sites for the oxidation of the fuel gas at the anode and for the reduction of oxygen molecules at the cathode. Thus, these electrode layers must have a high open porosity to guarantee sufficient supply of fuel and oxidant gases as well as a finely dispersed pore and material distribution to provide extended reaction sites at triple phase boundaries for the electrochemical reactions. These enhanced reaction sites are particularly required close to the interfaces of electrodes and electrolyte, preferably with a graded structure and decreasing pore sizes towards the interfaces.
Thermal spray technology is considered to be a suitable mass production method for solid oxide fuel cells. The development of nano-structured, highly efficient electrode layers to improve electrochemical cell performance is described in this paper. Nano-structured electrode layers were obtained by applying air plasma spraying (APS) with nano-structured powder feedstock for the SOFC anode and a thermal plasma chemical vapor deposition process (TPCVD) using inductively coupled RF plasma and liquid precursors for the cathode.

Experimental

Setup, feedstock and process conditions for APS
Nano-structured anodes were developed using pre-synthesized agglomerated powder consisting of nano-sized primary particles of NiO and YSZ in 60 to 40 vol% ratio. The powder was produced using co-precipitation and spray drying methods. The composite powder was sprayed using air plasma spraying (APS) by a standard F4-type gun with a V-type anode nozzle from Medicoat, Switzerland, on porous FeCrMnTi substrates (48 mm in diameter, 1 mm in thickness) from Plansee, Austria. The plasma enthalpy, heat transfer to particles and particle velocity were experimentally adopted to define spray parameters. The nano-structured deposit was characterized in terms of its structure, gas permeation, high temperature conductivity and electrochemical performance. These characteristics of a nano-structured anode were compared to the conventional one having particle size range around 1 µm.

Setup, feedstock and process conditions for TPCVD
The experiments were performed using a vacuum reactor and a PL50 induction plasma torch from TEKNA Plasma Systems, Sherbrooke/Canada which is operated with a radio frequency generator from Himmelwerk, Germany, at 500 kHz. The RF power was varied in the range from 20 to 30 kW, the chamber pressure was between 12 and 38 kPa and spraying distance between 150 and 600 mm. The plasma gas composition was varied over a wide range from argon/hydrogen mixtures to plasma mainly consisting of oxygen. The precursors were fed with a rate between 1.5 and 3 ml/min by a peristaltic pump using two channels to avoid pulsing. The material was directly injected into the hot plasma core by means of a gas-assisted atomizer. Argon flow rates in the range of 2-10 slpm were used to atomize the precursors. Aqueous solutions of metal nitrates of different concentrations were used as precursors for the preparation of perovskite-type cathode coatings by means of TPCVD.

Results and Discussion

APS of nano-structured SOFC anodes

Promoting short dwell time of particles in medium enthalpy plasma led to partial melting of the surface of agglomerated powder whereas the interior of the agglomerates was conserved. The partially molten surface, which was no-longer nano-structured, led to the adhesion of impacting particles on pre-deposited layer. The interior of the agglomerates remained composed of a network of nano-sized particles and pores as shown in Fig 1. The connective pore network in the deposits led to significantly higher permeability for gases compared to the conventional NiO+YSZ layers (Fig. 2) whereas the electrical conductivity at 800°C (cell operating temperature) for conventional and nano-structured deposits were comparable [1]. However, the conductivity of the nano-structured anode tends to increase for extended period of testing which was explained by phase I of sintering of Ni. During the electrochemical testing at 800°C using 50 to 50 vol% H_2+N_2 mixture as fuel gas, the cells consisting of nano-structured anodes showed 0.8 Ωcm² as polarization resistance instead of 1.08 Ωcm² for the cell with conventional anode which was about 25% improvement.

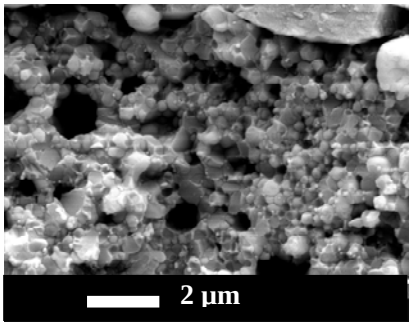

Fig. 1 SEM of the fractured cross section of the nano-structured anode deposit

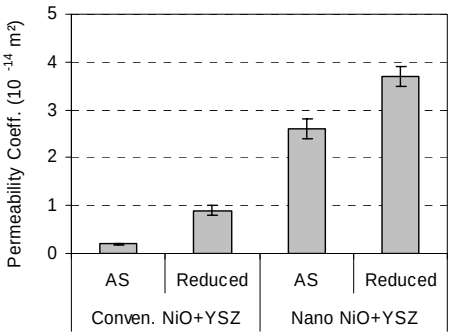

Fig. 2 Comparison of permeability coefficient of conventional and nano-structured anodes

TPCVD of nano-structured SOFC cathodes

Aqueous solutions of metal nitrates which contain the relevant elements La, Pr, Sr, Mn, Fe and Co were used as precursors for the preparation of highly porous perovskite-type cathode coatings by applying the TPCVD method. The solutions vaporize completely in the plasma and condense through heterogeneous nucleation on the substrate surface forming a columnar microstructure that is shown in SEM images of fracture surfaces in Fig.3 [2]. This structure provides a large surface area and an open porosity offering efficient vertical as well as horizontal gas migration paths. This is an ideal microstructure for application as SOFC cathode enabling excellent gas permeability and creating a lot of reaction zones. Deposition rates of up to 30 µm/min were achieved which is orders of magnitudes higher than most of the comparable values found in the literature for TPCVD of oxide layers. Phase purity of the perovskite coatings is not easy to be achieved but we succeeded in preparing pure perovskite phase PSFC (praseodymium strontium cobalt iron oxide), checked by XRD, by replacing La by Pr in the perovskite structure.

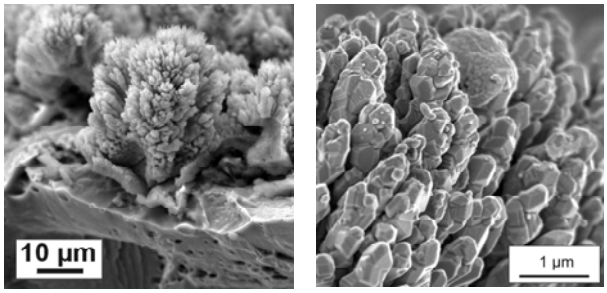

Fig. 3 SEM images of fracture surface of a TPCVD perovskite coating

Conclusion

Nano-structured anodes (fuel electrode) and cathodes (air electrode) for solid oxide fuel cells were developed by plasma deposition technologies exhibiting improved permeability and enlarged reaction zones, thus, leading to enhanced cell performance.

References

1.Ilhan, Z. and Ansar, S.A. Solid oxide fuel cell with nano-structured fuel electrode. MRS Spring Meeting 2007, on CD-ROM, San Francisco, (2007)

2.Schiller, G., Müller, M., Bouyer, E. and v.Bradke, M. RF plasma synthesis and deposition of SOFC materials. Proc. of 16th Int. Symposium on Plasma Chemistry, Taormina, Italy, Paper 121 (2003)