Electrophoretic Deposition of Thin Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] Thin Films

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Abstract – **Experimental setup for electrophoretic deposition of ogranic materials was constructed and tested.**

Electrophoretic deposition of thin MEH-PPV films was carried out at a constant current of 1 mA. To keep the deposition current constant it is necessary to increase the voltage applied on the electrodes. This effect agree with the theoretical model for electrophoretic deposition of wide-gap or insulator materials.

SEM investigation of the film surface morphology shows that the films consist of hollows of about 30 nm size and wide smooth areas in between. The flexibility of the electrophoretic deposition method allows further process optimization to densify the film structure and reduce the surface roughness.

Keywords – **Molecular electronics, Organic semiconductors, Electrophoretic deposition, Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV).**

I. INTRODUCTION

The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found applications during the past 40 years mainly in traditional ceramic technology [1]. A DC electric field is applied across a colloidal suspension of charged particles depositing a film of particles on the oppositely charged electrode. Electrophoretic deposition (EPD) is essentially a two-step process: electrophoretic transport and deposition. In the first step, charged particles in a liquid are forced to move toward an electrode by applying an electric field across the solution. These charged particles may be generated in one of two ways: the "solution approach", where material is dissolved in a solvent, or the "suspension approach", where material particles are dispersed in a nonsolvent. Colloidal suspension is a solution in poor solvent of material, where the material exists as solid nano-particles [2].

The suspension approach to EPD is primarily used for forming thick (1, 30, 100 μm) films, whereas the solution approach could produce thin (bellow 1 μm) films. The suspension approach is more frequently used for film deposition.

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In the second step, the particles deposited on the electrode surface form a homogeneous film via coagulation.

A post-EPD processing step is usually required, which includes a suitable heat-treatment (firing or sintering) in order to densify the deposits and to decrease the porosity. The drying of the film produced in suspension approach, conducted in the non-solvent vapor expected to yield polymer films with novel microscopic structures. In this case the stage of film formation is separated from the solidification [3].

The advantages of EPD are that [1]:
(i) The deposition rate is high;
(ii) Coatings can be made in any shape;
(iii) The film is dense and uniform;
(iv) The thickness of the film can be controlled by the deposition condition;
(v) Phe process is simple and easy to scale up.

EPD needs a stable suspension with particles charged so as to respond to an applied electric field [4].

This stability of the suspension can be obtained by the following processes [5]:
(i) Selective adsorption of ions onto the solid particle from the liquid;
(ii) Dissociation of ions from the solid phase into the liquid;
(iii) Adsorption of dipoles at the particle surface;
(iv) Electron transfer between the solid phase and the liquid phase due to differences in the work function.

Examples of electrophoretic thin film deposition can be found in the literature, including metals, polymers, carbides, oxides, borides and glasses [4].

In the recent years more succesfull atempts are made to deposit polimer materials e. g. polimer photonic crystals [6] and polymeric donor-acceptor composites [7]. Polymer EPD incorporates the separate phenomena of colloid formation in suspension (solidification), colloid propulsion to the deposition sites (electrophoresis), and colloid aggregation and adhesion onto a substrate (deposition) [8]. These combined processes can facilitate the formation of nanostructure in thin polymer films. Additionally, EPD provides substantial control over the film thickness, marked enhancement of the deposition rate, and improved film composition homogeneity, compared to other wet casting-nanostructured thin film deposition methods [9]. Unlike other wet casting techniques that cannot readily produce polymer films with combined low surface roughness, long-range film thickness homogeneity, and a distinct

nanostructure, EPD process can produce casts of polymers with all of these characteristics.

Electrophoretic deposition, is one of the most widely used coating methods capable of patterning.

Recently there are great efforts for production of large area low-cost organic solar panels and cheap organic light emitting diodes as well. The advantages of the EPD technique suggest good solutions.

