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Effect of HCl on electrophoretic deposition of yttria stabilized zirconia particles in organic solvents

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Abstract

This study investigates the electrophoretic deposition (EPD) of YSZ particles onto a metal substrate from an organic solvent, the conductivity of which was manipulated by HCl additions. The green density is dependent on electrical conductivity and deposition time. It was found that a uniform coating with up to 67% relative green density could be produced after 10 min deposition from a 20 g/L suspension with electrical conductivity in the range of 10–15 μS/cm (0.5–0.7 mM HCl concentration). Direct measurements of the green YSZ coating density were supported by micro-indentation data using a spherical indenter.

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1. Introduction

It is commonly accepted that suspension dispersion has a decisive effect on the green density of deposits produced by electrophoretic deposition (EPD).[1,2] Well dispersed, homogeneous and deagglomerated particles are more able to pack into a dense deposit, in common with all colloidal processing techniques[3] in which pH, ionic strength and solid concentration all influence dispersion.[4] Optimum packing also requires sufficient time for particles to rearrange during EPD. For instance, Chen et al.[1] observed a porosity gradient, with a more porous structure close to the substrate where deposition was more rapid.

The pH, ionic strength and solid concentration parameters (which are all interrelated with suspension conductivity) can influence the rate of EPD and all three can vary during the EPD process,[3] especially for a static suspension (i.e. without ultrasonic-vibration or stirring). Anné et al.[5] developed a mathematical model to describe the deposition yield during EPD, taking into account the influence of the solid loading in the suspension and the deposition efficiency. They described the electric field as a function of the current in the deposition cell and the conductivity of the suspension, allowing a changing electric field during the deposition experiment as a function of time to be accounted for. Anné's equation suggests that the potential over the deposit is influenced by the ratio of the conductivity of the suspension and deposit. Therefore, we consider that a highly conductive suspension and a poorly conductive deposit are beneficial for the formation of coatings with a uniform thickness on an electrically non-uniform substrate surface.

Ferrari and Moreno[6] reported that the deposited mass per unit area is proportional to zeta potential divided by conductivity if the concentrations of particles in suspension, electric current and deposition time are fixed. Their model suggests the sticking probability of particles to particles within the deposit is unity, which leaves suspension conductivity as the controlling parameter for EPD. When the particles have a high enough zeta-potential to deposit, the electrophoretic deposition-rate and deposition-probability must decrease with increasing suspension conductivity. Again, it is assumed that the particles are the majority current carriers, and the free-ions in the system are ignored.

In the extreme case of an artificially changed suspension, Ji et al.[7] reported that the wet density of EPD coatings increased after immersing an as-deposited wet coating in a pure solvent under a D.C. electric field. They referred to this as electric field densification (EFD). They attributed the increase in packing density of EPD wet coatings to the rearrangement of particles by electro-osmotic flow, and considered the rearrangement ability of deposited particles to be proportional to the strength of the local electric field in the deposit. The local electric field around a deposited particle is distorted by the presence of charges on the particle surface, causing an electro-osmotic flow that can

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pull particles together to form aggregation.[8–10] However, the EFD had limited effect on green and free sintered coating densities despite the significant increase in wet coating density.[11] To our knowledge, there has been little study on effect of the EPD suspension conductivity or/and EPD time on the density of the EPD coating after drying, which we term as green density in this study.

In this work, suspensions were prepared by dispersing submicrometer yttria-stabilized zirconia (YSZ) particles in a mixed organic solvent with HCl addition. With application of a D.C. electric field, the YSZ particles were deposited on an electrode substrate in the prepared suspensions without stirring. The suspension conductivity and pH value as well as the green density were recorded to investigate the particle packing mechanism. Micro-indentation with a spherical tipped indenter was used to quantify the mechanical properties of the EPD green coatings, in relation to the green density and the EPD condition. The mechanical properties of the EPD powder compacts are expected to be determined by a range of issues, such as porosity, void size, particle shape, and particle binding, which can be related to the density.[12]

