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THE PRODUCTION OF THIN FILMS OF LiMn_2O_4 BY ELECTROSPRAYING

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Abstract—Electrospraying comprises the generation of an aerosol by applying a high voltage to the surface of a liquid, which contains certain precursor materials. The method was used commonly to form nanocrystalline oxidic ceramic powders. The method here is modified in order to deposit thin films, using the aerosols as the adsorbing species. This novel technique is shown to have a high deposition rate and a high efficiency relative to well-established thin film deposition techniques such as chemical and physical vapor deposition (CVD and PVD). In addition, the method allows easy control of the stoichiometry and microstructure of the deposits. The synthesis of LiMn_2O_4 having the spinel structure and which is used as a cathode material in rechargeable lithium batteries is described.

1. INTRODUCTION

Electrospraying of electrostatic spray pyrolysis uses an electrostatic field to generate an aerosol. Initially, electrostatic spray pyrolysis was developed for the synthesis of nanocrystalline ceramic powders (Vercoulen *et al.*, 1993). A brief background of the electrostatic aerosol generation will be given in the next section.

The high formation rate (Vercoulen *et al.*, 1993) involved in this process along with the formation of the aerosols gave us the idea to adapt this process to use it in thin film technology to obtain high deposition rates. In comparison to other thin film deposition techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), electrostatic spray pyrolysis offers the following advantages:

- high deposition rates,
- excellent control of (overall) stoichiometry,
- easy to develop as a continuous process,
- wide range of precursors (selection on toxicity possible),
- high deposition efficiency and
- easy coverage of large areas.

In addition, the deposited films often reveal a considerable porosity, which offers the possibility of adapting the method to synthesize anode and cathode materials for solid oxide fuel cells (SOFCs). Smooth dense films can be obtained if solvent evaporation occurs on the surface of the substrate. Smooth dense films are highly desirable in thin film all-solid state batteries. However, if a liquid electrolyte is used in combination with a porous cathode, the current exchange area will be considerably enhanced and the diffusion length decreased. Here we shall describe the synthesis of lithium manganese oxide having the spinel structure (LiMn_2O_4), which is known as a cathode material for rechargeable lithium batteries (Hunter, 1981).

2. ELECTROSPRAYING AND PYROLYSIS

If an electric field of sufficient strength is applied to the surface of a liquid, fine charged droplets are emitted. This electrospraying has been known for many years. However, more

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recently, it has been recognized that depending on the viscosity, electrical conductivity and surface tension of the liquid, the liquid flow rate, the effective field strength, the geometry of the system, and the surrounding dielectric different functioning regimes exist (Cloupeau and Prunet-Foch, 1990). For the application of thin film deposition, the regime controlled by space charge as described by Meesters *et al.* (1992) and Meesters (1992), seems the most promising, due to the high frequency of droplet emission in the micron size range. A pendular droplet, to which a high electrostatic field is applied, deforms to a conical shape which is commonly called a Taylor cone (see inset of Fig. 1). For the by space charge controlled regime the generation of micron-sized droplets at the tip of the cone, using liquids of modest conductivity, i.e. in the order of 10^{-5} S m^{-1} is reported (Meesters *et al.*, 1992; Meesters, 1992). For an experimental configuration with a grounded needle discharged and a metal shielding ring they measured a droplet emission frequency of 10^8 – 10^{10} droplets per second and a droplet size, depending primarily on the properties of the liquid, in the order of one micrometer. The droplets carry a high charge and the mean droplet size decreases with increasing liquid conductivity. The exact break up mechanism for this regime is not understood yet, but it is likely that it is caused by electric instability. It is clearly demonstrated that in many respects the phenomena which occurs at the tips of the cone are similar to those occurring in a corona discharge which occurs at the tip of a needle. There is in particular a close similarity in the current–voltage characteristics of the liquid cone and that of a sharp needle. Space charge proves to be a controlling mechanism for the stability of the cone.

However, for the production of thin films the configuration with ring and needle is not used, but a single grounded plate is used instead. So, it is not understood how far we can compare our spray mechanism with the above-mentioned regime.

3. THIN FILM DEPOSITION BY ELECTROSTATIC SPRAYING

As will be pointed out in detail in the next section, we used ethanol as the liquid in which manganese acetate tetrahydrate ($\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$) and thoroughly dried lithium chloride (LiCl) were dissolved. The conductivity of the liquid depends strongly on the concentration of the dissolved salts, but Meesters *et al.* (1992) observed that spraying occurs with pure ethanol. Increasing the conductivity of the liquid by adding salts, and thus ions, reduces the droplet size. The negatively charged droplets are attracted towards a grounded substrate

Fig. 1. Set-up for electrostatic spray pyrolysis. The figure has been drawn reasonably to scale (see marker). The inset of the figure is the shape of the conically formed liquid drop at the nozzle due to the applied high voltage, also known as the Taylor cone.

