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# Controllable deposition of gadolinium doped ceria electrolyte films by magnetic-field-assisted electrostatic spray deposition

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## ABSTRACT

This paper describes a simple and low-temperature approach to fabrication of dense and crack-free gadolinium doped ceria (GDC) thin films with controllable deposition by a magnetic-field-assisted electrostatic spray deposition technique. The influences of external permanent magnets on the deposition of GDC films were investigated. The coating area deposited using two magnets with the same pole arrangement decreased in comparison with the case of no magnets, whereas the largest deposition area was obtained in the system of the opposite poles. Analysis of as-deposited films at 450 °C indicated the formation of uniform, smooth and dense thin films with a single-phase fluorite structure. The films produced in the system using same poles were thicker, smaller in crystallite size and smoother than those fabricated under other conditions. Additionally, the GDC film deposited using the same pole arrangement showed the maximum in electrical conductivity of about $2.5 \times 10^{-2}$ S/cm at a low operating temperature of 500 °C.

## 1. Introduction

During the last two decades, considerable effort has been devoted to research and development in solid oxide fuel cells (SOFCs). They promise a high conversion efficiency of chemical energy to electric power with negligible pollution and are attractive for use in the co-generation of electric power [1,2]. However, their high operating temperature hinders their commercialization due to difficulties in material selection and other problems, such as high operation costs. Lowering the operating temperature of SOFCs can provide higher thermodynamic efficiency, enhanced durability of cell performance, and the use of cheaper stainless steel interconnects. Currently, one of the critical targets for the commercialization of SOFCs is lowering the operating temperature to an intermediate-to-low temperature range of 500–800 °C without sacrificing cell efficiency [3,4]. In general, there are two approaches to reduce the operating temperature: the use of alternative electrolyte materials with higher ionic conductivity and the decrease in electrolyte thickness. Doped ceria materials have been considered as potential solid electrolytes for SOFCs due to their relatively high ionic conductivities even at low temperatures [5,6]. Furthermore, various fabrication techniques have been developed for the preparation of SOFC components, such as physical vapor deposition [7], chemical vapor deposition [8], electrochemical vapor deposition [9], metal-organic chemical vapor deposition [10], sputtering [11], and flame assisted vapor deposition [12]. These methods generally require special raw materials and targets, sophisticated equipment and a well-controlled atmosphere, therefore increasing the capital investment and fabrication costs.

An alternative thin-film forming method is electrostatic spray deposition (ESD), in which a liquid flowing through a capillary nozzle can be subjected to a high voltage to produce a spray and move towards a grounded substrate, upon which it ultimately deposits and builds up a solid layer. This method has several advantages, such as a simple setup, non-vacuum conditions, inexpensive and non-toxic precursors, and a well-controlled structure and composition [13–15]. Gadolinium doped ceria (GDC) electrolyte films for SOFCs have been prepared using the ESD technique [16–19]. Nevertheless, controlling the deposition coverage area is still difficult. Our earlier studies have shown that the geometry of the nozzle tip drastically influences the deposition area and the agglomeration of particles on samarium doped ceria electrolyte films prepared by the ESD process [20]. Previous studies of reactive magnetron sputtering have reported that the distribution of the discharge above the sputtered targets of the dual magnetron depends on the magnetic field, resulting in controlling the deposition area and film thickness [21]. Control of the deposition area, thickness, and uniformity without crack is also hard to achieve simultaneously. Until now, no studies have been performed that examined the thin film fabrication with magnetic-field-assisted ESD technique. We, therefore, investigated the effects of the magnetic field arising from external

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permanent magnets on the deposition of GDC thin films based on ESD technique. In addition, the use of magnetic-field-assisted ESD technique to fabricate dense and crack-free GDC thin films at a low temperature was also examined.

## 2. Experimental details

### 2.1. The magnetic-field-assisted ESD setup

A schematic diagram of the equipment used in this work is shown in Fig. 1(a). This system is mainly composed of four parts: (1) two bar magnets (6 × 10 × 0.8 $cm^3$) having a magnetic induction intensity (B) of 0.025 T placed 6 cm above the substrate; (2) an electrostatic spray unit, including a high direct current (DC) voltage power supply and a stainless steel nozzle (0.0394 cm inner diameter); (3) a liquid feeding unit, including a syringe pump and a liquid container; and (4) a temperature control unit, including a temperature controller and a heating element. A DC voltage of 15 kV was applied between the nozzle and a stainless steel (316 L) substrate. A precursor solution was emitted at the orifice of the nozzle and, consequently, a spray was deposited as a thin layer on the substrate.

