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NANOELECTROSPRAY TECHNOLOGY FOR FUNCTIONAL LAYER DEPOSITION

A. Jaworek, A.T. Sobczyk, A. Krupa, T. Czech, M. Lackowski

Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, POLAND
jaworek@imp.gda.pl, FAX +48 58 3416144

ABSTRACT
The results of experimental investigations of the formation of thin metal-oxide functional layers deposited onto a metal or polymer substrate using nanoelectrospray technique have been presented in the paper. Al_2O_3 or MgO nanoparticles suspended in methanol or methanol-ethylene glycol mixture were used in these experiments. An advantage of electrospray technique used for thin layer formation is that the material can be directly deposited onto a substrate enabling micro- and nano-thin film formation after solvent evaporation. The deposition process can be carried out in ambient atmosphere, in air or other gas, and at low temperatures. Electrospraying facilitates the production of very thin layers, which can be crack-free and more homogeneous than those obtained by other methods. The process is simple, flexible, and cheap. The growth rate of the layer can be faster than in chemical or physical vapour deposition. Depending on the layer thickness and required uniformity, the growth rate can vary from 0.1 μm/h to 100 μm/h. The technique can be used for nanocomposite material production because nanosized particles can merge tightly with reduced number and size of voids and cracks in the final product.

INTRODUCTION

Electrospraying is a well-known technique of liquid atomisation by subjecting a liquid jet at a capillary-nozzle outlet to electric field of high intensity. Due to the electrical forces, the liquid meniscus elongates, forming a fine jet, which is next atomised into fine droplets. The droplets obtained by this method are electrically charged and, depending on the mode of spraying, can be of submicron size with narrow size distribution. The mode of spraying and the droplets' size can be controlled via setting the liquid flow rate and voltage applied to the nozzle.

Electrospraying is a useful tool for thin film deposition for functional layer formation. Using electrosprayed nanoparticles as building blocks provides a new route to create functional layer the different composition and properties depending on the particles size and shape, and the process of deposition. The deposition process and further thermal processing define the arrangement of the particles on the substrate, and the layer properties. Al_2O_3 or MgO nanoparticles suspended in methanol or methanol-ethylene glycol mixtures were used in the presented experiments. Metal oxides thin films can be used as active catalysts and catalytic supports. In the paper, we present the results of experimental investigations of the formation of thin metal-oxide layers deposited via nanoelectrospraying onto stainless steel or aluminium substrates, or polymer fibers.

NANOELECTROSPRAY

Nanoelectrospray refers to the kind of electrospray producing droplets of the size smaller than a few micrometers, which, after solvent evaporation, allow the production of nanosized species. There are two main configurations of electrospray systems: the nozzle - substrate system (Fig.1a), when the electric filed is produced between these two electrodes, and nozzle - extractor - substrate system (Fig.1b) in which the nozzle is placed in the axis of an aperture of an extractor electrode and the electric filed is produced between the nozzle and the extractor. In this case, the droplets are deposited onto a substrate placed beneath the extractor, or can be borne with a flowing gas for further processing. In each case the capillary can be oriented horizontally or vertically, upwards or downwards.

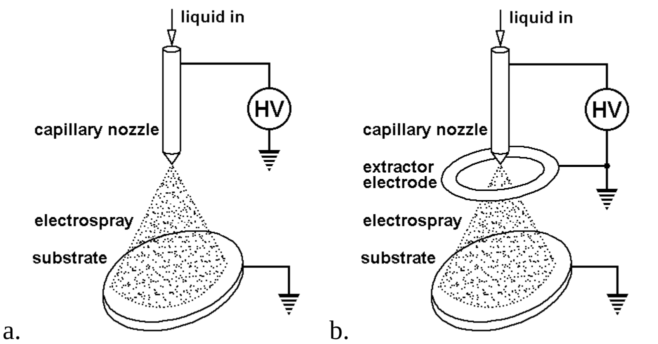

Fig. 1. Schematic of main configurations of electrospray systems.

