Morphology control of thin LiCoO_2 films fabricated using the electrostatic spray deposition (ESD) technique

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Electrostatic spray deposition (ESD) is a technique recently developed for the fabrication of inorganic thin films. Several process steps involved in an ESD process are overviewed. A variety of surface morphologies of LiCoO_2 thin layers fabricated by this technique are presented, indicating correlations between the morphologies and deposition conditions.

Electrostatic atomization of liquids has been investigated for many years. It has been applied in crop spraying¹ and for painting. However, recently it has been used for the preparation of particles of metal oxides by pyrolysing solution spray droplets.^{2,3} Compared with other spray techniques, *e.g.* ultrasonic or mechanical atomization, it has the advantage that non-sized droplets may be produced under proper conditions. More recently, it was used for preparing thin films of metal oxides, such as LiMn_2O_4 , Y_2O_3 -stabilized ZrO_2 , BaCeO_3 , LiCoO_2 ,⁴⁻⁶ and a CdS -polymer composite film.⁷ This technique may be termed electrostatic spray deposition (ESD), and it has also been called electrostatic spray pyrolysis (ESP) in our previous reports. In addition to the very simple set-up, which is a common advantage of spray film-fabrication techniques over techniques using vacuum systems, *e.g.* physical vapour deposition, the high deposition efficiency attained using this technique appears to be another attractive feature. This is mainly due to a well defined trajectory of spray droplets directed towards the substrate by the electric field. In this respect, it is similar to the so-called corona spray technique.^{8,9} However, in the ESD process, the charged aerosol is generated more directly and usually consists of monodispersed primary particles, while the corona spray techniques produces its spray by other means, *e.g.* ultrasonically combined with electrical discharge.

Like other spray deposition techniques, the electrostatic spray deposition technique usually atomizes a precursor solution into an aerosol, which is then directed to a heated substrate to form a thin layer. The history of applying the ESD process to deposit thin films is short, so that only a few reports exist concerning the deposition mechanism. Here we present the results of LiCoO_2 thin layers prepared by ESD of ethanol solutions containing lithium and cobalt precursors. The focus will be on the control of the morphology of the layers by controlling the deposition parameters. Furthermore, a number of different morphologies produced by this technique will help us to find a unified deposition mechanism model.

Processes involved in ESD

There are several physical and chemical processes involved in the ESD of layers, occurring either sequentially or simultaneously. Possible sequential steps are (see also Fig. 1): spray formation; droplet transport, evaporation, disruption; preferential landing of droplets; discharge, droplet spreading, penetration of droplet solution, drying; surface diffusion, reaction.

All of these processes can influence the morphology of the deposited layer. They are described below separately.

Spray production

In the ESD technique a capillary-plate configuration is usually adopted.¹⁰ The precursor solution is placed in a container which is connected to a metal capillary tube. When a voltage is applied to the capillary, an electrostatic field is immediately set up across the capillary and the grounded plate. This field also penetrates the liquid surface and acts on the ions in the solution. In the case of a positive potential at the capillary, positive ions move to the surface of the solution at a rate which depends upon the electrical relaxation time constant τ , which in turn depends upon the electrical conductivity κ and the absolute permittivity of the solutions $\epsilon (= \epsilon_r \epsilon_0$, where ϵ_r is the relative permittivity of the solution and ϵ_0 is the absolute permittivity of free space), as shown in eqn. (1):

$$\tau = \frac{\epsilon}{\kappa} \quad (1)$$

For ethanol solutions, the absolute permittivity is approximately $2 \times 10^{-10} \text{ F m}^{-1}$.¹¹ The resistivity of an ethanol solution containing a salt has typical values between 10^{-2} and 1 S m^{-1} , therefore its electrical relaxation time is 2×10^{-8} – $2 \times 10^{-10} \text{ s}$, which means the surface charge can develop fully in $\ll 1 \mu\text{s}$, while this surface charge completely shields the bulk of the solution so that there is no free charge inside the solution. The surface charge density σ is given by $\sigma = \epsilon_0 E$, where E is the electric field strength. The surface charge causes an outward electrostatic pressure on the solution, which is opposite to the

