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Preparation of functional layers for anode-supported solid oxide fuel cells by the reverse roll coating process

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ABSTRACT

The roll coating technique represents a novel method for applying functional layers to solid oxide fuel cells (SOFCs). This fast process is already used for mass production in other branches of industry and offers a high degree of automation. It was utilized for coating specially developed anode (NiO + 8YSZ, 8YSZ: 8 mol% yttria-stabilized zirconia) and electrolyte (8YSZ) suspensions on green and pre-sintered tape-cast anode supports (NiO + 8YSZ). The layers formed were co-fired in a single step at 1400 °C for 5 h. As a result, the electrolyte exhibited a thickness of 14–18 μm and sufficient gas tightness. Complete cells with a screen-printed and sintered $La_{0.65}Sr_{0.3}MnO_{3-\delta}$ (LSM)/8YSZ cathode yielded a current density of 0.9–1.1 A cm^{-2} at 800 °C and 0.7 V, which is lower than the performance of non-co-fired slip-cast or screen-printed Jülich standard cells with thinner anode and electrolyte layers. The contribution of the cell components to the total area-specific resistance (ASR) was calculated by analyzing the distribution function of the relaxation times (DRTs) of measured electrochemical impedance spectra (EIS) and indicates the potential improvement in the cell performance achievable by reducing the thickness of the roll-coated layers. The results show that the anode-supported planar half-cells can be fabricated cost-effectively by combining roll coating with subsequent co-firing.

1. Introduction

Significant advances have been reported for increasing the performance of planar SOFCs and their durability by employing new materials with an optimized microstructure and modern coating technologies [1–6]. Recent examples include plasma-sprayed protective coatings on the interconnects, which allowed degradation rates as low as 3 mV/1000 h [5], and thin-film electrolytes with a thickness of 1.0–1.5 μm applied by sol–gel technology yielding the highest performance of SOFCs to date [6]. In addition, high-throughput manufacturing processes that allow low manufacturing costs are required to bring the SOFC technology to market. Among all SOFC cell designs, planar anode-supported cells yield the highest power output. They are therefore mainly used to build stacks with high power densities, e.g. for mobile and smaller stationary applications. Tape casting is considered a viable industrial manufacturing process for anode and electrolyte substrates and is already widely used [1,7]. The functional layers are commonly applied by screen printing [8–10] or wet powder spraying [2,11]. Whereas wet powder spraying suffers from a relatively large overspray, and spraying hazardous materials like NiO represents a safety issue, screen printing is a batch processes and therefore limited in speed. Interesting alternatives to both methods are to laminate tape-cast functional layers on a support in its green state [12] or to directly tape cast complete half-cells starting with the electrolyte (reverse tape-cast cell [7]). With these methods, it is possible to apply thin coatings with a thickness of a few micrometers on green tapes over their total length before the multi-layer system is decollated and co-fired.

Roll coating represents a scalable and very simple coating technique. It allows continuous coating on either sintered or green substrates; even contoured coatings are feasible with appropriate rolls (gravure coating [13] or relief printing). Defect-free wet coatings of 12–1200 μm thickness can be applied with industrial machines at speeds of approx. 1–500 m min^{-1}, utilizing coating liquids with a large range of viscosities (0.05–500 Pa s) [14]. With sol–gels as coating liquids, dried thicknesses as low as 1 μm were reported [15], thus demonstrating the feasibility of coating thin films by reverse roll coating. Whereas the roll coating process is widely used in the paper, textile, metal, optical and electronic industry, and also in the manufacturing of PEM fuel cells [16], it has yet not been applied to SOFC manufacturing.

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Table 1
Materials and composition of the anode and electrolyte suspension used.

	Solid content	Solvent	Binder
Anode	22.4 wt.% NiO (J.T. Baker)17.6 wt.% 8YSZ (TZ-8Y)	58 wt.% dibasic esters	2 wt.% ethyl cellulose 45–55 mPa s
Electrolyte	40 wt.% 8YSZ (TZ-8Y)	58 wt.% dibasic esters	2 wt.% ethyl cellulose 45–55 mPa s

Depending on the orientation of rotation of the applicator roll relative to the sample being coated, two varieties of the roll coating process can be distinguished: forward and reverse roll coating. During reverse roll coating, the applicator roll rotates opposite to the transport direction of the sample. This coating method, which was first described by Münch [17], can achieve an even distribution of the coated liquid on irregular surfaces [18] and is known to display less surface instabilities, such as ribbing phenomena, than forward roll coating, especially if non-Newtonian liquids are processed [19,20]. Recognizing these advantages, the layers in this work were applied using reverse roll coating. Both green tapes and pre-sintered anode supports were coated with an anode and electrolyte layer prepared from submicron powders utilizing an advanced, commercially available laboratory reverse roll coater with a maximum transport speed of 60 m min^{-1}. In this work, transport speeds of 5 m min^{-1} were used, which is already much higher than the coating speeds of any other coating process Jülich has utilized in the past.

Advanced analysis of the electrochemical impedance spectra allowed us to correlate the observed microstructural properties of the manufactured cells, e.g. the layer thickness, with the electrochemical performance [21]. Utilizing the distribution function of relaxation times (DRTs), the ASR of single cell components could be calculated and used for the interpretation of the obtained data.

