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2009 J. Phys. D: Appl. Phys. 42 132001

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Electric current during electrophoretic deposition of conjugated polymer

Kazuya Tada¹ and Mitsuyoshi Onoda

Division of Electrical Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2201, Japan

E-mail: tada@eng.u-hyogo.ac.jp

Received 18 March 2009, in final form 25 May 2009

Published 12 June 2009

Online at stacks.iop.org/JPhysD/42/132001**Abstract**

The electric current during the electrophoretic deposition of a conjugated polymer based on polyfluorene has been studied. Thin slab vessels provide a simple path for the colloidal particles during deposition as well as minimum suspension consumption, and the transient currents during the electrophoretic deposition from a suspension containing 1.0 g l^{-1} of the polymer in those vessels reveal clear breaks corresponding to the transit time. The electrophoretic mobility of the colloidal particles in the suspension has been estimated to be $7.0 \pm 0.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The deposition of a uniform film of the polymer over a 9 cm^2 utilizing the thin slab vessel has also been demonstrated.

(Some figures in this article are in colour only in the electronic version)

One of the most significant features of conjugated polymers in the field of semiconductor electronics is solubility, since inks made of soluble semiconductors enable the printed electronic devices such as light-emitting devices, photocells and field-effect transistors [1–7]. Although the preparation of thin films of conjugated polymers by spin-coating is a daily task in laboratories, this method is considered to be a material-consuming process, since a large portion of the solution placed on the substrates is blown away during the spinning. New technologies, including the ink-jet printing, are proposed [8–10]. However, they place the ink in a dot-by-dot manner, and most of them involve nozzles which can clog, and both these features diminish the usefulness of the methods in industrial production of large-area devices.

Electrophoretic deposition is a classical technology of coating [11–13]. The principle of the method is quite simple: the electric field generated in a suspension accelerates the charged colloidal particles in the suspension, and the particles eventually hit the surface of the electrodes having opposite charge to deposit on them. Thus, this method can coat a large area at once without nozzles. We have proposed electrophoretic deposition as a method to obtain

nano-structured conjugated polymer films [14–16], and have recently mentioned a way to obtain smooth and dense films suitable for electronic devices such as light-emitting devices [17]. In the course of the study, it has been found that coating the electrode with poly(ethylene-3,4-dioxythiophene):poly(styrenesulfonate) (PEDOT), which is known as a useful hole-transporting material in the polymer-based devices, has a detrimental effect on the deposition of the polymer [18]. This clearly indicates that understanding the basic process of electrophoretic deposition including the characterization of polymer suspension is important for the development of electrophoretic deposition as a coating process of conjugated polymers.

In this paper, electric current during the electrophoretic deposition of a conjugated polymer, poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)] (PDOF-MEHPV), is studied. It is found that the electric current profile strongly depends on the shape of the deposition vessel. A preliminary estimation of the electrophoretic mobility of the colloidal particles is also attempted.

PDOF-MEHPV, purchased from American Dye Source, and aqueous dispersion of PEDOT, from Aldrich, were used as received. The suspension containing 1.0, 0.5, 0.2, 0.1, 0.05 g l^{-1} of PDOF-MEHPV was made by simply mixing

¹ Author to whom any correspondence should be addressed.