2. Experimental procedure

2.1. Suspension preparation

Scanning electron microscopy (SEM, XL30 FEG, Philips, Netherlands) shows that the mean primary particle size of the 8 mol% yttria-stabilized-zirconia powder (YSZ, >99%, cubic phase, HSY-8.0, Pi-KEM, UK) was 0.20 μm with a standard deviation of 0.05 μm (50 particles were measured), however most particles were agglomerated. Size measurement using laser diffraction (Micro Trac X100, Malvern, Worcestershire, UK) revealed a model agglomerate size of around 0.27 μm with 90% of the agglomerates smaller than 1 μm (Fig. 3). We used a mixture of absolute ethanol (Et-OH, >99%, Sigma–Aldrich, UK) and acetylacetone (ACAC, >99%, Sigma–Aldrich, UK) with a molar ratio of 7:4 as the solvent for all suspensions.[13] This mixture is referred to as "the mixed solvent" throughout this paper. HCl (0.1 mol/L in distilled water) was used to adjust suspension pH and conductivity. Suspensions, with solid concentration in the range of 20–100 g/L (0.3–1.5 vol%) were prepared by weighing YSZ in a glass beaker, adding 40 ml of the mixed solvent and an appropriate amount of HCl, followed by 120 s ultrasonication using an ultrasonic probe (22.5 kHz, MICROSON, Ultrasonic Cell Disruptor, Misonix, Famingdale, NY). The suspension stability was evaluated by the relative sedimentation height (R.S.H.) method over 1800 min.

2.2. EPD of YSZ coatings

The green coatings were deposited on vertical Fecralloy substrates (Fe 72.8, Cr 22, Al 5, Y 0.1 and Zr 0.1 (wt%), Goodfellow, UK). EPD was carried out in freshly prepared suspensions with a constant D.C. electric field of 50 V cm^{-1} applied (Consort-E863, Belgium). The distance between a platinum counter electrode (anode) and Fecralloy foil (cathode) was 10 mm. The deposition time is varied within the range of 2–14 min to achieve green coatings with thickness in the range of 100–500 μm after ambient drying overnight.

2.3. Characterization methods

2.3.1. Conductivity measurements

Potentiometric conductivity measurements were carried out using a D.C. conductivity meter (InLab 720 probe, S47, Mettler Toledo, UK). The conductivity probe was held in the suspension vertically. The measured values may underestimate the real values if sedimentation takes place during measurement as the contribution of charged particles to the electric conductivity can be significant. In this work, conductivity readings were stable within 3 min of immersion in suspension, and all the measured suspensions remained stable, with less than 2% sedimentation over 30 min, so sedimentation was not thought to influence conductivity measurement. The physical measurement accuracy of the conductivity meter was within ±1% over the range from 4 μS/cm to 120 μS/cm and within ±2% from 1 to 4 μs/cm. Errors between measurements, calculated from the standard deviation of three repeated measurements, were within ±0.05 μS/cm for conductivities below 5 μS/cm and within ±0.3 μS/cm in the range from 5 μS/cm to 80 μS/cm.

2.3.2. Zeta potential

The zeta potential of the suspension at different pH was measured using the electrokinetic sonic amplitude method (ESA 9800, Matec Applied Science, USA). The variation of zeta potential with increased YSZ concentration is expected to be negligible as the quantity of HCl addition far exceeds the quantity of H$^+$ adsorption in the YSZ suspension without the addition of HCl. Zeta potential given in this paper is the mean value of five measurements, the standard deviation of which was within ±3.5 mV.