Fig. 1 Processes involved in ESD. 1, spray formation; 2, droplet transport, evaporation, disruption; 3, preferential landing; 4, discharge, droplet spreading, penetration, drying; 5, surface diffusion, reaction.

inward directed pressure from the surface tension. This leads to surface instabilities, which are normally called Rayleigh–Taylor instabilities.¹² Taylor has shown that when the electric field is strong enough, the electrostatically stressed liquid surface can be distorted into a stable conical shape (Taylor cone).¹³ The cone surface is equipotential but the net electric field E_{surf} that exists at the surface of a Taylor cone is given by eqn. (2):

$$E_{\text{surf}} = 300 \left(\frac{8\pi\gamma \cot \alpha}{r} \right)^{1/2} \quad (2)$$

where γ is the surface tension of the liquid with respect to the surrounding gas, α the semi-vertex angle of the cone, and r the radius.

An ideal Taylor cone has a semi-vertex angle of 49.3°. At the very apex of a Taylor cone the liquid surface is unstable since according to eqn. (2) the electric field would tend to be infinite with r close to zero. In order to compensate for this ‘infinite’ electric field, the Taylor cone will emit charged droplets immediately after the application of an electric potential. In the so-called cone-jet mode¹⁴ (as shown in Fig. 1) these primary charged particles are usually monodispersed. Having considered capillary equilibrium, liquid continuity and momentum and charge continuity at the jet, Ganan-Calvo deduced the following relation for polar liquids [eqn. (3)]:¹⁵

$$d \propto \epsilon_r^{1/6} \left(\frac{Q}{\kappa} \right)^{1/3} \quad (3)$$

where d and Q are the diameter of the droplets emitted at the jet (the primary droplet size) and the feed rate or flow rate of the solution, respectively. As a result, the primary droplet size depends on the flow rate, the conductivity and the permittivity of the solution.

Aerosol transport

An electrostatically produced charged droplet of mass m will be attracted towards a grounded substrate by a Coulombic force qE_{sp} , where q and E_{sp} are the droplet charge and the electric field strength in the travelling space, respectively. Simultaneously, a gravitational force, mg (where m is the mass of the droplet and g is the gravitational acceleration constant), and a viscous drag force $3\pi\eta vC$ (where η is the dynamic viscosity of air, v is the drop velocity and C is a correction coefficient) also act on the droplet. The trajectory as well as the flight time taken from the nozzle to the substrate for this droplet will be determined mainly by these forces. The gravitational force may be neglected in the case of electrostatic spraying because droplets produced in this way are very small.

Assuming a homogeneous electric field in the travelling space (i.e. a constant E_{sp}) and a short nozzle-to-substrate distance L so that the drag force and the solvent evaporation can be neglected, the flight time t can be calculated according to eqn. (4):

$$t \approx \left(\frac{2Lm}{qE_{\text{sp}}} \right)^{1/2} \quad (4)$$

On the other hand, if L is long enough, the equilibrium between the Coulombic force and the drag force determines the terminal velocity of the droplet, i.e.:

$$v = \frac{qE_{\text{sp}}}{3\pi\eta C} \quad (5)$$

and

$$t \approx \frac{3\pi\eta CL}{qE_{\text{sp}}} \quad (6)$$

In addition, there are space-charge forces arising from the

repulsive interaction between charged droplets. Moreover, the real situation is further complicated by: (i) the non-uniform temperature profile and the resulting thermophoresis force; and (ii) the evaporation of the solvent and the resulting possible droplet disruption (see below). These factors also change the flying speed and time.

