



The Physical Characterisation of Coating via Electrophoretic Deposition (EPD) with Voltage and Duration Variables for Solid Oxide Fuel Cell Application - A Review

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Abstract: This review covers the basics of electrophoretic deposition (EPD) techniques and its effect on the physical characterisation for solid oxide fuel cell (SOFC) application. SOFC have gotten a lot of attention in recent years as a future alternative energy generation technology because of their ability to utilise hydrocarbon fuels and high efficiency. On top of that, the characterisation of coating often affected by the variation of voltage (30V, 50V, 70V and 100V). The higher the voltage (100V), the more deposition weight obtained. The thickness and morphology of the coating layer were determined by using Scanning Electron Microscopy (SEM). The duration of deposition (1.5 minutes to 3 minutes) also crucial as it can influence the thickness of the coating layer which in the range 11.90 μm to 29.30 μm . Therefore, this paper will benefit future works on SOFC application.

Keywords: SOFC, EPD, physical characterisation

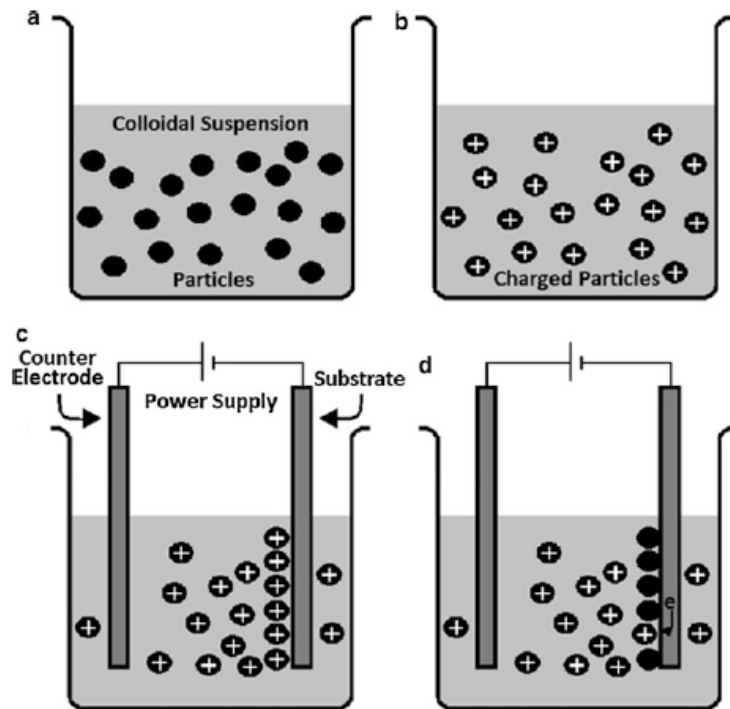
1. Introduction

Recently Solid Oxide Fuel Cells (SOFCs) have sparked a lot of interest for commercialisation as the next generation of energy devices because of their excellent power efficiency, a generally clean final product, and fuel flexibility [1]. SOFCs have the benefit of being able to use a variety of fuels, including hydrogen, hydrocarbons, and carbon monoxide [2]. One method for achieving this aim is to lower the ohmic resistance of SOFCs by reducing the electrolyte thickness to an optimal amount. As a result, several ways for producing thin gas-tight layers of stabilised zirconia as the traditional electrolyte material have been presented [3]. Wet procedures are the most appealing of the offered techniques because of their low production costs and high mass productivity [4]. Electrophoretic Deposition (EPD), which has been intensively investigated for the production of electrolyte and other components of SOFCs due to its simplicity, rapid film generation, and little or no additives, is one of the most promising wet techniques [5].

Electrophoretic deposition (EPD) is a material processing technique using the deposition of charged particles in a stable colloidal suspension on a conductive substrate, acting as one of the two oppositely charged electrodes in the EPD cell [6]. The deposited particles form the intended material or device [5]. EPD is an interesting technique in academia and industry because of its highly versatile application, simple apparatus and equipment, short processing time, cost-effectiveness, ease of modification, desirable dense packing of particles in the final piece, high quality of the microstructures produced, easy production of geometrically complicated shapes, and simple control of thickness and morphology an interesting technique both in academia and industry [7,8,9].

In EPD, the state of suspended particles and their evolution during the process can be controlled and manipulated. Moreover, an appropriate and accurate choice of processing variables could enable the production of dense and homogeneous or porous microstructures [10,11]. A combustible substrate that can be removed by further heating in the sintering process is used for fabricating complicated shapes [9,10]. However, the operator must be wary of potential fractures caused by drying and sintering when it comes to coatings. The impartible nature of the method causes these thermally generated fractures, and resolving this challenge is critical to the ultimate surface quality [12].