2.3.3. Green coating density measurement

Green density ρ_d was calculated by a mass and volume method:

$$\rho_d = \frac{m_d}{A \cdot l_d} \tag{1}$$

The mass of dry (m_d) coatings was measured using a balance (Ohaus AB-S, Leicester, UK) which had a precision of 10 ng. l_d is the thickness of the green coating and A is the coating area. For the green coatings with uniform surface, the l_d was measured by a magnetic thickness gauge (±2 μm, Ecotest Plus, Sheen Instruments, UK). For the green coatings with rough surface, the l_d was measured by changing focus under an optical microscope (Olympus BH, Tokyo, Japan). The thickness of the deposit was quite uniform for deposition time below 2 min as the electric field was uniform over the deposition area. However for deposition time exceeding 5 min the deposit became appreciably non-uniform. The thickness gradually increased along the gravity direction due to sedimentation. In addition, there is an increase in the surface roughness of green coating with

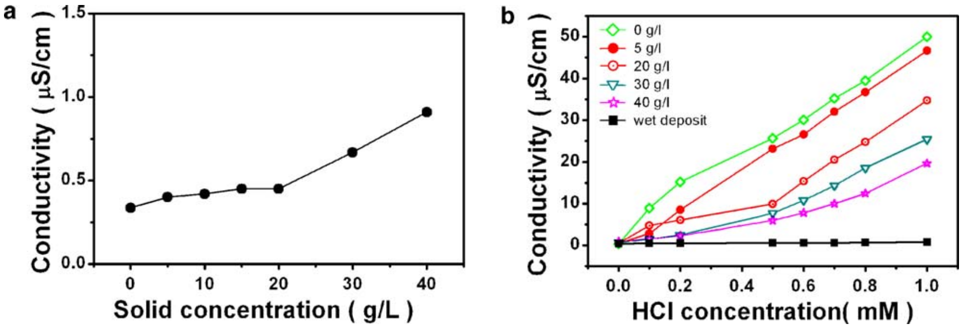

Fig. 1. Electrical conductivity as a function of (a) solid concentration and (b) HCl concentration of yttria-stabilized zirconia suspension. Error bars are not shown as they were less than 1% so are smaller than the symbols.

greater HCl concentration of the EPD suspension. The mean thickness of green coatings with rough surfaces may be overestimated when measured using a thickness gauge. Therefore, more consistent measurement of deposit thickness was made using the change in focus under an optical microscope using a smaller area of deposit, the area of which was determined by image analysis (Axiovision Rel. 4.8 software), to allow accurate characterization of green density. The green densities were obtained by taking the mean value from 3 coatings fabricated under identical conditions. The results are reproducible to ±5%.

2.3.4. *Micro-indentation measurement*

In order to characterize the particle packing of green coatings experimentally micro-indentation with a spherical indenter was carried out on the top surface of green coatings at room temperature. Instrumented indentations were made at a load of 500 mN, applied at 400 mN min^{-1} and maintained for 10 s using a 200 μm radius diamond sphere (MHT, CSM, Switzerland). For each sample, 10 separate indents, spaced 1 mm from each other, were made on the investigated surface.

3. Results and discussion

3.1. *Characterization of suspension*

Fig. 1(a) shows the electrical conductivity as a function of the solid concentration of YSZ suspensions without the addition of HCl. The mixed solvent alone has an electrical conductivity of around 0.33 μS/cm and this increases gradually as YSZ is introduced. This increase results from the greater dissociation of the solvent ions due to the YSZ surface, as follows. The surface of fine YSZ particles tends to adsorb hydroxyl groups from moisture in air or residual water in the mixed solvent and to form amphoteric hydroxyl groups of $(\mathrm{Zr–OH})_0$. Greater adsorption of H^+ in the presence of $(\mathrm{Zr–OH})_0$ encourages greater dissociation of acetylacetone ($\mathrm{CH_3COCH_2COCH_3}$) into $(\mathrm{CH_3CO})_2\mathrm{CH}^-$ and H^+ causing higher suspension conductivity.[7,14]

Fig. 1(b) shows the suspension electrical conductivity as a function of HCl concentration for suspensions with various solid concentrations. The suspension electrical conductivity considerably increases with the HCl concentration, but decreases with increased solid concentration. The electrical conductivities of the mixed solvent and the suspensions increase linearly with the HCl concentration. Compared with a steep increase of the electrical conductivity with the HCl concentration in the mixed solvent alone (represented by green diamonds), the increase becomes more gradual with increased solid concentration. The adsorption of dissociated HCl to the YSZ particle surface instead of remaining in solution moderates the conductivity increase in suspensions compared to the mixed solvent alone.

