



# Oxide ceramics with unidirectional pore channels by electrophoretic deposition



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## ABSTRACT

Disc-shaped alumina, alumina-toughened zirconia, and mullite green bodies, few millimetres in thickness, with parallel aligned pore channels were produced by an electrophoretic deposition method that takes advantage of the gas generation by electrolysis in aqueous suspensions. Appropriate amounts of an anionic polyelectrolyte, chosen on the basis of zeta potential measurements, and ammonia solution were used as additives. Adding ammonia promoted the gas evolution at a given polyelectrolyte amount. The electrolyte content influenced the porosity values and the diameters of the pore channels. Volume fractions of the pore channels in the sintered bodies up to 40% were determined by computed tomography in combination with 3D image analysis. The maxima of the pore diameter distributions of the sintered samples were in the range between 200 and 300  $\mu\text{m}$ .

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## 1. Introduction

The method used for fabricating ceramic green bodies with unidirectional pore channels is a combination of two processes: electrophoretic deposition (EPD) of powder particles from aqueous suspensions and simultaneous gas generation by electrolysis.

### 1.1. Electrophoretic deposition of ceramic materials

Electrophoretic deposition is the motion of particles in a liquid medium under the influence of an electric field due to their surface charge and the formation of a deposit at the oppositely charged electrode or an ion-permeable substrate, such as a membrane, in front of this electrode. Powders with particle sizes in the range from nanometres to a few micrometres can be used for EPD, but the method is particularly suitable for submicron and nano-sized powders. The possibility to achieve a dense and homogeneous particle packing in the deposits from well-dispersed, stable suspensions is one of the main advantages of EPD. Free-standing ceramic green bodies, functionally graded materials, ceramic laminates, fibre-reinforced composites, and coatings can be produced by elec-

trophoretic deposition [1–4]. The use of aqueous suspensions has economic advantages over that of organic dispersion media and is more environmentally friendly. However, in contrast to the aim of the present work, gas bubble formation by electrolysis of water has to be prevented in most applications of EPD. Several approaches for solving this problem were developed, such as the above-mentioned deposition at a membrane placed between the electrodes [5]. In recent years, the EPD using asymmetric AC or pulsed DC fields instead of a continuous DC field has been attracting increasing interest as promising method for producing “bubble-free” thick deposits from aqueous suspensions [6–13].

EPD requires a sufficiently high electrophoretic mobility and suspension stability for the movement of the particles towards the deposition electrode and for a high packing density and homogeneity in the deposits. These requirements can be fulfilled by adjusting a pH value and/or adding a deflocculant that leads to high values of the zeta potential and, consequently, to suspension stabilisation by double-layer repulsion. Polyelectrolytes, such as polyacrylates or polymethacrylates, are common deflocculants in ceramic processing [14,15]. They can impart suspension stability by combined double layer and steric repulsion (“electrosteric stabilisation”).

Either the voltage applied between the electrodes or the current is kept constant during the EPD. In constant-voltage EPD, the increasing potential difference across the deposit causes a decrease in current and in the effective field strength, the driving force for the particle movement, with time [1,16]. The decrease in the effective field strength can be avoided under constant-current conditions

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[1]. However, the field strength at a given current depends on the conductivity of the suspension.

### 1.2. Gas evolution by electrolysis

Electrolysis of water produces hydrogen by cathodic reduction and oxygen by anodic oxidation. According to Faraday's first law of electrolysis, "the quantities of substances involved in the chemical change are proportional to the quantity of electricity which passes through the electrolyte" [17]. The efficiency of water electrolysis can be enhanced by adding electrolytes (acids, bases, salts) that increase the electrical conductivity. For example, concentrated potassium hydroxide is used in industrial hydrogen production by water electrolysis. For choosing suitable electrolytes it is important to consider that the electrochemical oxidation/reduction of the electrolyte ions may be thermodynamically or kinetically favoured over that of water, depending on the standard potentials and further factors such as overpotentials at the used electrode materials and the concentration [18]. In order to produce hydrogen gas at the cathode, the reduction of metal ions of the electrolyte must not prevail. Sodium bromide (NaBr) in aqueous solution is an example for a salt which does not increase gas evolution at the anode; on the contrary, it is used in industrial electrophoretic enamelling in order to avoid anodic gas formation because the oxidation of the bromide to sodium bromate ( $\text{NaBrO}_3$ ) is favoured [19]. The products of electrolysis reactions competing to that of water can also be gaseous, such as ethane and carbon dioxide evolved at platinum anodes by Kolbe electrolysis of acetate solutions [20].