### 2.2. The effect of external permanent magnets on deposition

#### 2.2.1. The deposition coverage area

A precursor solution with Gd:Ce mole ratio of 0.1:0.9, stoichiometric amounts of gadolinium nitrate hexahydrate (99.99%, Aldrich Chemical) and cerium nitrate hexahydrate (99.99%, Aldrich Chemical) dissolved in ethanol (99%, Fluka) at a total concentration of 0.01 M, was pumped towards the nozzle at a flow rate of 1 ml/h. The substrate temperature, the deposition time, and the nozzle-to-substrate distance were set at 100 °C, 2 h, and 9 cm, respectively. To evaluate the influence of the external magnetic field on the deposition area, the spraying was operated under three conditions: without and with two magnets (same and opposite poles). The distance between the two magnets was kept at 8 cm. Two arrangements of magnet position, same and opposite magnetic poles, were located, as illustrated in Fig. 1(b). These films were labeled as NM, SP, OP for the deposition with no magnet, same pole magnets and opposite pole magnets, respectively.

#### 2.2.2. The fabrication of GDC films using magnetic-field-assisted ESD

The same precursor solution used in Section 2.2.1 was fed into the nozzle at a flow rate of 1 ml/h. For each deposition, the distance between the nozzle and the substrate was 9 cm, while the deposition

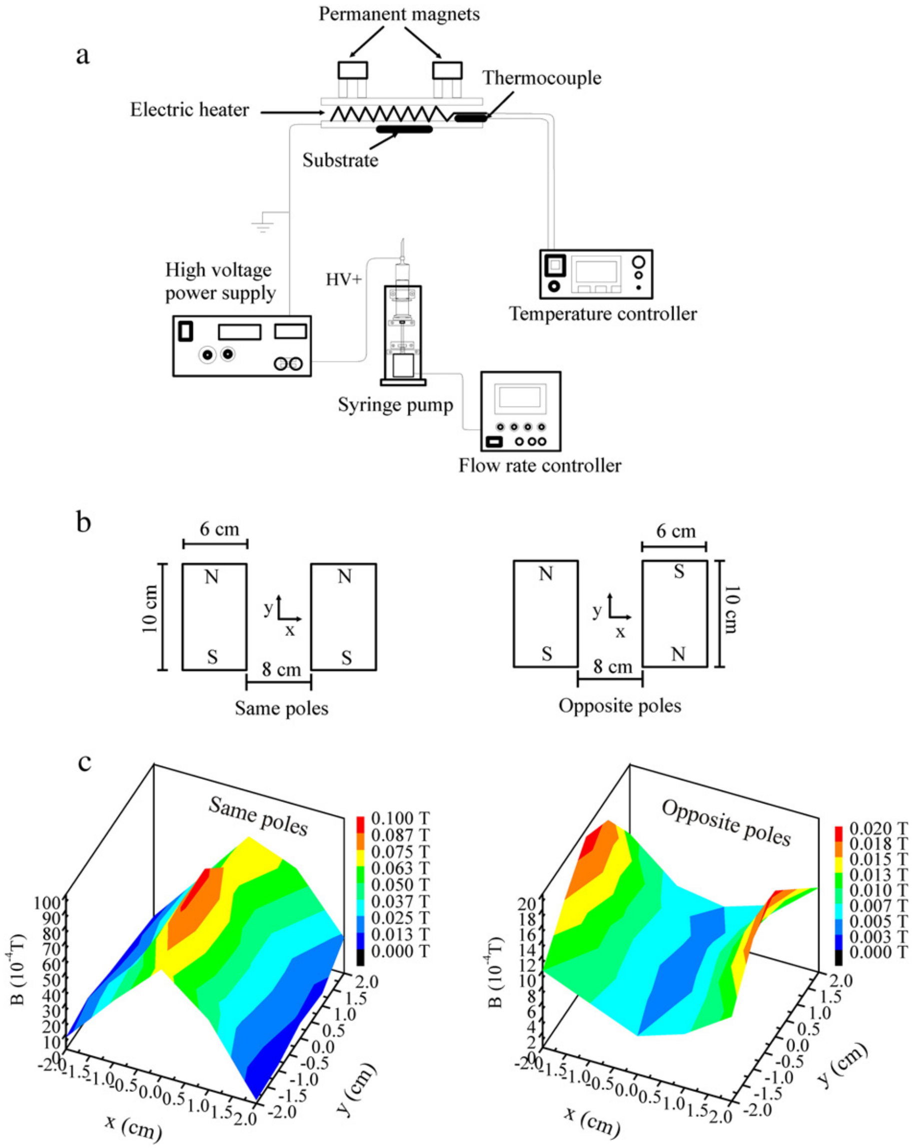

**Fig. 1.** (a) Schematic view of magnetic-field-assisted ESD setup, (b) the arrangement of two permanent magnets and (c) 3D maps of magnetic induction intensity at a given area.