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Development of novel metal-supported proton ceramic electrolyser cell with thin film BZY15–Ni electrode and BZY15 electrolyte

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ABSTRACT

Metal supports for planar MS-PCEC were manufactured using tape-casting of low-cost ferritic stainless steel. A coating protecting the metal support against oxidation was applied by vacuum infiltration and a buffer layer of $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_{3-\delta}$ (LSTN) was further deposited to smoothen the surface. The $BaZr_{0.85}Y_{0.15}O_{3-\delta}$–NiO (BZY15–NiO) cathode and the $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ (BZY15) electrolyte were applied by pulsed laser deposition (PLD) at elevated substrate temperatures (at 700 °C and 600 °C, respectively). The main challenges are related to the restrictions in sintering temperature and atmosphere induced by the metal support, as well as strict demands on the roughness of substrates used for PLD. Reduction treatment of the half cells confirmed that NiO in the BZY15–NiO layer was reduced to Ni, resulting in increased porosity of the BZY15–Ni cathode, while keeping the columnar and dense microstructure of the BZY15 electrolyte. Initial electrochemical testing with a Pt anode showed a total resistance of 40 $\Omega \cdot cm^2$ at 600 °C. Through this work important advances in using metal supports and thin films in planar PCEC assemblies have been made.

Introduction

Hydrogen production via electrolysis of water has positive environmental impact compared to reforming of fossil fuel without CO_2 capture. The total energy demand of the process drops considerably when water shifts from liquid to gas phase and higher operation temperatures are beneficial. Water electrolysis using proton-exchange membrane (PEM) cells operates at 70–80 °C and requires a large amount of electricity [1,2], making hydrogen production with solid oxide electrolysis cells (SOECs) more viable [3,4], particularly when waste heat from industry or renewables sources (*e.g.*, solar or geothermal plants) are utilized as the heat source.

For SOECs based on conventional oxygen-ion conductors, the need to remove water from the produced hydrogen, the low electrode stability, and the high operating temperature (750–1000 °C which is higher than that of the waste heat from industries), limit the deployment. Proton ceramic electrolyser cell (PCEC) alleviates these challenges by producing electrochemically pressurized, dry hydrogen at operating temperatures between 500 and 700 °C, and the dry H_2 produced avoid risk of oxidation of hydrogen electrode (cathode). Introduction of thin film electrodes and proton conducting electrolyte on a

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metal support (MS-PCEC) enables better thermal conduction (reduced thermal stresses) and the possibility for additional reduction in the operating temperature due to reduced resistance of the thin film functional layers. Lower operation temperatures open up for the use of cheaper materials such as steel-based interconnects and metal-supported electrodes. PCEC further avoids steam corrosion of the metal support and oxidation of the Ni electrode observed for SOECs [5], since the oxygen activity in the produced H_2 (dry) at the metal support is below the stability range of the oxides. Overall, PCEC is favourable for coupling to renewable energies and increased lifetime [6].

Porous metal supports are expected to have high potential for mobile applications because of their relatively high resistance to thermal and mechanical stress [7]. They also enable the use of well-established joining techniques such as welding and brazing [8]. Metal-supported cells, however, call for low temperature processing routes since the metal alloy can only withstand sintering up to ~1300 °C without partly densification and/or melting. This is not compatible with the processing of high temperature proton conducting ceramics such as barium zirconate-based materials (*e.g.*, $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ = BZY15), which typically require sintering temperatures ≥ 1500 °C. These restrictions therefore exclude traditional powder based synthesis of BZY15–Ni cermet electrode and BZY15 electrolyte and other processing routes must be developed for the fabrication of MS-PCEC. To the authors knowledge, no reports on MS-PCEC or MS-PCFC have been published.