Solvent evaporation and droplet disruption

Alcohol solutions have been used frequently in the ESD process. Solvent evaporation during the flight of a solution droplet is inevitable, especially under heating conditions. The evaporation rate for small volatile drops can be calculated by using eqn. (7):¹⁶

$$\frac{dd}{dt} \approx - \frac{4D_v M}{R\rho d} \left[\frac{P_\infty}{T} - \frac{P_d}{T_d} \right] \left[\frac{2\lambda + d}{d + 5.33(\lambda^2/d) + 3.42\lambda} \right] \quad (7)$$

where d is the droplet diameter, D_v the diffusion coefficient of the vapour of the solvent in air, M the molecular mass of the solvent, R the gas constant, ρ the density of the solution, P_∞ the partial vapour pressure of the solvent away from the droplet, P_d the partial vapour pressure at the droplet surface, T the ambient temperature, T_d the droplet temperature which is normally $< T$ due to cooling by evaporation, and λ the mean free path of air. For a charged droplet, it is not clear whether the evaporation time is influenced by the charge. Even if it is negligible, the calculation of the evaporation time is still difficult because the system is not isothermal, and, thus, T and T_d change from place to place.

Evaporation of the solvent results in shrinkage of the droplet, keeping the total charge the same.¹⁷ A charged droplet may be disrupted into a few smaller droplets, after reaching a maximum attainable charge density, q_R , for a liquid droplet with radius a . This is the so-called Rayleigh limit,¹⁸ which can be expressed as shown in eqn. (8):

$$\frac{q_R}{m} = \frac{q_R}{4\pi a^3 \rho / 3} = \frac{6}{\rho} \left[\frac{\gamma \epsilon_0}{a^3} \right]^{1/2} \quad (8)$$

The disruption of a droplet (‘mother droplet’) usually occurs with the ejection of a few highly charged, very tiny drops (‘daughter droplets’).

Therefore, for solutions with rather volatile alcohols as solvents and/or a long nozzle-to-substrate distance and/or a high deposition temperature, the effect of droplet disruption should be taken into account. In that case, there is no longer a monodispersed particle size distribution.

In contrast, for solutions with a relatively non-volatile solvent and/or a short nozzle-to-substrate distance and/or a low deposition temperature, the monosized distribution may remain during droplet flight.

Preferential landing of droplets on the substrate

In the strong electrostatic field, induced charges exist on the surface of the grounded substrate, with a sign opposite to that of the droplets or the nozzle. The charge distribution generally is not uniform, but depends on the position relative to the nozzle and, in particular, on the local curvature of the surface. The charges concentrate more at the places where the curvature is greater. Therefore, the electric field there is stronger than at other places. When a charged droplet approaches the surface, it will be attracted more towards these more curved areas; this is referred to as ‘preferential landing’. This action will cause agglomeration of the particles, especially when the incoming droplets are small (see below). Also, this means that the roughness of the substrate surface may influence the morphology. An increase in the surface roughness will lead to more particle agglomeration.

Discharge, spreading and penetration of solution droplets on the surface

As soon as a charged droplet contacts with the surface of the substrate or the earlier formed layer, it starts to discharge by transferring the charge to the grounded substrate either immediately or through the layer to the substrate. This process is very fast according to eqn. (1) when the electronic conductivity of the substrate (usually a metal in ESD) and the deposited layer is relatively high. In this case, the discharge process is not expected to determine the morphology of the layer. However, in the cases of using insulating substrates or depositing insulating layers, the discharge may proceed slowly and, hence, it influences the morphology. Nevertheless, when wet droplets reach the substrate surface (see below), the discharge process could also be completed through electrical conduction in the concentrated solution on the surface.