The electrical conductivity of wet deposits is hard to measure. Therefore 3100 g/L suspensions with solid volume fractions up to 0.4 were used to represent the wet deposits. This corresponds to ~40% wet density which our preliminary results suggested to be representative. The measured electrical conductivities of the 3100 g/L suspensions show little difference with varied HCl concentrations, and are in the same order of magnitude as the electrical conductivity of wet deposits that was calculated from measured specific resistance of wet deposits reported in Anné's study.[15]

Fig. 2 shows both the zeta-potential (ζ) and the electrical conductivity of a 5 g/L YSZ suspension as a function of HCl concentration. The zeta-potential measurement shows that YSZ particles are positively charged in the mixture of ethanol and acetylacetone (78 mV). As HCl was added to the suspension there was a very rapid rise in the zeta potential from ~78 mV to 132 mV at 0.2 mM HCl, at higher HCl concentration the zeta potential gradually decreased to 72 mV. The Derjaguin equation[16] predicts that the electrostatic repulsion depends on the product of the dielectric constant (ε_r) and the square of the surface potential. Thus, the surface potential in the mixed solvent ($\varepsilon_\mathrm{r} = 25.0$) should be about twice of that in water ($\varepsilon_\mathrm{r} = 78.54$) to

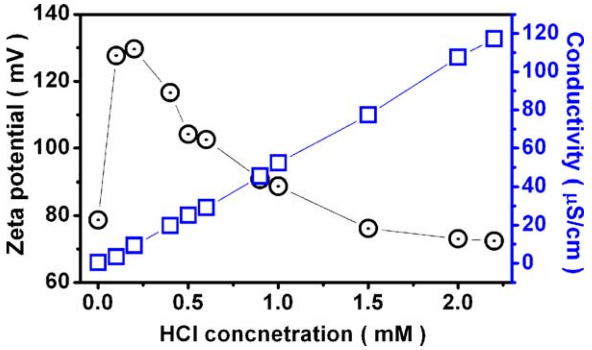

Fig. 2. Both zeta-potential ([ζ], ○) and electrical conductivity (□) as a function of HCl concentration in 5 g/L suspension.

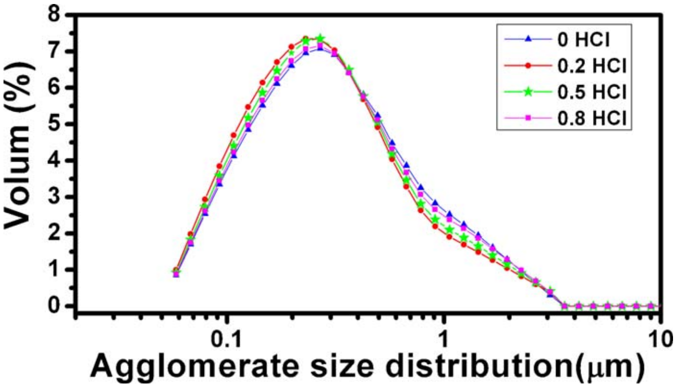

Fig. 3. Agglomerate size distribution for suspensions with various HCl additions.

provide the same repulsion: i.e. if 40 mV is adequate in water, 80 mV should be adequate in the mixed solvent.[16] Here a relatively small addition of HCl is sufficient to impart a relatively strong charge on the YSZ particles in the mixed solvent resulting in a high zeta potential of 132 mV. The zeta potential is substantially reduced at the HCl concentrations above 0.5 mM. This effect can be related to the compression of the electrical double layer (reduction of the Debye length) with increasing ionic strength.