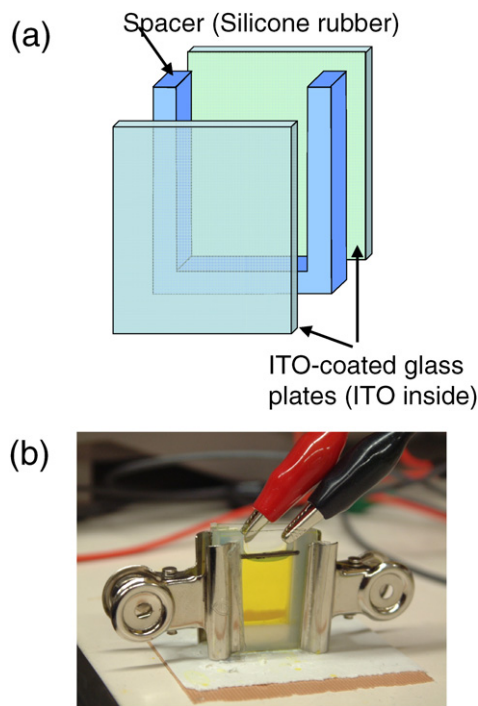


Figure 1. (a) Schematic and (b) photograph of the thin slab vessel used in this study.

equivalent volumes of toluene solution of the polymer and acetonitrile. A mixture of acetonitrile and toluene with a 1:1 volume ratio without the polymer was used as a control.

Indium-tin-oxide (ITO) films coated on glass plates were used as the electrodes. As mentioned in the previous paper, the electrophoretic deposition of PDOF-MEHPV occurs on the positively biased electrode [17]. Both bare and PEDOT-coated (approximately 50 nm in thickness by spin-coating) ITO electrodes were employed as deposition electrodes. A bare ITO electrode served as a counter electrode. The electrophoretic deposition was carried out in a glass cuvette, which is usually used for optical spectroscopy, with an optical path of 1 cm at the initial stage of this study, and later in thin slab vessels consisting of two ITO-coated glass plates with a silicone rubber spacer for reasons to be mentioned later. The scheme and the photograph of the thin slab vessel are shown in figure 1. The deposition area was approximately 1.0 cm × 1.5 cm and the electrode spacing was 5 mm throughout this study.

The measurement of electric current was carried out using a Keithley 6517A electrometer. The voltage, ranging from 100 to 300 V, was applied between the deposition and the counter electrodes using the internal high voltage power supply of the electrometer.

Figure 2 shows the transient currents during the electrophoretic deposition on bare ITO electrodes at 200 V measured by using the glass cuvette. Although the current for suspensions increases with increasing polymer concentration, the current profiles are apparently featureless regardless of the polymer concentration. During this experiment, it was observed that the suspension which resides behind the

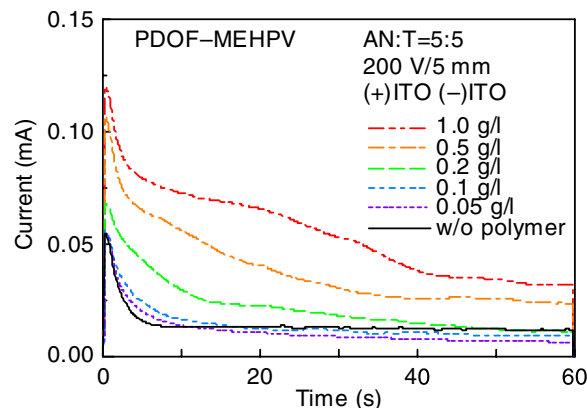


Figure 2. Transient currents during the electrophoretic deposition on bare ITO electrodes at 200 V in a glass cuvette having an optical path of 1 cm filled with suspensions containing various amounts of the polymer.