(see Section 4), and, therefore, enhance the deposition efficiency compared to CVD and PVD. By the time the aerosol reaches the substrate the liquid is evaporated completely from the droplet, as can be illustrated by the following calculation.

Meesters (1992) found the terminal velocity of a charged particle in his configuration for spraying to be in the order of 5 m s^{-1} at atmospheric pressure. Neglecting the electric wind ($< 1 \text{ m s}^{-1}$ for the current values we used, typically below 1 mA (Cutler *et al.*, 1986)), the time for a particle emitted from the cone to reach a substrate 2 cm further away is 4 ms. The time for complete evaporation can be approximated by Hinds (1982)

$$t_{\text{evap}} = \frac{RT\rho_p d_{p0}^2}{8DM(P_d - P)}, \quad (1)$$

where t_{evap} is the evaporation time of an initial micrometer-sized ethanol droplet, R is the gas constant, T is the absolute temperature (K). As the distance between the nozzle and the heated substrate is in the order of 1 cm in our set-up, the temperature may be taken as the average between room temperature and the deposition temperature ($350\text{--}400^\circ\text{C}$), which is approximately 200°C , ρ_p is the density of particle. This may be approximated by the density of the solvent, in our case ethanol with a density of 785 kg m^{-3} was used. d_{p0} is the initial particle diameter: approximately $4 \mu\text{m}$, (Section 5), D is the gas-phase diffusion coefficient of evaporating species, for ethanol in air about $10^{-5} \text{ m}^2 \text{ s}^{-1}$, M is the molecular weight of evaporating species (ethanol: 46 g mol^{-1}), P_d is the pressure of evaporating species directly over the particle surface. The droplets are assumed to be at the boiling point of the solution during evaporation, irrespective of the concentration. At the atmospheric boiling point this is $101,325 \text{ Pa}$ and 200°C and P is the partial pressure of evaporating species in the surrounding atmosphere (assumed to be zero in our experiment).

Substituting the above-collected data yields an evaporation time of approximately 0.2 ms, i.e. much smaller than the 4 ms it takes for the particle to reach the substrate. It is assumed that the solid particles formed in the gas phase do not change after deposition. As a result, the average particle size of the LiMn_2O_4 grains in the deposited film will be determined only by the droplet size and the precursor concentration. As a consequence, the films deposited this way will tend to be highly porous. For battery application this may be regarded as an advantage as was already mentioned in the introduction.

4. EXPERIMENTAL ASPECTS

A solution is made of manganese acetate tetrahydrate ($\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$) and thoroughly dried lithium chloride (LiCl) in ethanol (absolute, $>99.8\%$, Baker). $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ was chosen as the manganese precursor because of the favourable chemistry of manganese acetates proved earlier by Barboux *et al.* (1991). The lithium compound (LiCl) was thoroughly dried using standard techniques. This drying step was carried out to be sure that the weighted solid lithium compound contains the desired amount of lithium.

Spraying was possible with precursor solutions of $5 \times 10^{-4} \text{ M}$ LiCl and 10^{-3} M $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ up to 0.05 M LiCl and 0.1 M $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ in ethanol. Actually, a small excess of lithium was chosen to prevent formation of other phases but the spinel-phase LiMn_2O_4 . A 0.5 M LiCl and 1.0 M $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ solution could not be tested as $\text{Mn}(\text{OH})_2$ precipitates readily from this solution. The stoichiometry for the cathode material was chosen to be LiMn_2O_4 as the $\text{Li}_2\text{Mn}_2\text{O}_4$ phase is not stable in air.

For the spray pyrolysis deposition the set-up shown in Fig. 1 is used. Note that the set-up is an open system and did not use a specific reaction chamber. This makes the method suitable for scanning or writing large surface areas as it is not restricted to chamber sizes as is in PVD and CVD. In contrast to the commonly used equipment for aerosol formation by electrospraying, the set-up used here for thin film application was turned upside down, the nozzle being in upward position. The equipment consists of a resistance-heated substrate holder to which a conductive substrate is mounted underneath. The substrates used were 1 mm thick $18 \times 22 \text{ mm} \times \text{mm}$ object glasses coated with a several nanometers thick film of