This paper aims to construct a simple laboratory setup for electrophoretic deposition of thin organic films and deposit thin poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) films by electrophoretic technique.

II. OUTLINE OF THE THEORY

A. Basic considerations

Counter ions from the liquid form a charge cloud around a charged particle masking their surface charge (Fig. 1).

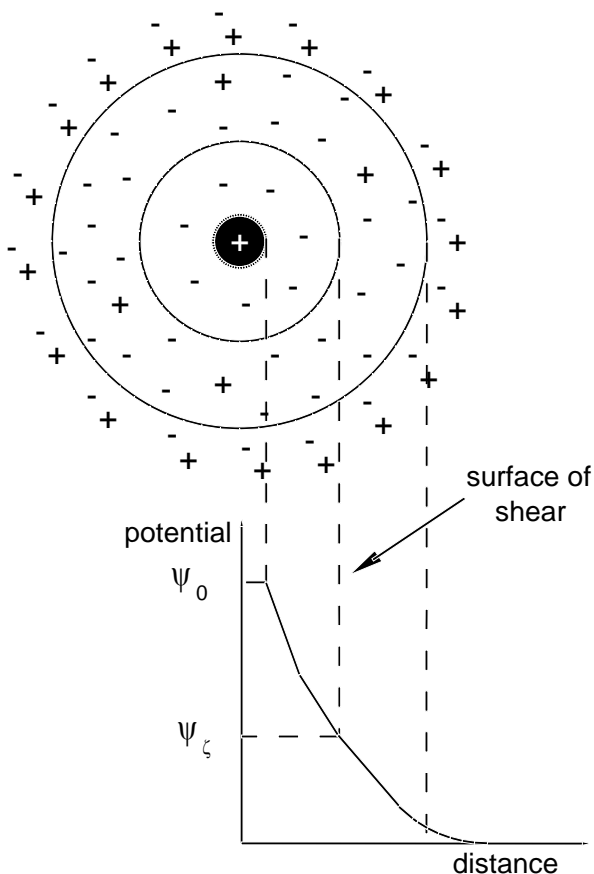

FIGURE 1. DOUBLE LAYER SURROUNDING A CHARGED PARTICLE FORMING THE ZETA POTENTIAL AND EVOLUTION OF THE ELECTRIC POTENTIAL FROM THE SURFACE POTENTIAL, Ψ_0, TO ZERO FAR FROM THE PARTICLE – ACCORDING TO REF. [10]

This ionic atmosphere is called 'diffuse-double layer'. When an electric field is applied, these ions and the particle move in opposite directions. However, the ions are also attracted by the particle, and as a result, a fraction of these ions surrounding the particle will not move in the opposite direction but move along with the particle. Hence, the speed of a particle is not determined by the surface charge

but by the net charge enclosed in the liquid sphere, which moves along with the particle forming a 'lyosphere' shell. The potential at the surface of the lyosphere, the limit between the liquid moving with the particle and the liquid, which does not move with the particle, is termed zeta potential (ζ) and is the main parameter determining the electrokinetic behavior of the particle [10]. It is experimentally accessible.

B. Kinetics of the Electrophoretic Process

Fig. 2 shows schematically the mechanism of coagulation / deposition of oxides via lyosphere distortion and thinning.

The overall-positively charged oxide particle / lyosphere system was moving toward the depositing electrode in an EPD cell (for example, the cathode; Fig. 2). Fluid dynamics and the applied field could distort the double layer shell, thinning ahead and widening behind the particle. Cations in the liquid could also move to the cathode with the positively charged particles. The counter-ions in the extended tails would be neutralized. As result of this reaction, the liosphere around the tail of the particle would become so thin so that the next incoming particle (which has a thin heading liosphere) could approach close enough for coagulation / deposition [11].