Recently the electrospraying technique was found as a useful tool for nanotechnology [1]. The following groups of nanotechnology applications can be met in the literature:

1. Surface coating [2]. The electrosprayed droplets can be directly deposited onto a substrate enabling micro- and nano-thin film forming. The deposition process can be carried out in an ambient atmosphere, in air or other gas, and at low

temperature, without complex reactors and high-vacuum systems. Using the electrospray deposition technique, highly pure materials can be produced, with structural control at the nanometre scale. From the literature it is known that electrospray facilitates the production of very thin layers, which can be crack-free and more homogeneous than those obtained by other methods. The process is simple, cheap, flexible, and the growth rate of the layer can be faster as compared to chemical or physical vapour deposition. This technique was, for example, used by us for metal-oxides layer deposition onto a metal substrate or a polymer fabric.

2. Fine particle production [3]. From fine electrosprayed droplets, the micro- and nano-particles can be produced via solvent evaporation from a solution or colloidal suspension. The size of such particles can be controlled by changing the concentration of the dissolved or suspended substance. This technique is particularly useful for the production of metal oxides or ceramic powders from the colloidal suspension. It was reported in the literature that electrospraying allows fine powder production from various materials, including bio-substances, without significant changing chemical composition and physical properties of the material to be sprayed.

3. Electroencapsulation [4]. Encapsulation is a process for capturing solid particles or liquid droplets as a core material in a solid or liquid envelope (shell) made of another material. Employing electrical forces can increase the effectiveness of micro- and nano- encapsulation. The electroencapsulation can be accomplished by 1. Impacting of two droplets streams charged to opposite, positive and negative polarities, 2. Electrospraying/evaporation of a colloidal suspension with subsequent shell material solidification, 3.·Electrospraying of colloidal suspension into a bath with gelatinising or polymerising agent, 4. Electro-coextrusion, which is a process of simultaneous electrospraying of two different liquids from two coaxial capillaries. Electroencapsulation appears to be promising in the pharmaceutical, cosmetics, and food industries, and in biotechnology, where this low-temperature process preserves heat-sensitive biological materials, as reported in the literature.

4. Electrospray forming and direct writing [1]. Electrospray forming is a process by which fine, liquid or semi-solid droplets of a material to be deposited are placed layer-by-layer onto a substrate using electrospraying to form a bulk product or thick coating. Direct writing is a maskless process of drop-by-drop deposition of a material in a liquid or semi-solid phase to draw a pattern on a substrate. Both these techniques can be used for nanocomposite material production because nanosized particles can merge in the way similar to sintering with reduced number and size of voids and cracks in the bulk product. A complex structure in submicron scale can be built on a substrate, for example, for microelectronics, by controlled drop-by-drop deposition of a material or simultaneous deposition of various materials.

5. Electrospinning [5,6]. Electrospinning is a process of stretching a thin fiber from a viscous liquid, usually a polymer. Electrospinning is used for the fabrication of non-woven fabrics from nono-thin fibers. In recent years, electrospinning was tested as a tool for the production of scaffolds for tissue regeneration and for bone repairing.

In this research, nanoelectrospraying technology was employed for the deposition of nanothin functional layer on a metal substrate or polymer fiber. In this paper, functional layer means a deposited material and its structure which are tailored for fulfilling a required functions in physical, chemical or biological processes the layer is designed for. Examples of functional layers are anodes or cathodes for fuel or solar cells, or lithium batteries, dielectric or semiconducting films in micro and nanoelectronic devices, catalysts, electrochemical sensors or MEMS piezoelectric microactuators [1]. Metal, polymer films or fibers, glass, semiconductors or carbon structures are the examples of substrates used for functional layer deposition.