2. Experimental

2.1. Substrates

The porous ceramic substrates were prepared by tape casting starting from commercially available 8YSZ powder (FYT13.0-005H, Unitec Ceramics Ltd., Stafford, U.K.) and NiO powder (Mallinckrodt Baker Inc., Phillipsburg, NJ). The tape casting slurry was based on a solvent mixture of ethanol/methyl ethyl ketone. Additionally, it contained a dispersant (Nuosperse FX9086, Elementis Specialities Inc., Hightstown, NJ), a binder (polyvinyl butyral) and plasticizers (polyethylene glycol/Solusolv S-2075, Solutia Deutschland GmbH, Frankfurt, Germany). First, 60 wt.% NiO and 40 wt.% 8YSZ powder were homogenized with the dispersant in the solvent. Further organic additives, such as the binder and plasticizer, were then added in an adequate ratio to produce a slurry with well-adapted rheological properties [7,23]. Then, the slip was degassed. Due to lack of availability of this newly developed slip, some coatings were applied on a tape produced with a slightly different recipe described in Ref. [24]. For this recipe partly different organics and a graphite pore former was used. Both tapes displayed the same performance during electrochemical quality assurance tests (as the cell performance is governed by the functional layers) and can be, in this respect, considered interchangeable. All tapes were cast by the well-known doctor blade process (FGA 500, SAMA Maschinenbau GmbH, Weißenstadt, Germany) and subsequently dried. Finally, the green substrate tapes with a thickness of 0.58 mm were cut into dimensions of 200 mm × 120 mm. Some tapes, prepared from the recipe described in Ref. [23], were used in the green state as coating supports. Other tapes, prepared from the recipe according to Ref. [24], were debindered and pre-sintered at 1230 °C for 3 h, thereby shrinking to dimensions of approx. 184 mm × 110 mm × 0.53 mm. This cell format was chosen because such cells can be used in lightweight stacks in future work [25].

2.2. Coating and sintering

The ceramic starting material for the production of the anode layer was a mixture composed of 56 wt.% NiO (Mallinckrodt Baker Inc., Phillipsburg, NJ) and 44 wt.% 8YSZ (TZ-8Y, Tosoh Corp., Tokyo, Japan). Before mixing the two powders in ethanol, the NiO was ground in ethanol to an average grain size of about 0.3 μm. The 8YSZ powder was calcined at 1230 °C for 3 h and then wet ball-milled to 0.5 μm. The calcined 8YSZ was used for the anode and electrolyte layer. The roll coating suspensions for both layers were prepared in the same way. A mixture of succinic, glutaric and adipic acid dimethyl esters, also known as dibasic ester (DBE), was chosen as the solvent (INVISTA Resins & Fibers GmbH, Hattersheim am Main, Germany). Low vapor pressure, low price and good environmental compatibility render DBE a suitable organic solvent for industrial applications. Another important fact is that it does not react with the rubber coating of the applicator roll. The solvent was mixed with an ethyl cellulose binder to prevent drying cracks in the coatings and to reach a promising green density and strength. The dry ceramic powders were added to the binder solution, and then homogenized with 10 mm zirconia grinding balls for 170 h on a roller bench to achieve an agglomerate-free suspension. The detailed composition of the anode and electrolyte suspension is summarized in Table 1. The lick roll always remained in contact with the applicator roll and rotated in the same orientation and at the same speed as the transport roll to ensure a constant thickness of the wet film on the applicator roll regardless of the presence of a substrate. Green tapes as well as pre-sintered tapes were directly coated with an anode functional layer by roll coating. After drying for 2 h in a dust-free hood, the electrolyte layer was applied in the same way. All coatings were performed with a laboratory reverse roll coater type RRC-BW 350 from Mathis AG (Oberhasli, Switzerland, Fig. 1a). The functional layers were either applied to the air side or the foil side of the tape to see whether this has any influence on the properties of the functional layers or bending of the cells after sintering.

Fig. 1(b) illustrates the roll coating process. The dip roll rotates in a liquor trough filled with the suspension. Then the suspension is transferred from the dip roll to the rubber-coated applicator roll. The distance between these two rolls influences the coating thickness, and can be precisely set with two precision clock gauges. The speed of both rolls is variable and can be adjusted by two digital displays. From the applicator roll, the suspension is directly applied to the substrate. The substrate is moved under the applicator roll by the rubber-coated transport roll, enabling homogeneous coating of the whole sample surface. The speed of the transport roll is also infinitely variable. The distance between the applicator roll and transport roll can be set according to the substrate thickness. The rotational direction of the transport roll can be chosen in the same or in the opposite direction relative to the applicator roll. Here, all coatings were applied in the reverse mode. Table 2 summarizes the coating parameters used in this study. The different thicknesses of green tapes and pre-sintered substrates resulted in slightly different gap settings. All tests were carried out using cells with a roll-coated anode and electrolyte layer and compared with traditional screen-printed layers. In order interpret the electrochemical impedance spectroscopy data better, cells with a roll-coated electrolyte and no anode layer were also prepared and tested.