The fact that in many reports on EPD little attention is given to the deposition mechanism clearly shows that even
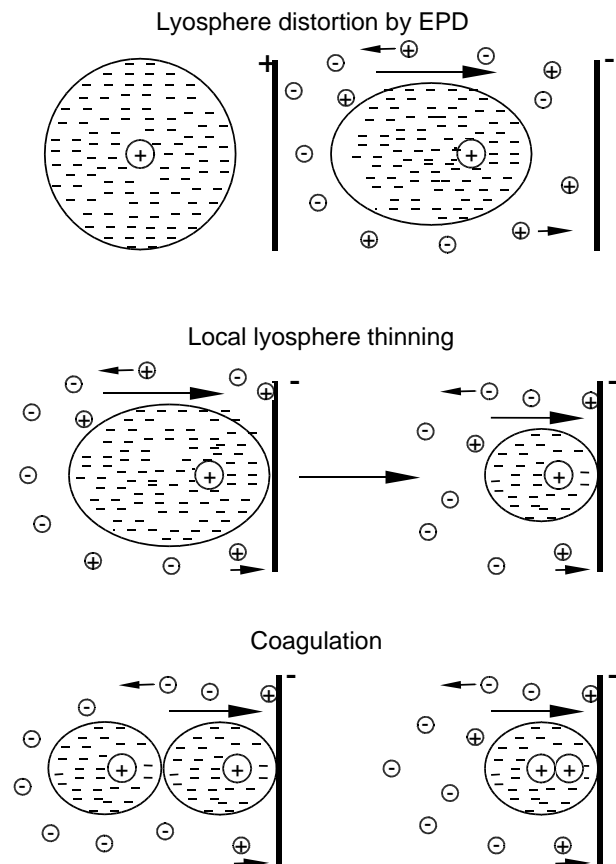

FIGURE 2. SCHEMATIC REPRESENTATION OF THE DEPOSITION MECHANISM BY LYOSPHERE DISTORTION AND THINNING – ADOPTED FROM REF. [5]

if a full understanding of the mechanism is lacking, EPD is already successfully used.

However, a better understanding would reduce experimental work required to determine the optimal parameters of EPD [4].

III. EXPERIMENTAL DETAILS

A. Description of the Setup

An original electrophoretic cell was constructed with capability for controlled immersing of the electrodes into the solution. This option will be used in future experiments expecting that drying the film between two deposition
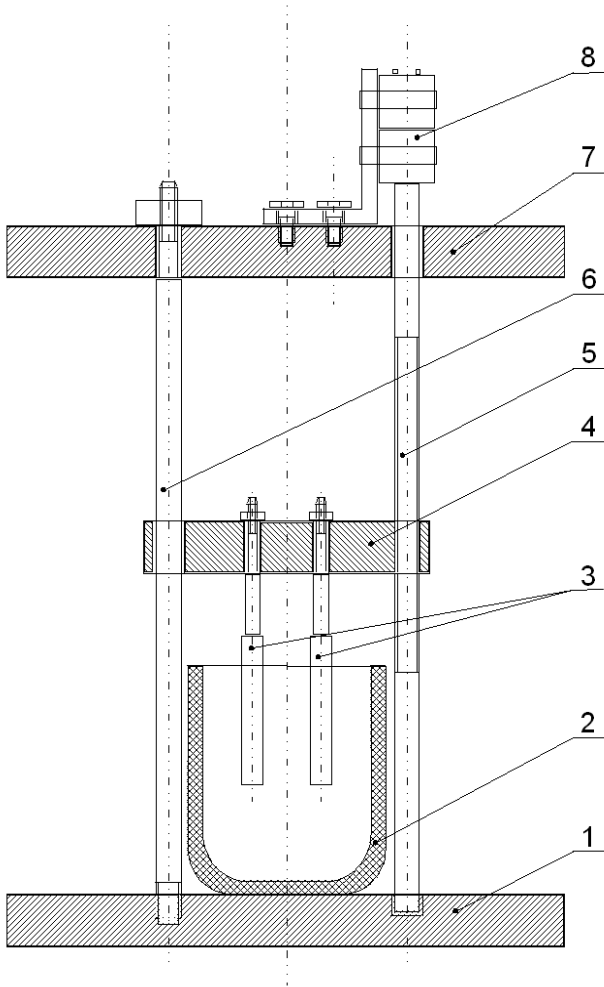