If the evaporation of all of the solvent has not been completed when a droplet reaches the surface of the heated substrate, the solution wets the surface of the substrate or the earlier deposited layer. This is usually true when using a high boiling point solvent or depositing at low temperatures. The type and dynamics of spreading depend strongly upon the so-called spreading coefficients [eqn. (9)]:^{19,20}

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (9)$$

where γ_{sv} , γ_{sl} and γ_{lv} denote the interfacial tensions between the substrate and ambient gas, between the substrate and the drop liquid, and between the drop liquid and ambient gas, respectively. If $S < 0$ only partial wetting occurs with equilibrium reached at a finite contact area. If $S \geq 0$ the drop spreads until it completely covers the surface. The value of S is intimately related to the spreading rate. For $S = 0$, $r^9 \propto t$ where r is the radius of the contact circle and t is the time, so the rate of evolution of the drop slows rapidly. If $S > 0$, $r^4 \propto t$. Therefore, the choice of substrate will affect the spreading rate of the liquid droplet, and may finally affect the morphology of the layer. The spreading rate is also influenced by the viscosity of the liquid. Qualitatively, the spreading rate decreases with increasing viscosity. However, even if $S > 0$ in a ESD process, the spreading may not be complete when the simultaneous drying process proceeds rapidly. This is why many lamellar particles are usually formed in an ESD layer.

When cracks or pinholes are formed in the earlier deposited layer, the subsequently arriving solution droplets may penetrate into these defects by capillary action. Therefore, the earlier formed defects are 'repaired' in this way, and a crack-free layer is easily obtained. This appears to be another advantage of the ESD technique.

Decomposition, reaction and surface diffusion of the solute(s)

The decomposition and reaction (either partial or complete) of the solute(s) may have occurred before the droplets reach the substrate, which is expected if the surrounding temperature is high enough and dried droplets have been formed. Rearrangement of these dry particles on the substrate surface by surface diffusion is not expected at moderate deposition temperatures $< 500^\circ\text{C}$ used in this ESD experiment. In this case, a grain-like structure is expected to be formed instead of a very dense morphology.

On the other hand, at relatively low temperatures the spreading of solution droplets on the surface and the following process, which is actually a wet chemical process of an alcohol solution of metal salt precursors, determine the layer morphology. For the spreading process, the viscosity change of the solution droplets is important. For the wet chemical process, there are many factors which influence the morphology. Specifically, among them are the solution chemistry including the solvation state, for instance whether there is complexation of the metal ions by the alcohol, evaporation and/or reaction

with ambient gas of the solvent on the heated substrate, nucleation and precipitation of the solutes, and dissociation and chemical reaction of the solutes. This may be the only way to form a relatively dense morphology except at an extremely high surrounding temperature at which the whole droplets will be vaporized before reaching the substrate surface. Other morphologies, like a unique porous structure found in our experiment (see below), can also be formed by using different solutes and/or different solvents. Furthermore, unlike a normal wet chemical process such as a sol-gel process, this method proceeds *via* the continuous repetition of many small steps. Therefore a crack-free layer is more easily formed due to the aforementioned defect-repairing mechanism.

In general, the final morphology of the layer depends upon the relative rate of spreading, precipitation, decomposition and reaction. For example, if the spreading is slow but the precipitation and the decomposition are fast, the morphology will be granular. The ideal conditions for the formation of a dense layer include at least: (i) the particles arriving at the substrate must still be wet (solutes); (ii) the solubilities of the solutes in alcohol must be sufficiently large; and (iii) the spreading of the solution droplets must be rapid.

Experimental

Ethanol (100%) solutions of $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were prepared separately. The solutions were mixed in a molar ratio of $\text{Li}:\text{Co} = 1:1$; these solutions were used as the precursors. The Li (or Co) concentrations were 0.003 to 0.05 mol dm^{-3} . To investigate the solvent effect, mixtures of alcohols, ethanol ($\text{C}_2\text{H}_5\text{OH}$) and butyl carbitol ($\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$), were also used. A horizontal ESD set-up with capillary-plate configuration was used in most cases (Fig. 2). Circular stainless-steel (and sometimes platinum or aluminium) disks (1.4 cm in diameter) were chosen as the substrate and acted as the 'plate'. A heating element was used to control the substrate temperature. A positive high voltage up to +15 kV was applied to the nozzle (a hollow needle or 'capillary') through which the precursor solution was forced to flow by the pressure difference between the top level of the precursor solution and the solution at the needle orifice, and from which a positively charged spray was generated. The flow rate was controlled using valve G. The nozzle-to-substrate distance was 6 cm. Another set-up with a vertical configuration was also used to obtain a special morphology.

