CONDUCTIVITY MEASUREMENTS WITH MULTILAYERED LANGMUIR BLODGETT FILMS PRODUCED BY 4-METHYLBENZENETHIOL ENCAPSULATED GOLD NANOPARTICLES AND TWO KINDS OF PEO DERIVATIVE CONTAINING LI^+ IONS

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ABSTRACT

Langmuir – Blodgett (LB) thin film technique has been used to fabricate thin films of thiol-coated gold nanoparticles and lithium-doped poly(ethylene oxide) (PEO) derivative matrix. These thin films have been fabricated on interdigitated gold electrodes. Electrical measurements have been made using these thin films containing 4-32 layers. I-t measurements for all films showed that the current passing through is stable with time. The I-V measurements showed that the current passing through the Langmuir-Blodgett films is in the μA and nA (for 0-5V bias) region for nanoparticles and PEO respectively and that the presence of ions in the films modifies the conductivity.

Keywords: Langmuir – Blodgett (LB) thin films, nanoparticles, polyethyleneoxide (PEO), Electrical conductivity

ÖZET

Thiol ile kaplanmış altın nanoparçacıklar ve lityum dop edilmiş polyetilen oksit (PEO) matrisi Langmuir – Blodgett (LB) ince film üretiminde kullanılmıştır. Bu ince filmler interdijite altın elektrotlar üzerine oluşturulmuştur. 4-32 tabaka içeren bu filmler kullanılarak elektriksel ölçümler yapılmıştır. Tüm filmler için yapılan I-t ölçümleri akımın zamanla sabit olduğunu göstermiştir. I-V ölçümleri LB ince film üzerinden geçen akımın nanoparçacıklar ve polyetilen oksit (PEO) için sırasıyla μA ve nA (0-5V aralığı için) mertebesinde olduğunu ve film içinde iyon varlığının iletimi değiştirdiğini göstermiştir.

Anahtar kelimeler: Langmuir – Blodgett (LB) ince filmler, nanoparçacıklar, polyetilen oksit (PEO), elektriksel iletkenlik

1. INTRODUCTION

Conducting polymers are of interest because of their relatively high conductivity (compared to most organic materials), their low density and their processibility. There are a number of interesting applications of conducting polymers such as biomolecular electronic devices [1] and optoelectronic devices [2]. Another branch is molecular electronics which includes diodes, field effect transistors and sensors [3]. An example of a conducting polymer is poly(ethylene oxide) (PEO) and its complexes with inorganic or organometallic salts which are of considerable interest for applications as solid state ion conductors or mixed conductors in electrochemical devices of different kinds. Solvent-free polymer electrolytes which are based on (PEO) derivatives are relatively stable polymers which can dissolve lithium salts to yield semi crystalline or fully amorphous complexed phases [4]. That material also attracts

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interest as an alternative to conventional liquid electrolyte solutions in which the polymer behaves as the medium through which the ions are transported [5-7].

Bulk gold is metallic in nature while colloidal gold nanoparticles with radii in the range 2-4 nm have electronic properties. Such nanoparticles may find applications in many areas including optoelectronics, chemical biosensors etc. [8] and potential application in sensing [9].

Langmuir-Blodgett thin film technique is an excellent method to fabricate monolayer thick organic films [10-11]. The poly(ethylene oxide) polymers and gold thiols have been investigated for their conductivity properties and found to form LB films [12]. The results of such studies showed that nanostructured electronic devices can be developed for applications such as zener diodes [13]. In this study, the conduction behavior of Langmuir-Blodgett films of thiol-coated gold nanoparticles and poly(ethylene oxide) derivative polymers has been investigated as a function of the number of transferred layers. Langmuir-Blodgett thin films have been transferred onto interdigitated gold electrodes using 4-methylbenzenethiol encapsulated gold nanoparticles and two kinds of poly(ethylene oxide) derivatives. Lithium ions have been embedded in the poly(ethylene oxide) matrix. Because of the transport behavior of lithium ions through the helical structure of the poly(ethylene oxide) matrix, an increase in current is expected. The dependence of the current on film thickness has also been investigated.