EXPERIMENTAL

The electrospray system used in our experiments consisted of a stainless-steel capillary nozzle and an aluminium disk electrode of diameter of 150 mm. A schematic of experimental set-up is shown in Fig. 2. The length of the capillary was 10 or 15 mm. The distance between the nozzle tip and the disk was changed between 20 and 35 mm. Stainless steel or aluminium were used as substrates. The table holding the substrate was electrically heated to facilitate the liquid evaporation. The temperature was varied between 30 and 60^{o}C, depending on the layer to be deposited.

The capillary nozzle was connected to a high voltage supply SL600W/30kV/PN (Spelmann) of positive polarity, while the disk electrode was grounded. The suspension to be electrosprayed was supplied from a syringe pump mounted above the capillary nozzle. The spray process was recorded using CCD camera PANASONIC NV-GS 400.

Metal oxide suspensions in methanol or a mixture of methanol and ethylene glycol were used in the experiments. The solvents were supplied from POCH Gliwice (Poland). MgO particles of 40.3 g/mol (pure grade) were purchased from POCH Gliwice (Poland). Al_2O_3 particles of 99.9% purity were purchased from Alfa Aesar.

The suspensions were prepared by stirring 5 g of the commercial powder in a mixture of different mole fraction of ethylene glycol and methanol in a glass vessel for 2 h. Next the suspension was loaded into the syringe which was mounted in syringe pump AP22 (Ascor - Poland).

The suspension was electrosprayed for a time from 5 to 30 min. The produced structures were tested under a scanning electron microscope EVO-40 (Zeiss).

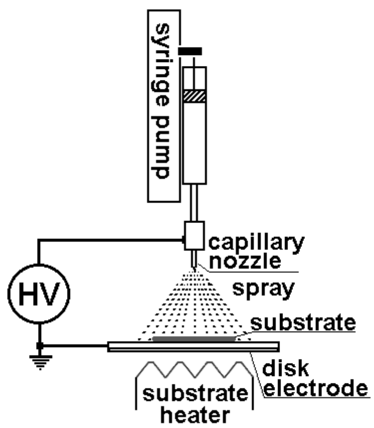

Fig. 2. Schematic of electrospray system used in the experiments.

RESULTS

An example of electrospray plume of droplets for the spray system operating in the cone jet mode is shown in Fig. 3.

Fig. 3. Cone-jet mode of electrospraying of methanol. Capillary: 0.45 mm o.d., 0.25 mm i.d., flow rate 0.1 ml/h, voltage 8 kV, capillary-substrate distance 30 mm.

Table 1. Liquids physical properties.

Parameter	Methanol	Ethylene glycol in methanol (26 wt.%)
Density, kg m^{-3}	792	861
Surface tension, N m^{-1}	21×10^{-3}	24.4×10^{-3}
Viscosity, mPa s	0.563	1.202
Electric conductivity, S m^{-1}	8.2×10^{-5}	5.9×10^{-5}
Relative permittivity	32	32.7
Estimated droplet size (Eq.1), µm	2.85	2.97

Based on scaling laws of electrospraying, Gañan-Calvo [7] and Gañan-Calvo et al. [8] have obtained the following equation for the size of droplet in the cone-jet mode:

$$d = \alpha \left(\frac{Q^3 \varepsilon_0 \rho_l}{\pi^4 \sigma_l \gamma_l} \right)^{1/6} \qquad (1)$$

where Q is the liquid flow rate, ε_0 is the permittivity of the free space, ρ_l, γ_l, σ_l is the liquid density, electric conductivity, and surface tension, respectively, and α was proposed to be equal 2.9. The properties of the liquids sprayed are presented in Table. 1. In the last raw, the size of droplets has been estimated form equation (1). The mean droplets diameter produced by our system is about 3 µm.