As shown in Fig.1, (a) colloidal particles are highly distributed and able to move freely and independently in a solvent suspension; (b) the surface charge of the particles is determined by the solvent's electrochemical equilibrium; (c) particles migrate electrophoretically through the bulk of the solution to the oppositely charged electrode (substrate), and (d) the substrate is coated by a neutralised, a firmly deposited layer of particles [13]. In principle, any particulate solid (ceramics, polymers, metals, and their composites) or biological entity (proteins, cells, enzymes, etc.) can be used in EPD as long as the particles can be stably suspended and produce a substantial surface charge in interaction with the solvent. As a result, EPD is a method in which the moving species are solid particles, the liquid medium's necessary conductance is minimal, and organic liquids are favoured. The liquid in EPD remains stationary while particles and ions move due to electrostatic attraction. It may also be utilised to create uniform deposits on large product sizes with excellent microstructural homogeneity for a range of equipment and complicated forms, and it can be done at room temperature.



- Four steps of EPD; (a) dispersion; (b) electrochemical charging; (c) electrophoresis; (d) deposition [13]

2. Physical Characterisation of Coating

2.1 Morphological Characterisation

Scanning Electron Microscopy (SEM) provides a high resolution, high magnification image of the sample material by emitting a finely focused electron beam to the sample. The beam interacts with the molecular composition of the sample [14]. Interactions create a series of observable electron energies that are analysed by a scanning electron microscope to generate a three-dimensional SEM that provides a high resolution, high magnification image of the sample material by emitting a finely focused electron beam onto the sample. This beam interacts with the molecular composition of the sample. These interactions produce a series of measurable electron energies that are analysed by SEM to create a three-dimensional image.

Borojeni *et al.*, [1] studied Yttria Stabilized Zirconia (YSZ) from Tosoh Co. (TZ-8Y) and used it as the ceramic powder and a mixture of acetylacetone (Merck Co.) and ethanol (Absolute-Merck Co.) was applied as the solvent in their studies. 0.5g of YSZ powder was added to 50 ml solvent, dispersed by an ultrasonic bath (Power Sonic 405, 350W) for 10 minutes and aged for one day till its chemical reaction arrived to an equilibrium [11,14]. Subsequently, the ultrasonic bath agitated the suspension to remove the sediment, followed by one-hour pre-sedimentation to eliminate large agglomerates. Before EPD testing, the suspension was agitated ultrasonically again for a few seconds to

homogenise [11]. The experiment was conducted at different voltage of 50V/cm, 75V/cm and 100V/cm with deposition duration of 3,2 and 1.5 minutes, respectively. Fig. 2 shows the morphological surface of the coating. However, there was no significant change in the packing structure of the films.

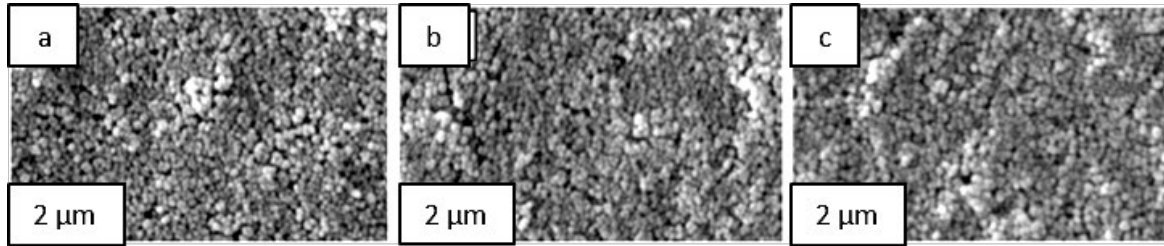


Fig. 2 - SEM micrograph of YSZ green films' surface deposited on NiO-YSZ a)50V/cm, 3min b)75V/cm, 2min c)100V/cm, 1.5min [1]

Molin *et al.*, [15] used commercially available $Mn_{1.5}Co_{1.5}O_4$ spinel powder with the mean particle size of $0.36 \mu m$ and a specific surface area of $12.0 m^2/g$ was obtained from American Elements (USA). The spinel powder was dispersed in a mixture of ethanol and deionised water (volume ratio of 60/40 of EtOH/H₂O) with a solid content of $37.5 g L^{-1}$. The suspension was homogenised by placing in an ultrasonic bath for 15 minutes (Bandelin Sonorex, Germany). It was advised for each deposition, a new suspension must be used. A 316 stainless steel sheet with similar dimensions to the Crofer 22 APU substrate was used as the counter electrode in the EPD cell. The voltage applied for the experiment is 50V/cm, with a deposition duration is 20s. Fig. 3 shows the morphological of EPD coating that looks quite porous on the surface, exhibiting well-connected grains with size around $1 \mu m$.