FIGURE 3. SHEMATIC DRAW OF THE ELECTROPHORETIC CELL CONSTRUCTED: PVC BASE (1), GLASS VESSEL OF THE ELECTROPHORETIC CELL (2), ELECTRODES (3), ELECTRODE CARRIER (4), SCREW MECHANISM (5), RULING SHAFT (6), UPPER HOLDER (7), ELECTRICAL MOTOR WITH REDUCTOR (8)

cycles will improve the film quality.

Shematic draw of the electrophoretic cell constructed is presented on Fig. 3. The glass vessel of the electrophoretic cell (2), ruling shaft (6), and the screw (5) for moving the electrode carrier (4) are mounted on a PVC base (1). The

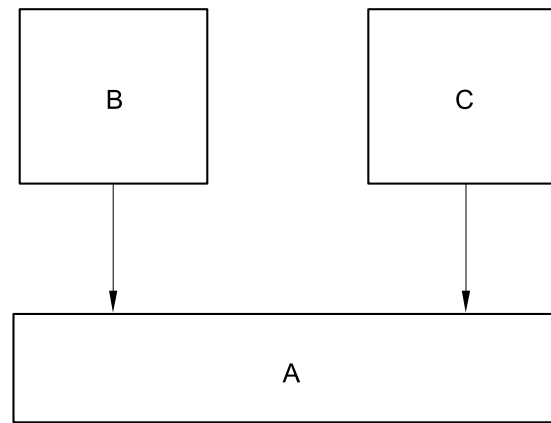linerar moving of the electrodes (3) in two oppisite

FIGURE 4. BLOCK-SCHEMA OF THE SETUP FOR ELECTROPHORETIC DEPOSITION: A-ELECTROPHORETIC CELL, B-MOTOR DRIVER UNIT, C-ADJUSTABLE VOLTAGE SOURCE

directions is provided by the electrical motor and reductor with reduction ratio 1:105. For both electrodes commercially ITO covered glass substrates were used.

Fig. 4 presents the block-schema of the electrical part of the setup for the electrophoretic deposition. It consists of electrophoretic cell (A), motor driver unit (B) and adjustable voltage source (C). The motor driving unit consists of contact relays for starting/stopping the motor and changing of the rotation direction. The voltage value applied on the electrodes in the electrophoretic cell is controlled in the range 0-300 V by adjustable commercial voltage source.

B. Experimental Conditions

1 ml 18 mg/ml solution of MEH-PPV in chloroform was prepared, by mixing with magnetic stirrer and heating in water bath. 9 ml acetonitrile was added to cause precipitation of MEH-PPV from the solution prepared. After the precipitation the color of the solution was changed but no apparently visible particles were observed. These changes supposed that the precipitated particles are of micro (nano) size.

The electrophoretic deposition was carried out immediately after the preparation of the solution at a constant current of 1 mA. The ITO covered substrates were placed at distance of 5 mm and were not moved during the deposition. The films were deposited on the positive electrode by applying voltage for 3 min. During the deposition process the voltage applied on the electrode and the flowing trough the solution current was measured by digital multimeters. About five minutes after mixing the solvents apparently visible particles were observed. Their size permanently increase forming sediments at the bottom of the evaporation vessel. In this stage of the process the solution becomes unusable for further deposition.

The thickness of the films obtained was measured by Talystep Hank Taylor Robson profilometer. The surface morphology images were obtained by Scanning Electron Microscope (SEM) Philips 515.

IV. Results and Discussion

The electrophoretic deposition was carried out immediately after preparation of the solution. To provide stable deposition rate the electrical current flowed trough the electrophoretic cell was kept constant.