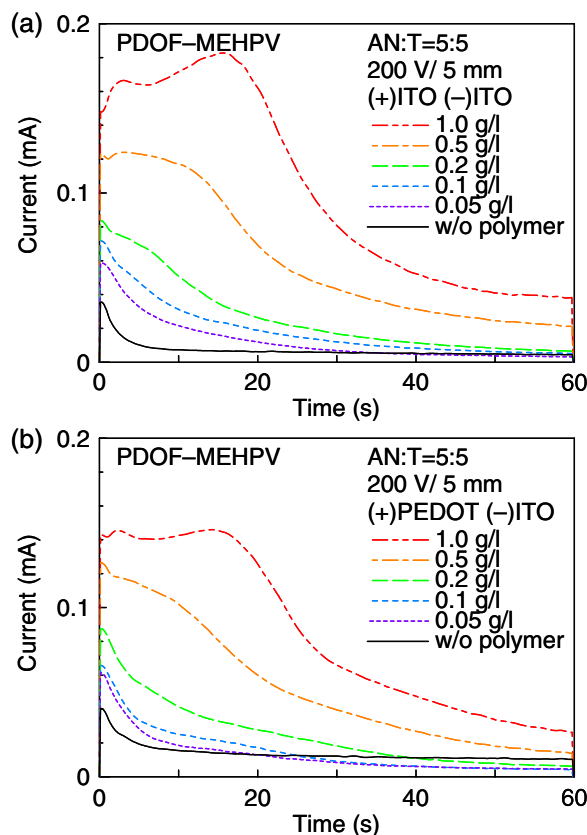


Figure 3. Transient currents during the electrophoretic deposition at 200 V in the thin slab vessels on (a) bare and (b) PEDOT-coated ITO electrodes with various polymer concentrations.

electrodes also contributed to the deposition. The path of those colloidal particles and that of the particles which initially exist between the electrodes are obviously different; the particles between the electrodes deposit faster than the particles behind the electrodes, since the latter particles must slip through the narrow gaps surrounded by the electrodes and the walls of the cuvette to reach the front of the electrode. The complicated deposition process taking place in the cuvette may make the current profile featureless. Thus, the thin slab vessel

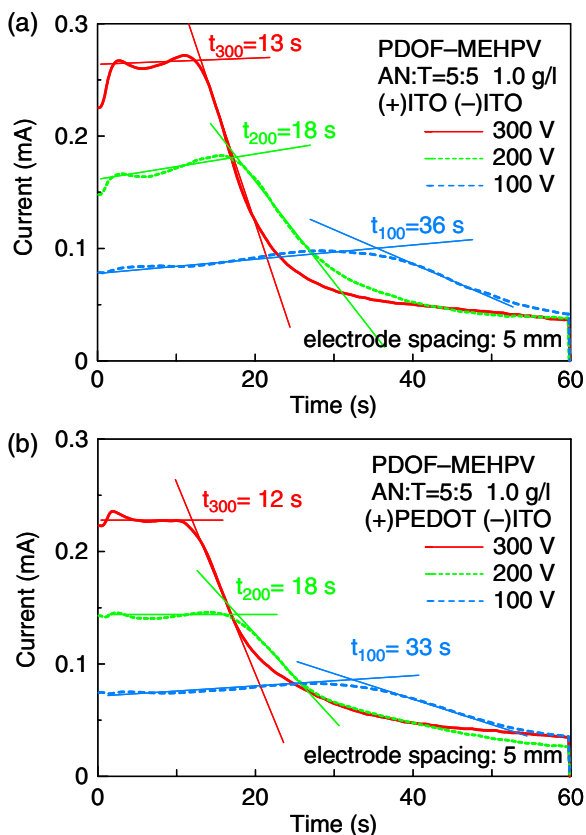


Figure 4. Transient currents during the electrophoretic deposition in the thin slab vessels charged with the 1.0 g l^{-1} suspension on (a) bare and (b) PEDOT-coated ITO electrodes at various voltages. The lines used for the estimation of transit times are indicated.

shown in figure 1, in which the suspension resides solely between the electrodes, was employed to measure the electric current.

The transient currents during the electrophoretic deposition on bare ITO electrodes at 200 V in the thin slab vessels are shown in figure 3(a). In contrast to the data in figure 2, the current profiles for the 0.5 and 1.0 g l^{-1} suspensions show clear breaks. Similar features can be found in the transient currents for the deposition on PEDOT-coated electrodes shown in figure 3(b). It is also noticed that the current profiles for the 0.05 and 0.1 g l^{-1} suspensions can be clearly distinguished, although the difference between the bare and the PEDOT-coated electrodes is not clear.