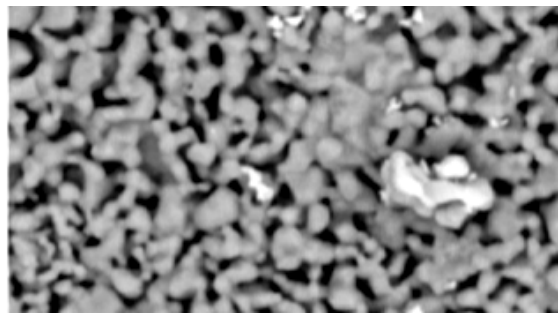


Fig. 3 - SEM image of EPD coating [15]

Choudhary *et al.*, [2] used $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$ (BZCY) as a material for EPD process. Two parallel conducting plates (stainless steel 304 of size $10 mm \times 30 mm$) separated by 10 mm gap were used as the electrodes. Prior to each deposition, the suspensions were ultrasonicated for approximately 20 min for a homogeneous mixture and to avoid any kind of agglomeration and settlement of large or heavy particles. EPD was performed at constant DC voltage of 30V, 50V and 70V with a deposition duration of 1 min to 5 min. The deposited samples were then carefully taken out from the suspension and allowed to dry overnight at room temperature and weighed to determine the deposit yield. Overall it can be seen that BZCY deposited coatings have finer and nicely closely packed microstructures, and surface morphology is overall homogenous. The deposition at each condition was crack-free even without any use of external agencies such as binders or charging agents.

Fig. 44 shows that BZCY deposited at 30V was less compaction as compared to higher voltages. The deposition of BZCY powders at 50V and 70V on conducting substrate were more evenly and compact enough [2]. The surface morphology of the BZCY deposited coatings has finer and nicely closely packed microstructures, and surface morphology is overall homogenous. While looking keenly and comparing these micrographs, it can be realised that film deposited at 30V showed less compaction than higher voltages at 50V and 70V. However, few pores were still present at higher voltage deposited BZCY film. Deposition at 70V produces the best coating.

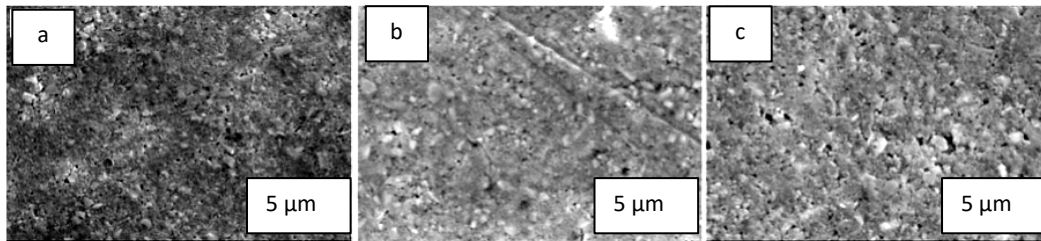


Fig. 4 - FESEM micrograph of BZCY deposited (green coating on conducting substrate) at the condition of (a) 30V for 2 min, (b) 50V for 2 min, and (c) 70V for 2 min [2]

2.2 EPD Deposition Thickness

According to Borojeni *et al.*, 2015 the deposition thickness obtained from EPD process is 5.21μm, where the voltage applied is 50V/cm with 3min deposition duration. Then at 75V/cm and 2min deposition duration, the thickness obtained is 11.9μm. Whereas, at 100V/cm with 1.5min duration, 29.3μm are obtained [1].

Molin *et al.*, 2017 state that the deposition thickness obtained from their experiment is 15μm with some porous layer in the outer part. The voltage applied is 50V/cm with 20s deposition duration [15]. While Choudhary *et al.* [2] shows an EPD process conducted with voltage applied at 30V, 50V and 70V with deposition duration is between 1 min to 5 min. The overall thickness deposition is measured out to be around 13μm. Table 1 summarises the previous findings in deposition thickness.

Table 1 - Material, applied voltage and duration of deposition

Author	Material	Voltage	Duration	Thickness
Borojeni, Raissi, & Maghsoudipour, 2015	Yttria Stabilized Zirconia (YSZ) from Tosoh Co. (TZ-8Y) was used as the ceramic powder and a mixture of acetylacetone (Merck Co.) and ethanol (Absolute-Merck Co.) was applied as the solvent in our experiments (1:1 by vol.).	25, 50, 75, 100V/cm	6, 3, 2, 1.5 min respectively	50V/cm, 3min = 5.21 μm 75V/cm, 2min = 11.9μm 100V/cm, 1.5min = 29.3μm
Molin <i>et al.</i> , 2017	Commercially available Mn _{1.5} Co _{1.5} O ₄ spinel powder (mean particle size of 0.36μm and a specific surface area of 12.0 m ² /g) was obtained from American Elements (USA)	50 V/cm	20s	has a 15μm thick Mn-Co layer with a more porous layer in the outer part
Choudhary, Anwar, Besra, & Anwar, 2019	BaZr _{0.4} Ce _{0.4} Y _{0.2} O _{3-δ} (BZCY)	30V, 50V and 70 V	1-5 minutes	The film thickness was measured out to be ~13 μm