To investigate the effect of the substrate, an unpolished alumina square plate partly covered with some aluminium foil was used as the substrate, in order to produce the same conditions, necessary for a good comparison. Besides this, a thin (0.1 mm thick) smooth yttria-stabilized zirconia [YSZ or cubic $(\text{YO}_{1.5})_{0.16}(\text{ZrO}_2)_{0.84}$] was also used as a substrate under similar deposition conditions.

Fig. 2 Horizontal ESD set-up

Fig. 3 Four types of layer morphology obtained by ESD. I, dense layer; II, dense layer with incorporated particles; III, porous top layer with dense bottom layer; IV, fractal-like porous layer.

Results and Discussion

We reported previously that there exists an almost proportional relationship between layer mass and deposition time for ESD derived layers.⁶ Furthermore, the growth rate in terms of the layer mass per unit time is found to be independent of the deposition temperature. Therefore, over-spray is apparently not a problem in ESD. The overall composition of the layer should be the same as that of the precursor solutions. Elemental analysis by atomic absorption spectroscopy (AAS) for an LiCoO_2 layer deposited at 340°C confirmed this conclusion. This is in fact one of the advantages of the ESD technique in comparison with other spray and non-spray deposition techniques.

In addition to a unique porous microstructure, four types of layer morphologies were observed in this study; they are schematically shown in Fig. 3. Type I is a relatively dense layer; type II is a relatively dense layer with some particles incorporated; type III consists of a relatively dense bottom layer containing some lamellar particles, and agglomerates of lamellar particles on top of this dense layer, forming a porous and sometimes fractal-like structure, while type IV is a very porous structure made of fractal-like agglomerates of tiny particles. These four types of morphologies are formed under certain deposition parameters, as will be described below.

Effect of deposition time

The effect of deposition time on layer morphology deposited at 340°C is shown in Fig. 4. It can be seen that the layer deposited within 1 h (ca. $1.5\ \mu\text{m}$ thick) is relatively dense, belonging to type II [Fig. 4(a)]. With increasing deposition time and thus increasing layer thickness the morphologies of the layers are shifted to type III [Fig. 4(b)]. With a deposition time of 6 h the top section of the layer is very porous [Fig. 4(c)].

This morphology development can be explained by considering the competitive effect between the rates of evaporation, decomposition and spreading. Probably most of the spray droplets arriving at the substrate are still wet. Initially these drops spread on the metal substrate surface at high speed, because the surface tension of a metal [γ_{sv} in eqn. (9)] is usually much greater than that of a metal oxide. Therefore, the solution droplets can spread rapidly. Also, the solubilities of $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in ethanol (100 g at 12.5°C and 21.5 g at 25°C , respectively) are sufficiently high. Combining the two factors, a continuous layer is formed. In the meantime, evaporation of ethanol and decomposition of the acetates $\text{Li}(\text{CH}_3\text{COO})$ and $\text{Co}(\text{NO}_3)_2$ take place, producing a relatively dense morphology. It has been proved by X-ray diffraction that LiCoO_2 is formed at this deposition

Fig. 4 Surface morphologies of layers deposited at 340°C for different deposition times: (a) 1; (b) 3; (c) 6 h. Precursor solution, $0.04\ \text{mol dm}^{-3}$ $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O} + \text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ethanol solution; substrate, stainless steel; applied voltage, 11 kV.

temperature, *i.e.* 340°C .⁶ Therefore, the reaction between the lithium intermediates such as Li_2O and cobalt intermediates such as CoO may also contribute to the formation of this dense morphology. The submicron-sized particles incorporated in the layer could be from the disruption of larger 'mother droplets' owing to the evaporation of ethanol during the droplet flight and the reaching of the Rayleigh limit. When these disrupted particles arrive at the surface they are likely to be dry. They can be incorporated into the continuous layer.

