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Application of sol gel spin coated yttria-stabilized zirconia layers for the improvement of solid oxide fuel cell electrolytes produced by atmospheric plasma spraying

Lars Rose [a,b,*], Olivera Kesler [b,c], Zhaolin Tang [d], Alan Burgess [d]

[a] University of British Columbia, Department of Materials Engineering, 309-6350 Stores Road, Vancouver, British Columbia, V6T 1Z4, Canada
[b] National Research Council, Institute for Fuel Cell Innovation, 4250 Wesbrook Mall, Vancouver, British Columbia, V6T 1W5, Canada
[c] University of British Columbia, Department of Mechanical Engineering, 2054-6250 Applied Science Lane, Vancouver, British Columbia, V6T 1Z4, Canada
[d] Northwest Mettech Corp., 467 Mountain Hwy, North Vancouver, British Columbia, V7J 2L3, Canada

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Abstract

Due to its high thermal stability and purely oxide ionic conductivity, yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material for solid oxide fuel cells (SOFCs). Standard electrolyte fabrication techniques for planar SOFCs involve wet ceramic techniques such as tape-casting or screen printing, requiring sintering steps at temperatures above 1300 °C. Plasma spraying (PS) may provide a more rapid and cost efficient method to produce SOFCs without sintering. High-temperature sintering requires long processing times and can lead to oxidation of metal alloys used as mechanical supports, or to detrimental interreactions between the electrolyte and adjacent electrode layers. This study investigates the use of spin coated sol gel derived YSZ precursor solutions to fill the pores present in plasma sprayed YSZ layers, and to enhance the surface area for reaction at the electrolyte-cathode interface, without the use of high-temperature firing steps. The effects of different plasma conditions and sol concentrations and solid loadings on the gas permeability and fuel cell performance have been investigated.

Keywords: Atmospheric plasma spraying; Sol gel; Spin coating; YSZ; Porosity reduction; OCV

1. Introduction

Fuel cells electrochemically convert the chemical energy in fuels to electrical energy, more efficiently and with much lower pollution than electrical generators based on combustion. Solid oxide fuel cells (SOFCs), with their high (>600 °C) operating temperatures, offer the advantage of high efficiency, especially in co-generation. The capability to use a large selection of fuels, including hydrocarbons and carbon monoxide, also gives SOFCs flexibility not found in low-temperature fuel cells that are poisoned by CO.

SOFC production typically includes wet ceramic techniques, such as tape-casting or extrusion and screen printing or slurry spraying, followed by at least one firing step [1]. Dense YSZ films for SOFCs can also be applied on tubular cells by chemical vapour deposition (CVD) [2]. However, vacuum-based deposition techniques such as CVD are very expensive. Spin coating combined with high-temperature firing steps (1300 °C) can also be used to produce stand-alone YSZ electrolyte layers with low (1–2%) porosity, but only by utilizing lower-conductivity compositions of YSZ that are not fully stabilized [3].

Plasma spraying (PS) is often used for the deposition of electrolyte or ceramic interconnect layers in tubular cells. PS offers the possibility to deposit ceramic, metal, or composite layers, without the need for high-temperature sintering. PS is also an easier method for coating large areas and complex shapes that are difficult to coat with planar wet ceramic deposition techniques. Consequently, PS is uniquely suited for deposition of patterned strip ceramic interconnects on tubular cells that cannot be fired at high-temperatures, to avoid interreactions between cathode and electrolyte.

* Corresponding author at: National Research Council, Institute for Fuel Cell Innovation Canada, 4250 Wesbrook Mall, V6T 1W5 Vancouver, BC, Canada. Tel.: +1 604 2213000x5538; fax: +1 604 2213001.
E-mail address: lars.rose@nrc-cnrc.gc.ca (L. Rose).

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More recently, plasma spraying has been studied as a technique with the potential to deposit all of the electrochemically active fuel cell layers on a low-cost, robust metallic interconnect (IC) support layer with no subsequent high-temperature firing step. This approach reduces the material cost of the fuel cell and minimizes the risk of oxidation of the metallic IC during processing [4]. By avoiding the lengthy high-temperature firing steps, the need for parallel production lines for mass production is also decreased. Material compatibility problems such as interreactions between layers at high sintering temperatures can also be avoided.