For the purpose of promoting gas generation in order to form pore channels during electrophoretic deposition of ceramic powders, the chemical composition of the gas would be in principle of secondary importance. However, impurities of the ceramic have to be avoided. Furthermore, the gas bubble composition is one of the factors which can influence their generation, growth, and release from the electrode during electrolysis of electrolyte solutions. Adsorbed species on the electrode, the surfactant properties of solution species, electrode roughness, buoyance, electrostatic forces if the bubbles are charged, and, of course, the applied voltage are further influencing factors [21]. In ceramic suspensions and, moreover, in combination with the electrophoretic motion of the particles to and their deposition at the electrode, the conditions become more complex.

### 1.3. EPD with simultaneous gas evolution for producing porous ceramics

The electrophoretic method that takes advantage of the gas evolution by electrolysis for producing ceramics with pore channels, which may be useful for applications such as filters, burner elements, or catalyst supports, is the topic of an US patent by Kerkar, published in 1994 [22]. As exemplary embodiment, the fabrication of alumina tubes with a wall thickness of about 1 mm and conical pores radiating from the inner to the outer surface of the tube is described. The green bodies were produced by anodic electrophoretic deposition from aqueous suspensions comprising the ceramic powder, sodium hydroxide solution, a deflocculant, a binder, and a defoaming agent. Graphite rods were used as deposition electrode and afterwards burnt out in an intermediate step during sintering. The narrow ends of the pores were about 1  $\mu\text{m}$ , the wide ends about 30  $\mu\text{m}$  in diameter. In a second exemplary embodiment, zirconia powder was used instead of alumina. Similar results were obtained. Furthermore, a graphite crucible and an alumina crucible with graphite paper and an additional graphite coating served as deposition electrodes for the EPD from the above-mentioned alumina slurry [22]. Nakahira et al. produced alumina tubes with radially aligned pore channels by cathodic EPD on

graphite rods. The pH values of the suspensions, adjusted by means of hydrochloric acid solution, were in the range between 2.5 and 4.0 [23].

Two types of aqueous suspensions were used in previous own investigations for preparing planar yttria-stabilised zirconia green bodies with parallel aligned channel pores by EPD at platinum foil or gauze. The particles of the first suspension type were positively charged. Electrophoretic mobility and suspension stability were already sufficiently high for a successful EPD without any additives, but small amounts of electrolyte were necessary in order to promote electrolysis and to enable the formation of channel-like pores by an appropriate rate of gas evolution at the deposition electrode, the cathode in this case. Acetic acid was chosen for this purpose because it could be removed from the deposit by thermal treatment without leaving residues [24–26]. The second suspension type contained an anionic polyelectrolyte (Dolapix PC 21/Zschimmer & Schwarz, Germany) and ammonia. Suspensions with this additive combination proved suitable for forming zirconia deposits with unidirectional pore channels by EPD at the anode [26]. The resulting porous structures obtained from both types of suspension composition could be controlled by the electrolyte content, the EPD parameters, and the structure of the deposition electrode [24–26].

Using the second suspension type but another commercial deflocculant, the application of the method to further oxide materials – alumina, alumina-toughened zirconia, and mullite – has been investigated in the present work.

## 2. Experimental procedure

The used powders are listed in Table 1. Aqueous suspensions with a solids content of 10 vol% were prepared by stirring for 10 min and subsequent ultrasonic agitation for 3 min by means of the ultrasonic homogeniser "Sonopuls HD 2200" (Bandelin, Germany). Heating during ultrasonication was avoided by a cooling bath. After the ultrasonic treatment, the temperature of the suspensions was adjusted to 21 °C.

Following additives were used:

- the deflocculant Dolapix CA (Zschimmer & Schwarz, Germany), which is an aqueous solution of an alkali-free, synthetic polyelectrolyte with an active ingredient concentration of approx. 25% and a pH value of approx. 8.5 according to manufacturer's information, and
- aqueous ammonia solution (25 %  $\text{NH}_3$ , BDH Prolabo, VWR International, Germany).

Suitable polyelectrolyte contents for preparing stable suspensions were chosen on the basis of electroacoustic measurements of the zeta potential using the "Multi-frequency zeta potential analyser PA Field ESA" (Partikel Analytik Messgeräte, Germany). The zeta potential curves have been recently published elsewhere [27]. In the present paper, only the zeta potential and, in addition, the simultaneously measured pH value and specific electrical conductivity of the alumina suspension as a function of the additive concentration are shown as an example for discussing the effect of the additives. In a first measurement, Dolapix CA was added by means of an automatic titrator in 50 steps up to a maximum amount of 2.5 wt%. (The Dolapix CA amount in this paper is expressed as a percentage of powder weight.) In a second measurement, the effect of ammonia solution on the zeta potential of a suspension containing a given Dolapix CA amount, chosen from the first measured zeta potential curve, was studied. The ammonia solution was added in 50 steps up to an amount of 0.1 ml per g of powder. The suspension

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