With the increase of deposition time and layer thickness, the spreading of the solution droplets will occur on the surface of the LiCoO_2 layer, which usually has a smaller surface tension than a metal (stainless-steel here). In other words, the wettability of the ethanol solution on the LiCoO_2 surface is less than that on a metal surface. Therefore, discrete particles may be formed on the surface owing to the slow spreading. Some extent of spreading of the solution leads to the lamellar particles. These discrete particles also increase the surface roughness, which enhances the possibility of preferential landing and agglomeration.

In addition, no crust or hollow particles have been observed when ethanol is used as the solvent. This suggests that the evaporation of ethanol and precipitation of the solutes proceed homogeneously.

Effect of deposition temperature

Fig. 5 shows the differences in morphology of layers deposited at different temperatures. As already shown in Fig. 4(c) the layer deposited at 340°C for the same deposition time is quite porous and consists of discrete agglomerates of lamellar particles, belonging to the type III morphology. At lower deposition temperatures [Fig. 5(a) and (b)] the morphologies of the layers are less porous and belong to type II, but consist of many large particles ($4\text{--}20\ \mu\text{m}$), most of which are also lamellar, 'buried' in an amorphous matrix. The continuous 'semi-transparent' matrix appears to be formed from the spreading of large droplets. This provides further evidence that the particles landing on the substrate surface are still wet drops. At these

Fig. 5 Surface morphologies of layers deposited at different temperatures for 6 h: (a) 230; (b) 280; (c) 400; (d) 500 °C. Precursor solution, $0.04 \text{ mol dm}^{-3} \text{ Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O} + \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ethanol solution; substrate, stainless steel in (a), (b) and (c), Pt in (d); applied voltage, 11 kV.

relatively low temperatures the incoming droplets are larger and heavier than those at a higher deposition temperature, owing to less solvent evaporation. Therefore, their movement direction cannot be changed considerably by the attraction of induced charges at the substrate surface to form agglomerates. There are hardly any agglomerates in the layer at the deposition temperature of 230 °C [Fig. 5(a)], while minor agglomeration occurs at the deposition temperature of 280 °C [Fig. 5(b)]. In addition, slower precipitation steps at low temperatures also favour the formation of the relatively dense morphology. With increasing deposition temperature, the agglomeration extent increases by increasing the effect of the preferential landing. The morphology of the layer deposited at 400 °C belongs to the type III. The agglomeration is substantial but the agglomerates still constitute small lamellar particles [Fig. 5(c)], implying that even at this temperature the incoming droplets are not completely dry. It seems that the incoming droplets are completely dried at 500 °C because lamellar particles are no longer observed and drying traces are absent [Fig. 5(d)]. Actually, the morphology of the layer is fractal-like, belonging to type IV. Therefore, with increasing deposition temperature the morphology of the deposited layer changes from type II to type IV, i.e. from relatively dense to highly porous.

Effect of precursor solution concentration

Fig. 6 shows two layers, both with type III morphology, prepared with two concentrations of precursor solution. The deposition times are different but the layer thicknesses are similar, i.e. ca. 0.8 µm , which is about the thickness of a layer deposited over 1 h from a 0.04 mol dm^{-3} precursor solution [Fig. 4(a)]. Therefore, the influence of the concentration on the morphology is not remarkable as long as the layer thicknesses are similar. However, more scattered agglomerates and lamellar particles are present, in the layer obtained with a $0.0038 \text{ mol dm}^{-3}$ solution [Fig. 6(a)] than that with a 0.01 mol dm^{-3} solution [Fig. 6(b)], and with a 0.04 mol dm^{-3} solution [Fig. 4(a)]. This is due to the fact that a longer