Fig. 3 shows the agglomerate size distribution for suspensions with various additions of HCl. The mean agglomerate size in the suspension without HCl addition is 0.27 μm. As HCl was added to the suspension, there is a slight change in the agglomerate size, e.g. from 0.27 to 0.24 μm with the addition of 0.2 mM HCl. Fig. 4 shows the relative sedimentation height (R.S.H.) for the 20 g/L suspensions with 0, 0.2, 0.5, and 0.8 mM HCl additions as a function of sedimentation time. The lowest sedimentation rate occurred in the suspension with 0.2 mM HCl due to the highest zeta potential of 132 mV (shown in Fig. 2). All the measured suspensions were stable over the time periods used for EPD, with negligible sedimentation (Fig. 4).

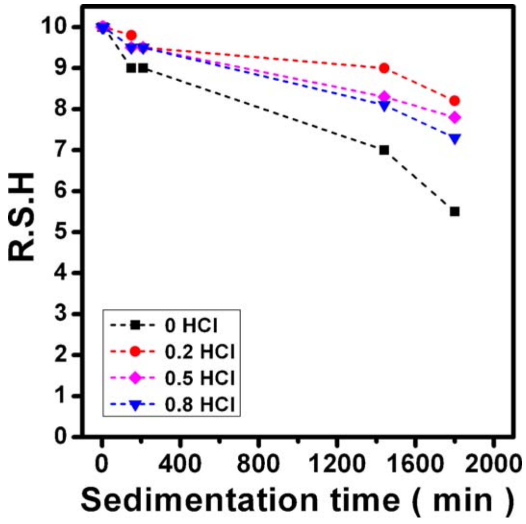

Fig. 4. Relative sedimentation height (R.S.H.) for the 20 g/L suspensions with 0, 0.2, 0.5, and 0.8 mM/L HCl additions as a function of sedimentation time.

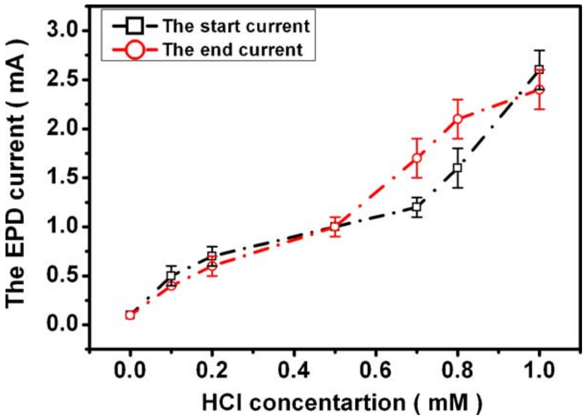

Fig. 5. The start and end current over 20 g/L suspensions for 10-min EPD process as a function of HCl concentration.

Fig. 5 shows the start and end current over 20 g/L suspensions for the 10-min EPD process as a function of the HCl concentration. Both start and end current of the suspensions increased with the HCl concentration of the starting suspensions. In addition, the current increased during EPD in the suspensions with HCl concentrations of 0.7 mM and 0.8 mM, which indicated that the sum of the deposit and suspension resistances decreased with deposition time. In this case, although the resistance of the deposit is expected to increase in proportion to its thickness, a larger reduction in resistance is expected in the suspension which is dependent on ionic strength and solid concentration of the suspension. However, further study is required to understand the mechanisms for reduction in the resistance during EPD.

3.2. Characterization of green coatings

Fig. 6(a) shows the green density of coatings deposited on the 20 g/L YSZ suspension for 5 min and 10 min as a function of electrical conductivity. With the increase in electrical conductivity and deposition time, the green coating density appears to increase with the electrical conductivity until 10 μS/cm, then decreased slightly after 17.5 μS/cm. In addition, with EPD from 5 min to 10 min, the density increased considerably. Fig. 6(b) shows the green density of coatings produced from the 20 g/L and 100 g/L suspensions for an 8 min deposition process as a function of suspension conductivity. The green density increased with suspension conductivity in the 20 g/L and 100 g/L suspensions. The solid concentration of suspension shows no obvious effect on the green coating density. Therefore, the deposition time and electrical conductivity have more significant effect on green density than the solid concentration in these suspensions.