Examples of various forms of electrosprayed layers are shown in Figs. 4-9. The layer can be formed from metal oxide particles (Figs. 4-6), or from pure metals (Figs. 7 and 8). The layer can be deposited at normal temperature and next annealed or calcinated at elevated temperatures (Fig. 7). Metal layer can be formed from nanosized metal powder suspended in a solvent but also from a precursor which is decomposed on a heated substrate. Such a process was used, for example, for the deposition of Ag layer on an Al substrate (Fig. 8). In this example, $AgNO_3$ was dissolved in water, electrosprayed and decomposed on the substrate at a temperature of 420^{o}C. Although the metal oxides are deposited at normal temperature, they could require sintering with substrate at elevated temperatures. Besides the metal substrates also other materials can be covered with a thin layer obtained from aerosol phase. An example of polymer fiber covered with MgO particles is shown in Fig. 9.

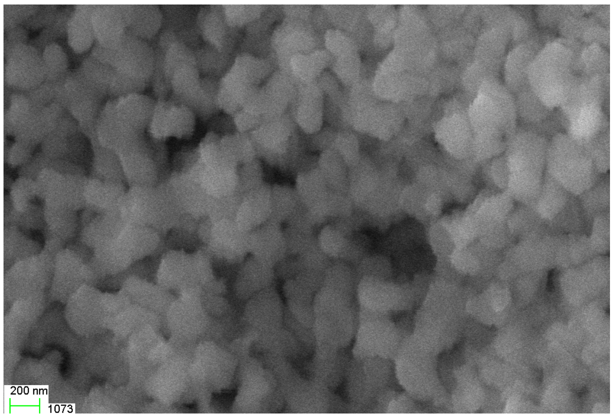

Fig. 4. α-Al_2O_3 layer deposited onto stainless steel substrate (solvent: methanol, voltage 17 kV, distance 25 mm, flow rate 18.5 ml/h, spraying time 10 min).

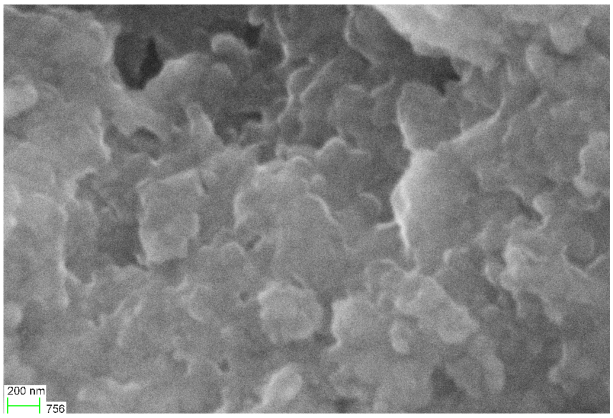

Fig. 5. MgO layer deposited onto aluminium substrate (solvent: methanol 100, voltage 20 kV, distance 25 mm, flow rate 18.5 ml/h, spraying time 6.5 min).

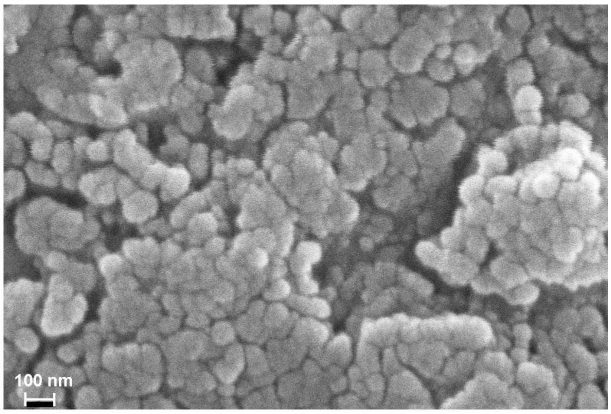

Fig. 6. MgO layer deposited onto stainless steel substrate (solvent: methanol, voltage 8 kV, distance 25 mm, flow rate 0.5 ml/h, spraying time 15 min).