substrate is masked by a platinum frame, leaving an exposed area of $17 \times 17 \text{ mm} \times \text{mm}$. A thermocouple is connected as close as possible to the conductive platinum surface to measure the surface temperature. The temperature is continuously recorded with an X-t recorder before, during, and after the deposition. The noise in the temperature signal has a typical amplitude of 25°C . This noise may be caused by the temporary instabilities of the Taylor cone, resulting in an unsteady electric wind and in fluctuations in the number of emitted droplets, and, so, the amount of evaporated solvent, and connected evaporation heat. If the thermocouple is shielded and mounted between the substrate and the heating element the noise decreases dramatically. However, in this case the temperature is not the surface temperature anymore. The manganese-lithium containing solution is stored in a 0.02 ml accurately calibrated glass tube to measure the adjusted volume. The adjusted volumes are about 3 ml per experimental run. The solution is supplied through an angular cut needle (the nozzle) with an internal diameter of 0.8 mm. The liquid flow rate is established due to a pressure difference between the nozzle exhaust and the liquid level in the glass tube, and is subsequently controlled by a leak valve which is placed on top of the glass tube. An 8 to 20 kV potential is applied by a high voltage source (Heinziger, Model HNCs 30.0001 ump), with a current never exceeding $50 \mu\text{A}$. The nozzle is the negative electrode. The spacing between the top of the nozzle and the substrate varies from 0.5 to 3 cm.

5. RESULTS AND DISCUSSION

The circular geometry of the spraying device is clearly reflected in the structure of the deposited film. In the center inhomogeneities are visible by eye. Scanning electron microscopy (SEM) graphs reveal the inhomogeneities to be large grains deposited on the surface (Figs 2 and 3). They are probably caused by temporary instabilities in the Taylor cone, releasing droplets larger than $1 \mu\text{m}$. The spraying occurs probably in the intermittent cone-jet mode. The temporary instabilities can also be a result of an insufficient flow rate of the liquid, as we were not able to adjust this liquid flow rate to the applied voltage. Further, a variation in the distance between the top of the nozzle and the substrate induces variations of the homogeneity of the film thickness. However, a detailed study of this phenomenon is not done yet.

The growth rates were calculated from the weight increases, and were found between 1 and $5 \mu\text{m h}^{-1}$.

The SEM micrographs of the film surface shows a porous structure, as predicted, with a fairly homogeneous size distribution of the crystallites. Their average size is $0.3 \mu\text{m}$. As the concentration of the solution is $0.05 \text{ M Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ ($\text{Li}/\text{Mn}=0.5$), the average size of the droplets of precursor solution emanating from the Taylor cone can be calculated to be $4 \mu\text{m}$, assuming completely dense particles (Meesters, 1992).

The cross-section of the film shows that the film thickness is rather constant throughout the area (1 cm^2) of the film (Fig. 4), however the layer thickness decreases towards the edges of the sample, reflecting the circular geometry of the spraying device (note that the exposed area of the sample was about 3 cm^2). In addition to this film, large grains, resulting from the instabilities in the Taylor cone, were visible. The smoothing of the film could be the result of the changing pattern of the electric field lines during deposition of the semiconducting

Fig. 2. SEM micrograph of an electrostatically sprayed LiMn_2O_4 thin film. The picture shows the area of the film which was present directly above the nozzle of the aerosol generator.

Fig. 3. SEM micrograph revealing the average primary particle size ($\approx 0.3 \mu\text{m}$) in the thin film of LiMn_2O_4 synthesized by electrostatic spray pyrolysis.

Fig. 5. X-ray diffractogram of a thin film of LiMn_2O_4 with the spinel structure deposited by electrostatic spray pyrolysis at 400°C .

material LiMn_2O_4 . In fact, it is attributed to the growth of this poor conducting material on the highly conductive substrate (Pt film on glass).

A typical X-ray diffractogram is shown in Fig. 5. The extra peaks are due to minor fractions of $\alpha\text{-Mn}_2\text{O}_3$, which is formed due to a slight deficiency in the Li/Mn ratio. If slightly higher molar ratios of Li/Mn are used, the depositions reveal to be pure LiMn_2O_4 . Actually, it is easy to obtain thin layers of oxidic materials having the desired stoichiometry. This makes the method of electrostatic spray pyrolysis highly favorable.

Using the total adjusted volumes and concentrations along with the the weight increase of the substrate the efficiency of the process using the set-up of Fig. 1 is calculated to be about 30%. The deviation from a 100% efficiency can be due to loss of droplets deposited in the area around the set-up, since the surroundings of the set-up is grounded too. A much higher efficiency can be expected in a closed system or using electrostatic lenses. In addition, part of the solution did not reach the substrate, but flew directly into the sewer (see Fig. 1). This amount of spoiled liquid lowers the total efficiency. However, if this spoiled liquid is collected, it can be used again for spraying.

6. CONCLUSIONS

Electrostatic spray pyrolysis is a novel low-cost and easy to use deposition method suitable for the deposition of LiMn_2O_4 cathodes for batteries at high deposition rates. A preliminary deposition rate of $1\text{--}5\ \mu\text{m h}^{-1}$ is observed in this work. The deposition rate may be enhanced by improvements to the set-up and a more fundamental knowledge of the processes governing the deposition. However, the present results clearly reveal the potential of this novel technique, which holds promise for the deposition of a wide range of structural and fundamental ceramics.

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