Fig. 7 shows the SEM images of typical surface morphology of the deposits produced in the 20 g/L suspensions with HCl concentration of 0.5 mM for 5 min and 10 min EPD, respectively, together with the images of indents generated from micro-indentation. The 5 min EPD produced a coating with approximately 1 μm open pores and loose packing as shown in Fig. 7(a), whereas the coating produced from 10 min EPD is uniform and more densely packed with pore size comparable to the particle size (Fig. 7(b)). The indents were generated by

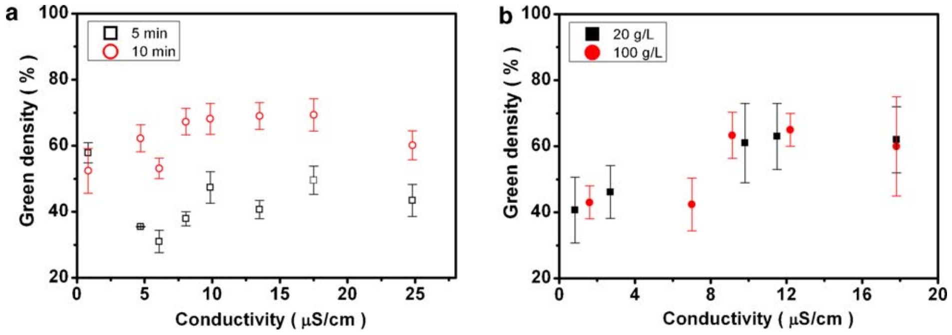

Fig. 6. The green density of coatings (a) produced in 20 g/L suspension for various deposition times and (b) produced in various solid concentrations for 8 min deposition time as a function of suspension conductivity.

the spherical indenter with a load of 500 mN, showing a larger impression in the coating (Fig. 7(a)) with green density of <55%, which is relatively free of cracks, and a smaller impression in the coating (Fig. 7(b)) with green density of >60%, where cracks were formed oriented at about 90° to each other.

Fig. 8 shows the indentation contact pressure (P_m) and elastic modulus (E) as a function of green density of coatings and deposition time. In powder compacts like the green coating, the contact pressure (P_m, load divided by projected contact area at the maximum load) is normally used to represent strength of the compact.18.[12] The contact pressure (P_m) and elastic modulus (E) increase appreciably with the green density and deposition time.

According to Section 3, the green density increases with the electric conductivity and deposition time for suspensions with less than 100 g/L solid loading, and the green density peaks at a conductivity of around 10–15 μS/cm for 20 g/L suspensions with a deposition time of 8–10 min. The measured contact pressures (P_m) and elastic moduli (E) shown in Fig. 8(b) are representative of the coating density and agree with the directly measured results shown in Figs. 6 and 7.