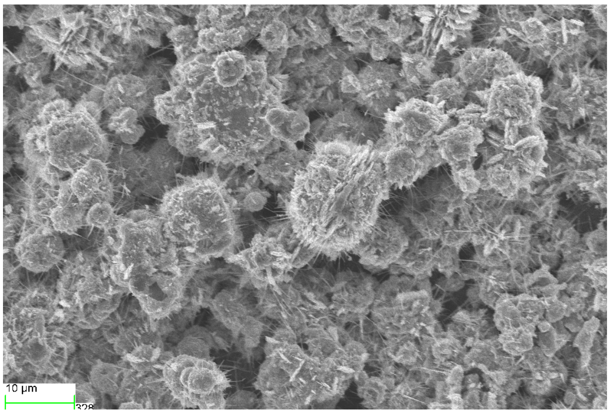

Fig. 7. SEM image of Zn layer deposited by electrospraying on an Al substrate and annealed at a temperature of $600^{o}C$ for a time of 15 min in air. (Zn suspension in ethylene glycol - methanol mixture, mole fraction of ethylene glycol 0.326, voltage 10 kV, capillary 0.6 mm o.d., 0.4 mm i.d., deposition time 9 min, distance 25 mm)

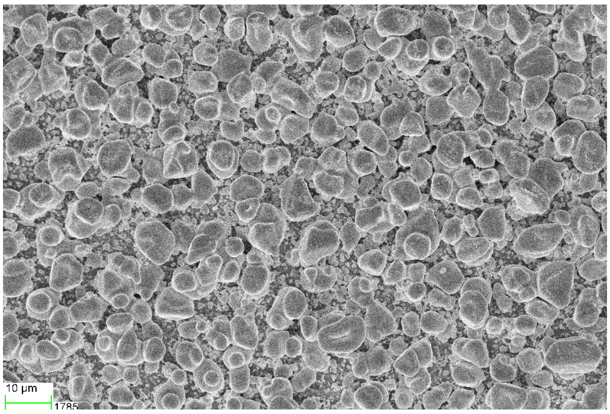

Fig. 8. SEM image of Ag particles deposited by electrospraying onto an Al substrate ($AgNO_3$ precursor, 20 wt.% in distilled water + methanol (1:1), voltage 7.5 kV, capillary 0.25 mm i.d., 0.45 mm o.d., distance 25 mm, flow rate 0.75 ml/h, substrate temperature $420^{o}C$, spraying time 5 min).

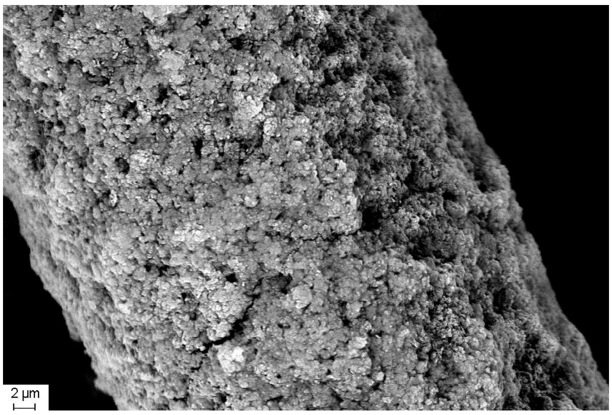

Fig. 9. MgO layer deposited onto polyamide fiber 30 µm dia. (solvent: methanol, voltage 5.1 kV, distance 25 mm, flow rate 0.3 ml/h, spraying time 15 min).

CONCLUSIONS

The paper provides experimental results of electrospray deposition of thin metal-oxide layers onto metal or polymer substrates. The layers were produced from colloidal suspension of the material to be deposited in an appropriate solvent, in the case of our experiments in methanol or methanol-ethylene glycol mixture. The layer morphology depends on the suspended material, the deposition rate, and the substrate temperature.

It was shown that electrospraying is a versatile tool for liquid atomisation and thin layer deposition from aerosol phase. Electrospraying has an advantage of uniform droplets generation with inexpensive equipment, which could operate at atmospheric conditions. The rate of droplets production and layer growth rate is easy to control via voltage and flow rate of the liquid. In our experiments, this technique was utilised for the formation of thin functional layers on metal or polymer substrates. The layers can play a role of protection films, electrodes, or catalyst.

ACKNOWLEDGMENT

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