Fig. 6 Surface morphologies of layers deposited at 350 °C for 2 h with solutions of different concentrations: (a) 0.0038 ; (b) $0.010 \text{ mol dm}^{-3}$. Precursor solution, $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O} + \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ethanol solution; substrate, stainless steel; applied voltage, 11 kV.

deposition time will result in an increased roughness, as shown in Fig. 4. Interestingly, there is no large variation in particle sizes when precursor solutions with different concentrations are used. According to eqn. (3) a lower concentration, and hence a smaller conductivity, will result in a larger primary particle size. However, the solid particle size after drying should also increase with the concentration of the precursor solution. The combination of these two opposing factors may lead to comparable final particle sizes for different concentrations.

Effect of electric field strength

Fig. 7 shows two layers deposited by applying 8 and 15 kV, respectively, to the nozzle. Their morphologies both belong to type III. However, it can be seen that the extent of particle agglomeration increases with decreasing electric field. Therefore, the layer from a stronger electric field [Fig. 7(b)] looks denser than that from a weaker electric field [Fig. 7(a)]. Also, the particle size using a weak electric field is smaller. This can be attributed to a shorter flight time of droplets under the stronger field according to either eqn. (4) or eqn. (6), and, hence, this results in less solvent evaporation and larger incoming droplets at the substrate surface. Another reason might be a stronger preferential landing effect existing in a stronger electric field.

Effect of substrate

Three layers deposited on different types of substrate are shown in Fig. 8. For the two layers simultaneously deposited on aluminium and alumina, their morphologies are quite different. The layer on aluminium [Fig. 8(a)] is rather dense whereas that on alumina [Fig. 8(b)] is not. The latter consists

Fig. 7 Surface morphologies of layers deposited at 350 °C for 4 h with different applied high voltages: (a) 8; (b) 15 kV. Precursor solution, $0.04 \text{ mol dm}^{-3} \text{ Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O} + \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ethanol solution; substrate, stainless steel.

Fig. 8 Surface morphologies of layers deposited at 350 °C for 2 h on different substrates: (a) Al foil; (b) Al₂O₃ plate (1 mm thick); (c) YSZ disk (0.1 mm thick). Deposition on the first two substrates was conducted simultaneously. Precursor solution, 0.04 mol dm⁻³ Li(CH₃COO)·2H₂O + Co(NO₃)₂·6H₂O ethanol solution; applied voltage, 11 kV.

of more agglomerates than that on the aluminium substrate. Note that originally present in the alumina substrate are some cracks or cavities, which enhance the preferential landing effect and accordingly lead to the formation of more agglomerates. In addition, a large difference in the dielectric property between aluminium and alumina may also cause the electric field to be stronger near aluminium than near alumina. This might also contribute to the different morphologies obtained on these substrates. However, under similar deposition conditions, a rather dense layer can also be formed on a thin (0.1 mm thick) and smooth YSZ substrate [Fig. 8(c)]. This suggests that the presence of cracks and cavities in the alumina substrate used in Fig. 8(b) is the main reason for the formation of agglomerates. The effect of the thickness of the ceramic substrate on the layer morphology is unclear and is worth further study.

Effect of solvent

As discussed above, the morphology of a deposited layer is largely determined by the droplet size and some physical properties, such as boiling point and spreading behaviour on the substrate, of incoming droplets, and in particular the solubilities of the precursor solutes. By changing the solvent composition, the layer morphology may also be modified. Fig. 9(a) and (b) show that the morphology changes from type IV to type III, when a mixture of 67 vol% ethanol + 33 vol% butyl carbitol is used as the solvent instead of 100% ethanol. The boiling point of butyl carbitol is *ca.* 230 °C, while that of ethanol is only 78 °C. Therefore, at 450 °C the droplets arriving at the substrate are probably dried particles when pure ethanol is used as solvent, but they are still wet in the instance of mixtures with a higher boiling point. When using 50 vol% ethanol + 50 vol% butyl carbitol as the solvent mixture at 250 °C the layer [Fig. 9(c)] is relatively dense, and hardly any particles can be discerned. It belongs to the type I morphology. Compared with the layers formed using pure ethanol solution [Fig. 5(a) or (b)] the morphology is denser.