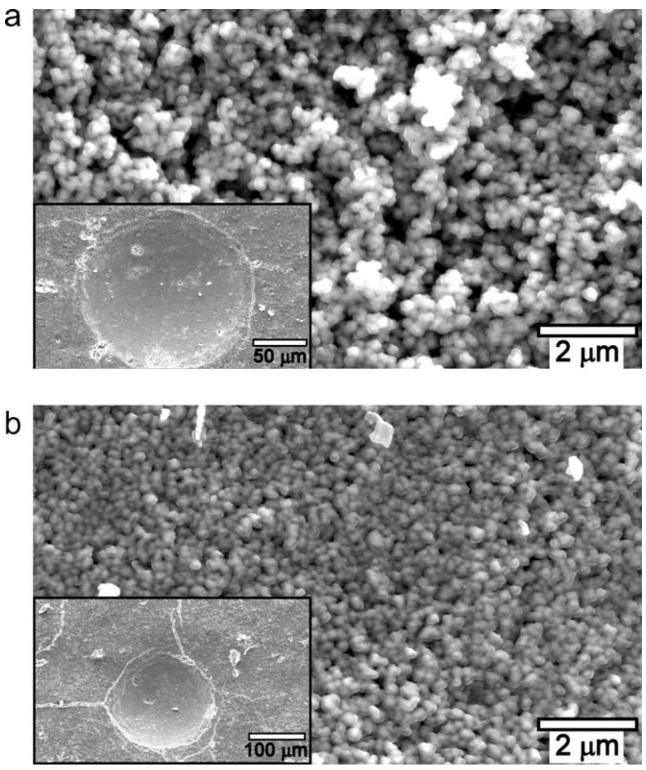

Fig. 7. SEM images of indentation impressions and surface morphologies in green coatings produced in 20 g/L suspension with 0.5 mM HCl concentration: (a) 5-min deposition and (b) 10-min deposition.

3.3. Particle packing during EPD

As Ji et al.[7] reported the local electric field around a deposited particle is distorted by the presence of charges on the particle surface, causing an electro-osmotic flow that can pull particles together to form aggregation. The aggregation velocity is proportional to the electro-osmotic velocity u.

$$u = \frac{\varepsilon \xi V_{\mathrm{d}}}{\eta l_{\mathrm{d}}} \tag{2}$$

where ε, ζ and η are, respectively, the dielectric constant and the zeta potential of ceramic particles and the viscosity of the solvent. In an EPD process, particle deposition and particle rearrangement occur at the same time. The deposit porosity is a combined result of the deposition rate and the rearrangement ability of particles.

In our EPD system, both free ions and charged particles act as current carriers.[7] Therefore, the electrical conductivity of the suspension and hence EPD current are effected by the content of charged particles and free ions. The magnitude of the potential drop over the deposit depends on the relative resistance of the deposit and the suspension.[15] The electrode polarization has been previously found to be negligible in the ethanol-based system.[5,15] We can define a factor Y as the ratio between the suspension resistivity, $r_{\mathrm{suspension}}$ (Ω m), and the deposit resistivity, r_{deposit} (Ω m).

$$Y = \frac{r_{\mathrm{suspension}}}{r_{\mathrm{deposit}}} \tag{3}$$

The $r_{\mathrm{suspension}}$ or r_{deposit} can be directly derived from the conductivity of the suspension or deposit as:

$$r = \frac{1}{\Lambda A} \tag{4}$$

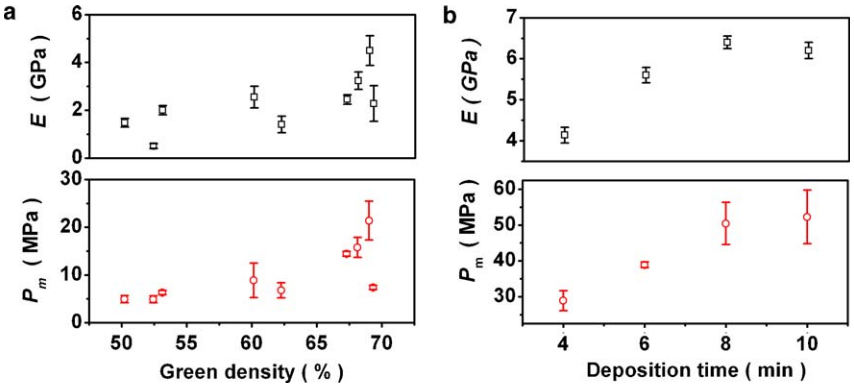

Fig. 8. Contact pressure (P_m) and elastic modulus (E) as a function of (a) green density of coatings fabricated in 20 g/L suspensions for 10-min EPD process and (b) deposition time for green coatings fabricated in 20 g/L suspension with 0.5 mM HCl concentration.