PS is a well-established technique to produce both powders and thick (micrometre to millimetre range) coatings [5,6]. Due to the large amount of heat generated in a plasma flame, nearly any material can be coated. Atmospheric plasma spraying (APS), performed in air at atmospheric pressure [7], offers significant advantages over vacuum plasma spraying (VPS). VPS is typically used to produce thin, dense, flat coatings, but can also create porous coatings with up to 15% porosity [8]. The necessity to create and maintain vacuum conditions during deposition increases capital and operating cost of VPS deposition. High gas flow rates through the torch, usually several hundred litres per minute, have to be pumped out of the chambers during deposition. Consequently, this batch processing technique is less favourable for mass production, both in terms of cost and scalability. APS, on the other hand, because it is performed in air under atmospheric pressure, has capital and operating costs that are approximately one order of magnitude lower compared to those of VPS [9].

The properties of PS coating layers vary significantly with feedstock types. Feedstocks can be liquids, powders, or solid rods [10]. For powder based delivery, particle shape, particle size, and size distribution are of importance [11]. Powders that are very small are susceptible to vapourization in the plasma torch or to difficulties with feeding. Large particles may not fully melt in the plasma, and may bounce off the substrate surface if they have remained solid or have re-solidified in flight. The wide range of feedstocks available for plasma spraying provides the process with the flexibility that is required for the spraying of different SOFC layers. These layers can consist of different combinations of materials, with widely varying porosity requirements. This flexibility makes the process potentially more readily adaptable to the fabrication of SOFCs compared to other deposition processes that utilize only one feedstock type.

PS processing is commonly used to create ceramic YSZ coatings for thermal barrier applications, typically with a porosity distribution from 5 to 15% [12]. Denser layers are possible with the use of appropriate spraying and feedstock parameters. For thermal barrier coatings (TBCs) to be effective, a large thermal gradient must exist over only a few hundred micrometer thick YSZ coating [13–15]. Formation of such a thermal gradient is facilitated by the use of porous PS YSZ coatings, since the porosity decreases the thermal conductivity of the coatings. In applying PS to the production of SOFC electrolytes or electrodes containing YSZ, on the other hand, a much more stringently controlled set of spraying conditions is required. Higher porosities are required for sufficient gas flow through the electrodes to ensure high performance and efficiency. Fully dense electrolyte layers that prevent gas crossover are needed to avoid reactant gas mixing. Gas leakage across the electrolyte leads to lower open circuit voltages (OCVs) and fuel combustion, resulting in lower fuel cell performance and efficiency compared to cells with dense electrolytes.

Coatings created by APS are difficult to produce in thin layers that are fully dense as deposited. Multiple methods have therefore been investigated to reduce the porosity of PS YSZ TBCs, and thereby improve their corrosion resistance and thermomechanical stability. Methods previously investigated include laser glazing [16,17], detonation gun spraying [17], phosphate solution sealing [17], drop coating of ceria-doped zirconia sols for sealing [18], silica sol infiltration of PS chromia coatings [19], and spark plasma sintering [20]. Furthermore, water based nitrate solution decomposition after simple specimen immersion [21,22] and forced vacuum impregnation [23] have been used to improve gas tightness of plasma sprayed coatings.

Sol gel (SG) processing is a well known ceramic fabrication technique that generally does not require high-temperature sintering to produce oxide materials. The SG technique is therefore particularly well-suited as a candidate for use in processing materials for SOFC applications [24]. SG processing is regularly used to produce both dense coatings [25] and powder materials [26]. SG processing is also used to produce high surface area components. Therefore, the technique is also potentially suitable for increasing the electrochemical activity of fuel cell electrode-electrolyte interfaces [27].

Spin coating, organic-based sols, and composite sols with suspended powder have not previously been reported to improve plasma sprayed coatings, TBCs, or SOFC electrolytes, nor to enhance the surface area of electrolyte-electrode interfaces. Investigations of the effects of varying sol concentrations and powder loadings have also not been reported previously in these applications. The present study investigates the densification and surface area enhancement of PS SOFC electrolytes on tape-cast NiO/YSZ substrates. Organic-based YSZ sols with varying chemical compositions and composite sol gel (CSG) slurries with varying solid loadings were applied to the PS YSZ layers by spin coating, and the resulting performance changes investigated.

2. Experimental procedure

2.1. NiO/YSZ substrates

NiO-YSZ anode support substrates were tape-cast (Engineering Associates Inc., model ephea223.5.1.T) on mylar sheet. A slurry with a total dry powder loading of 1 kg, with carbon sphere pore formers added to increase anode gas diffusivity, was produced by mixing and ball milling the slurry mixture components listed in Table 1.

The ethanol, toluene and fish oil were ball milled for over 15 h before adding the powders. The full mixture was then ball milled again for 24 h. Prior to tape-casting a 1.2 mm thick tape in a class 1000 cleanroom, the slurry was degassed in vacuum for 30 min. The resulting tape was dried at room temperature for