Fig. 9 Surface morphologies of layers deposited using precursor solutions with different solvent compositions: (a) 100 vol% ethanol solution (0.04 mol dm⁻³), at 450 °C for 2 h; (b) 67 vol% ethanol + 33 vol% butyl carbitol solution (0.04 mol dm⁻³), at 450 °C for 2 h; (c) 50% ethanol + 50 vol% butyl carbitol solution (0.02 mol dm⁻³), at 250 °C for 4 h; (d) 15 vol% ethanol + 85 vol% butyl carbitol solution (0.005 mol dm⁻³), at 230 °C for 2 h. (a)–(c): Li(CH₃COO)·2H₂O + Co(NO₃)₂·6H₂O precursor, using the horizontal set-up; (d) Li(CH₃COO)·2H₂O + Co(CH₃COO)₂·4H₂O precursor, using the vertical set-up.

This is due to slower evaporation of solvent during both droplets travelling in air and spreading on the substrate surface, and accordingly, the slower precipitation step. Therefore, by using high boiling point solvents the morphology of a layer becomes denser.

Fig. 9(d) shows the unique morphology of a layer deposited at 230 °C using a vertical set-up with a solution containing 15 vol% ethanol + 85 vol% butyl carbitol as solvent. Note that cobalt acetate instead of nitrate was used in this case. The layer is a highly porous and three-dimensional interconnected structure with a narrow pore-size distribution. The pore size is *ca.* 8 µm. It appears to be a stable structure as the network remains unchanged after annealing at 450 °C. The formation mechanism for this unique reticulate structure is not yet clear. However, the precipitation step must play a crucial role because it is found that such a structure cannot be obtained by using cobalt nitrate. According to our experiment, the solubility of cobalt nitrate in the solvent is much larger than that of cobalt acetate. Therefore, this morphology is probably formed during the spreading of wet droplets. In addition, there could be chelation between cobalt acetate and butyl carbitol, as the colour of the precursor solution is dark green, rather than pink which is the colour of cobalt acetate and the precursor solution using cobalt nitrate. The possible chelating effect might cause an increase in the viscosity of the solution during the spreading step. This may also contribute to the formation of the structure. Owing to the unique structure and its potential application, it is worth further study.

Conclusions

The electrostatic spray deposition (ESD) technique opens the opportunity to control the morphology of a layer. The mor-

phology of the layer deposited by ESD is determined by the spray droplet size (especially the size of the incoming droplets), the deposition temperature, the spreading rate of solution droplets on the substrate and, if at low deposition temperatures or using a high boiling point solvent, the solution chemistry including the precipitation process and the pyrolysis or reaction of the solutes.

The main factor which determines the layer morphology is the substrate temperature. The higher the substrate temperature, the more porous the layer. The layer deposited at elevated temperatures with ethanol as solvent is very porous and has a fractal-like morphology. At a moderate temperature and at an early stage the deposited layer on a metal substrate is relatively dense, but it becomes porous with increasing thickness. The concentration of the precursor solution has a minor effect on the layer morphology. Basically, it is easier to obtain a denser layer using a higher concentration compared to using a lower concentration. The electric field strength can influence the flying time of the charged particles. Above the onset voltage, the higher the applied voltage, the denser the layer. For a ceramic substrate, its surface roughness (or smoothness) can affect the morphology of a deposited layer. Cracks or cavities present in the substrate will lead to the formation of more agglomerates. At the same deposition temperature, a layer formed using a precursor solution with a high boiling point solvent is generally denser than one obtained using a low boiling point solvent. A unique porous structure, however, can be obtained with a high boiling point solvent.

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