where A (m^2) is the deposit surface area and Λ the conductivity (S/m) of the suspension. Inserting (4) into (3) gives

$$Y = \frac{r_{\text{suspension}}}{r_{\text{deposit}}} = \frac{\Lambda_{\text{deposit}}}{\Lambda_{\text{suspension}}} \qquad (5)$$

with $0 < Y < 1$ for isolated powder particles, and assuming a serial electrical connection of deposit and suspension, the voltage drop over the deposit is given by [15]

$$V_{\text{d}} = V_0 \frac{d_{\text{dep}}}{d_{\text{dep}} + (d - l_{\text{dep}}) \cdot Y} \qquad (6)$$

with l_{dep} being the thickness of the deposit, d the distance between the electrodes, and V_0 being the applied voltage. Assuming $l_{\text{dep}} = 0.2$ mm with $d = 10$ mm, $V_0 = 50$ V with the electrical conductivity ratio of the YSZ deposit and suspension (Y) obtained from Fig. 1(b), Fig. 9 shows the voltage drop over the deposit V_{d} and resistance ratio of suspension over deposit Y as a function of the HCl concentration, which indicates Y decreases rapidly with the HCl concentration until 0.1 mM, whereas that the potential drop over the deposit increases with the HCl concentration.

The increase in V_{d} over a fixed thickness deposit, as shown in Fig. 9, suggests promotion of densification of wet coatings with the addition of HCl due to an increase in electrical field. This, in addition to the increased particle zeta potential and dispersion, may explain the effect of the small HCl addition on green coating density. However, it is difficult to explain the effect of Y and V_{d} on the green coating density with further addition of HCl shown in Fig. 6(b) where the green density decreased with HCl concentration above 0.8 mM. There is a small increase in agglomerate size (Fig. 3) due to the reduced zeta potential (Fig. 2) caused by high ionic strength in the suspension with high HCl concentration which will have a detrimental effect on green density.

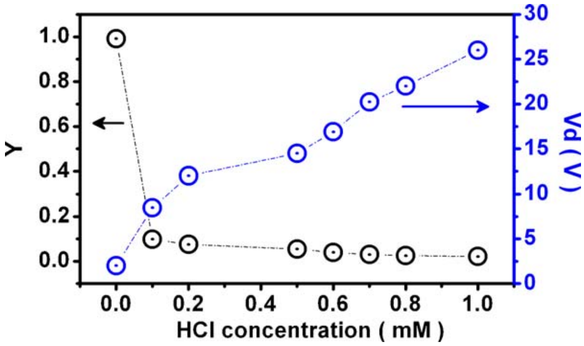

Fig. 9. The calculated potential drop over the deposit and $Y = \Lambda_{\text{deposit}}/\Lambda_{\text{suspension}}$ as a function of the HCl concentration during 10-min EPD procedure.

The deposition rate during the initial stage of EPD, is much higher than that in the latter period due to the high potential drop over the suspension. At beginning of EPD, time may be too short for particles to move into optimum positions at the substrate surface, resulting in a loose packing structure. Whereas, in the latter stage, more time is available for the particles to find optimal positions. A gradient structure is expected for EPD deposits, i.e., a loose bottom and a dense top, which has been observed in other experiments.[7,17] This may be a reason why a longer deposition time leads to a higher green density, although we have not found a gradient structure of the EPD green coatings produced in this study.

As solid loading is expected to influence deposition rate this factor may be expected to influence green density by altering the time available for particle re-arrangement. During EPD, particle consumption should further reduce the rate of particle deposition throughout the EPD process. However this and previous works have found no effect of solid loading on green coating.11.[4] Hence further study is required to understand how the solid loading affects the density and particle packing in EPD coatings.

4. Conclusions

This paper investigated how the HCl content of an EPD suspension affected particle packing in the green coatings produced from EPD. It is found that the green density increases with an initial increase in the HCl concentration. In addition, increase in the EPD time led to a significant increase in the EPD green coating density, which suggests that particle packing was influenced by time dependent re-arrangement in addition to the initial suspension dispersion state. The green density peaks at a conductivity of around 10 μS/cm achieved by the addition of 0.5 mM HCl for the 20 g/L suspensions with the EPD time of around 8–10 min. For the powder loading investigated, the YSZ content in suspensions showed little effect on the density of the green coating. The contact pressure (P_m) and elastic modulus (E) of green coatings increased with the green density and are consistent with the appearance of the SEM images of the green coating surface.

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