Figure 4(a) shows the transient currents during the electrophoretic deposition on the bare ITO electrodes from the 0.1 g l^{-1} suspension at various voltages. The transit time can be estimated as an intersection of the extension lines of the gentle and steep portions of the curve, as indicated in the figure. The case of PEDOT-coated electrodes shown in figure 4(b) also reveals similar features. As indicated in figure 5, the product of the voltage and the transit time has been found to be nearly identical regardless of the applied voltage, suggesting that the deposition process in the suspensions is governed by a simple drift-like process. Thus, the velocity of the colloidal particles v can be analysed by the equation $v = (d/\tau) = \mu(V/d)$, where d , τ , μ and V denote the electrode spacing, the transit

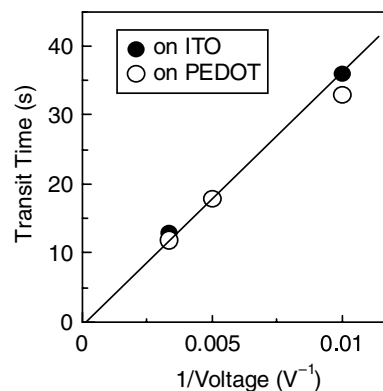


Figure 5. Relationship between the inverse voltage and the transit time estimated from figure 4.

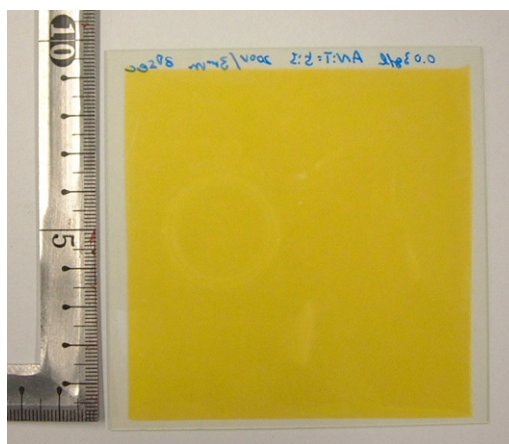


Figure 6. Photograph of a 9 cm-square PDOF-MEHPV film prepared by the electrophoretic deposition using the thin slab vessel.

time, the electrophoretic mobility of the colloidal particles and the voltage applied between the electrodes, respectively. With this expression, the electrophoretic mobility of the colloidal particles in the PDOF-MEHPV suspension is estimated to be $7.0 \pm 0.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ regardless of whether the electrode is coated with PEDOT, although it may fluctuate with experimental batches. This value has the same order of magnitude as those reported for suspensions of inorganic materials [12].

In contrast to the ready-made vessels, the volume of the suspension in the thin slab vessels is limited by the electrode plates used and the volume of the suspension is minimized. Encouraged by this feature, preparation of rather large-area film was attempted. As shown in figure 6, a uniform film over a square approximately 9 cm on a side was deposited by applying 300 V between the ITO electrodes 3 mm apart filled with a 0.03 g l^{-1} suspension of PDOF-MEHPV.

In conclusion, it has been clarified that the transient electric current during the electrophoretic deposition strongly depends on the shape of the vessel. With the thin slab vessel geometry, which provides a simple path for the colloidal particles during deposition as well as minimum suspension consumption, transient currents revealing clear plateaus and breaks have been recorded. The product of the applied voltage and the transit time has been found to be almost identical

regardless of the applied voltage. The electrophoretic mobility of the colloidal particles in the suspension has been estimated to be $7.0 \pm 0.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, regardless of whether the deposition electrode is coated with PEDOT. The deposition of a 9 cm-square PDOF-MEHPV film utilizing the thin slab vessel has also been demonstrated.

Acknowledgments

This work was supported in part by Grant-in-Aid for Young Scientists (B) (19760226) and the research grant from the IKETANI Science and Technology Foundation.

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