Fabrication of PCFC with a BZY electrolyte using traditional high temperature routes, shows high ohmic resistance of the electrolyte due to high grain boundary resistance resulting in large ohmic resistance and low power outputs of the cell [9,10]. Recently, highly conductive, grain-boundary free thin-film BZY electrolytes have been fabricated using pulsed laser deposition (PLD) [11,12]. PLD is a versatile method for optimized processing of electrode and electrolyte thin films for fuel cells and electrolyser cells at lower temperatures [11–18]. PLD has for instance been used to deposit thin electrolyte layers on porous YSZ–NiO electrode supports [19–21]. PLD fabrication has mostly been performed with small samples. However, recently, large-area deposition with PLD became available, in diameter up to 200 mm [22]. These systems are used for high-speed deposition of thin films such as piezoelectric $Pb(Zr,Ti)O_3$ (PZT) for micro-electronical–mechanical systems (MEMS) applications, ionic conducting YSZ for fuel cells or transparent electrical conducting layers on sensitive substrates, like flexible displays and OLEDs. PLD has the advantage of stoichiometric transfer and a strong bonding with the substrate of the deposited composition. PLD requires smooth surfaces for successful deposition of thin films. In a very recent work, a thin nano-crystalline electrode functional layer of BZY–NiO was deposited by PLD on a tape casted layer of BZY–NiO in order to reduce grain size and pore sizes and provide flat surface favourable for BZY electrolyte deposition by PLD [12]. Significantly improved power outputs were obtained from the fuel cell configuration with maximum power density of 740 $mWcm^{-2}$ at 600 °C.

As shown in our previous paper, the poor sinterability of BZY15–Ni on the metal support in reducing atmosphere and temperature ~1300 °C hindered the successful deposition of a dense electrolyte film [23]. In the current work it was therefore necessary to develop a smooth conducting buffer layer on the metal support with sintering temperature below 1200 °C. Reported results on $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_{3-\delta}$ [24] indicate that the material is a good candidate for such intermediary layers between the metal substrate and other thin film cell components implemented by PLD. Exsolution of metallic Ni nanoparticles during operation was even found to coincide with a dramatic (absolute) drop in the water splitting onset potential [25].

In this work, we present a fabrication procedure for manufacturing of single MS-PCEC cells with a thin electrolyte using scalable and flexible techniques. For the first time, MS-PCEC have been made with a cathode and an electrolyte deposited by PLD as illustrated in Fig. 1. The metal substrate is prepared by water-based tape-casting and protective Lanthanum–Manganese–Cobalt coatings are applied to avoid oxidation during cell fabrication and testing using vacuum infiltration [26]. A conducting buffer layer is deposited by spray-coating, while PLD is applied to grow thin layers of BZY15–NiO electrode and BZY15 electrolyte. The manufacturing process enables to decrease the total thickness of the electrolyser cell and eliminates the need for high temperature sintering steps above 1200 °C which are detrimental to the metal support. The oxidation of coated and uncoated metal supports has been studied by thermogravimetry and compared to elucidate effects of the coating on oxidation kinetics.

Experimental

The fabrication procedure is illustrated in Fig. 1. Highly porous and robust metal supports of low cost ferritic stainless steel (20.6% Cr) were prepared using aqueous tape-casting as described in Ref. [26]. The particle size distribution of the metallic powder from Höganäs AB, Sweden, was characterised by means of static image analysis with the Malvern Morphology G3 apparatus.

The green tapes were pre-annealed at temperatures between 1100 and 1300 °C in reducing atmosphere (4% H_2 in Ar) to obtain a support with sufficient mechanical strength for the cathode and electrolyte fabrication steps and at the same time preserve sufficient shrinkage capability to match densification of the buffer layer. A protective coating was applied on the sintered supports by vacuum infiltration of a lanthanum–manganese–cobalt solution with $La(Mn_{0.5}Co_{0.5})_{0.8}$ stoichiometry, followed by fast curing; 30 s at 900 °C in air [26].

A layer of $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_3$ (LSTN, CerPoTech, Norway) was deposited on the metal support with a SONOTEK spray coater. The final layer should have a defect free surface with roughness below 3 μm and without pores larger than 1 μm to allow the subsequent deposition of the electrolyte by PLD. Several LSTN suspensions, with varying solid content from 22 to 37 wt%, were prepared by dispersing LSTN powder in isopropanol for 1 h before 10 min sonification was applied using a BRANSON sonifier probe. It is essential to prevent extensive infiltration of LSTN powder into the support during spray coating and to smoothen the surface of the spray-coated layer promoting deposition of defect free layers with PLD. The number of spray-coating depositions applied to obtain a 40 μm