Analysis of thickness sections in the as-prepared state, shown in Table 1, indicates a clear difference in the voltage and duration times thickness. The thickness is between 5.21um to 29.3um. Since the thickness of the obtained layer by applying 75V/cm was closer to the optimum thickness for SOFC electrolyte [1]

2.3 EPD Weight Deposited

Faraday’s second law of electrolysis states that when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight [16].

Borojeni, Raissi, & Maghsoudipour, 2015 found that the weight he deposited had to be changed at the same time to counteract the effect of altering the field. According to Hamaker theory, the deposited weight can be calculated by the following equation below.

The equation is as shown :

$$W = f \int \mu c E s dt \tag{1}$$

Where;

W	: deposited weight
μ	: electrophoretic mobility of the particles
c	: concentration of the particles in the solvent
E	: applied electrical field,
s	: surface of working electrode,
t	: deposition time,
f	: efficiency factor

It was revealed that although E and t in their experiments did not change, the thickness of the deposited films was increased by increasing the applied electrical field. On the other hand, research conducted recently by Choudhary, Anwar, Besra, & Anwar [2] found that the deposition rate on conducting substrate was higher as compared to non-conducting substrate (anode) but both systems obeying Hamaker's law which indicates the linearity of yield with deposition time [12]. However, more deposition weight was also obtained at the higher voltage level [16,17]. Table 2 summarises the previous findings in weight deposition of EPD

Table 2 - Weight deposited in previous research

Author	Materials	Parameters	Weight Deposited
Borojeni, Raissi, & Maghsoudipour, 2015	Yttria Stabilized Zirconia (YSZ) from Tosoh Co. (TZ-8Y) was used as the ceramic powder and a mixture of acetylacetone (Merck Co.) and ethanol (Absolute-Merck Co.)	<ul style="list-style-type: none"> • 25, 50, 75, 100V/cm • 6, 3, 2, 1.5 min respectively 	deposited weight had to be varied simultaneously to offset the influence of changing the field. According to Hamaker theory, the deposited weight can be calculated by the following equation
$W = f \int \mu c E s dt$			
Choudhary, Anwar, Besra, & Anwar, 2019	BaZr _{0.4} Ce _{0.4} Y _{0.2} O _{3-δ} (BZCY)	<ul style="list-style-type: none"> • 30V, 50V and 70 V • 1-5 minutes 	The deposition rate on conducting substrate was higher as compared to non-conducting substrate (anode) but both systems obeying Hamaker's law which indicates the linearity of yield with deposition time
Mirzaei et al., 2016	Nanostructured MnCo ₂ O ₄ powder with 99% purity was supplied from Fuel Cell Materials (USA)	<ul style="list-style-type: none"> • 60V • 240s 	More deposition weight was also obtained at the higher voltage level

According to Table 2, During the 2 minute deposition time, a 75V/cm electrical field was applied. The thickness (12m) was close to the optimal electrolyte thickness (5-10m) for SOFCs. As a result, another parameter that influenced the deposited weight had to be changed simultaneously to counteract the field change. Where W is the deposited weight, μ is the electrophoretic mobility of the particles, c is the concentration of the particles in the solvent, E is the applied electrical field, s is the surface of working electrode, t is the deposition time, and f is an efficiency factor (in case all particles reaching the working electrode deposit on it, f regards as 1, otherwise f considers less than 1). If the deposition weight is relatively low, it may be assumed that the electrical field and particle concentration remained almost constant during the EPD process. Consequently, Et stayed constant in our tests, and deposition duration of 1.5, 2, 3, and 6 minutes were employed for fields of 100, 75, 50, and 25V/cm, respectively. Anticipated that the thickness of obtained layers in all experiments would be the same, and only the coatings' microstructure would be varied [1].

3. Conclusion

The characterisation of coating can be affected by the variation of voltage and deposition time. The best voltage variation is between 25V to 100V, and the best deposition time is between 20s to 6min. With those voltage and deposition time variation, it well evenly coating surface and micro size thickness can be obtained. Thus, it is suggested to use voltage and time deposition of 25V to 100V and 20s to 6min respectively to obtain the best coating through EPD process.

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