The voltage change as a function of the time passed (at a constant current of 1 mA) during the deposition of MEH-
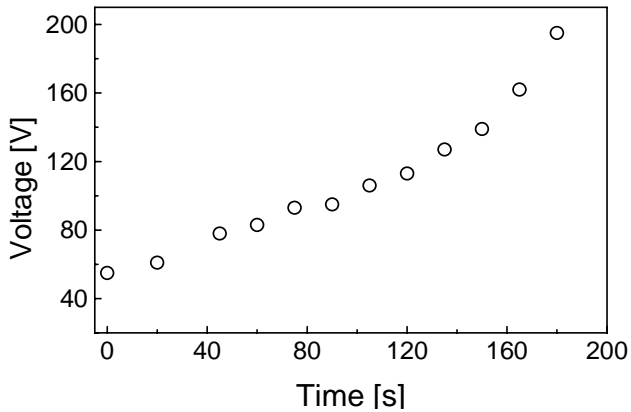

Figure 5. Dependence of the Voltage Applied on the Time Passed for the Electrophoretic Deposition of MEH-PPV Film

PPV is presented on Fig. 5. At the beginning of the deposition the voltage increase almost linearly which could be connected with a single process of decreasing the MEH-PPV concentration in the solution as the material is deposited on the electrode and segments are formed. The second nonlinear part of the curve could result from simultaneous action of two processes, i. e. solution dilution from one side and increased film thickness on the electrode. The second process could cause redistribution of the electric field between the increased film thickness and
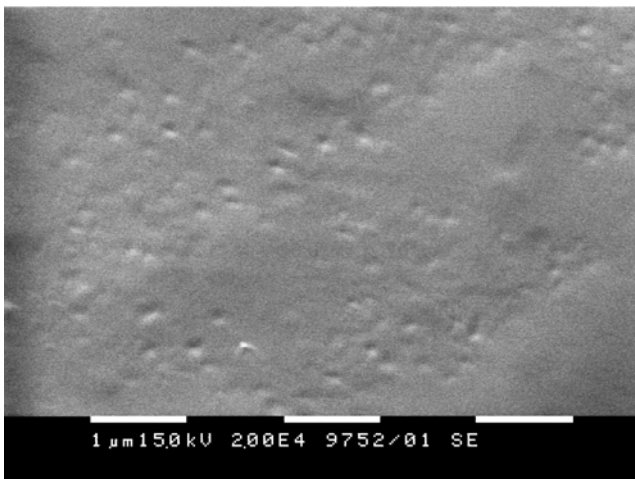

Figure 6. Surface Morphology SEM Image of Electrophoretically Deposited 465 nm Thick MEH-PPV Film

the solution. This effect follow the theoretical model for deposition of wide-gap or insulator materials.

SEM picture of the surface morphology of 450 nm thick MEH-PPV film is presented in Fig. 6. For more contrast imaging the sample was tilted at 40° during the

measurement. It was clearly seen a presence of hollows of about 30 nm diameter and relatively wide smooth areas in between. Hollows could result from hitting the film surface with relatively big and stable electrophoretic particles, which have no time to spill on the film surface and produce uniform film.

This investigation shows that it is possible by electrophoretic deposition to obtain smooth film surface. More optimization of the working conditions, e. g. solution concentration and deposition current should be done. To densify the film structure and consequently decrease the film roughness an intermediate drying between two deposition cycles could be applied. Such experiment is beyond the scope of this work.

V. Conclusion

Experimental setup for electrophoretic deposition of ogranic materials was constructed and tested.

Electrophoretic deposition of thin MEH-PPV films was carried out at a constant current of 1 mA. To keep the deposition current constant it is necessary to increase the voltage applied on the electrodes. This effect agree with the theoretical model for electrophoretic deposition of wide-gap or insulator materials.

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