2. EXPERIMENTAL PART

2.1. Materials

Three different kinds of molecules have been used in this study. Two of them are poly(ethylene oxide) derivatives and the other one is 4-methylbenzenethiol ($HS\text{-}C_6H_4\text{-}CH_3$) encapsulated gold nanoparticles. The polymers will be referred to using the code-names C1216 and C16 and the nanoparticles will be referred to as gold thiol. The chemical structures of these materials are shown in Figure 1. The syntheses of the molecules C1216 and C16 [14,15] and gold thiol [8] are described in previous studies. Full names of the materials C16 and C1216 are poly[tetraoxyethyleneoxymethylene (5-hexadecyloxy-1,3-phenylene) methylene] and poly[tetraoxyethyleneoxymethylene (5-hexadecyloxy-1,3-phenylene) methylene]-co-poly [tetraexyethyleneoxymethylene (5-dodecyloxy-1,3-phenylene) methylene] respectively.

The solutions prepared using chloroform as a solvent, for gold thiol, C1216 and C16 polymers have concentrations of 0.94, 1.816 and 1.06 mg ml^{-1} respectively. Lithium ions have been incorporated into the Langmuir-Blodgett films by dissolving 4.5 mg of $LiClO_4$ salt in the water subphase.

2.2. I-V Measurements

A computer controlled Langmuir-Blodgett film trough was employed to investigate the behavior of C1216 and C16 polymer molecules and the gold thiol incorporating lithium ions at the air/water interface. Films were deposited onto interdigitated gold electrodes with predetermined surface pressure and dipping speed; the electrodes were 2.88 x 2.88 mm^2 in dimensions and shown schematically in Figure 2. I-t and I-V measurements have been recorded using these films. In I-t measurements potential difference across two electrodes were fixed to 5V constant value and in I-V measurements the voltage was varied from zero to several volts using 0.1V steps. All experimental data were recorded at room temperature.

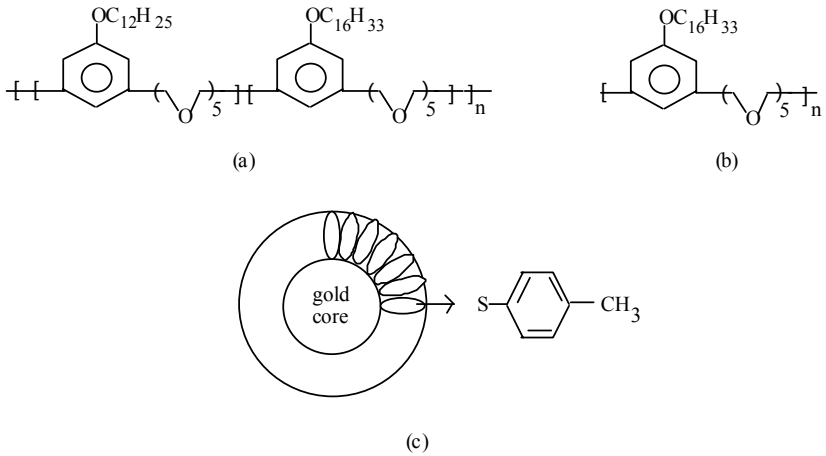

Fig 1: Chemical structures of the molecules coded C1216 (a) and C16 (b) and gold thiol (c).

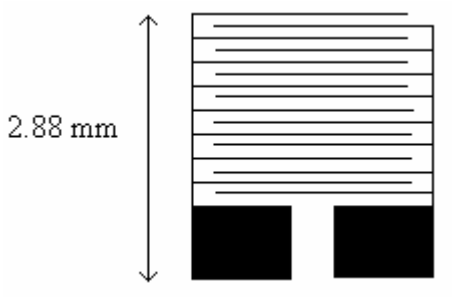

Fig. 2: Schematic figure of an interdigitated gold electrode.

3. RESULTS AND DISCUSSION

Figure 3 and Figure 4 shows I-t graphs of gold thiol and polymers for different number of layers. It is clear that the current passing through these Langmuir-Blodgett films is stable with time and in μA and nA region for gold thiol nanoparticles and polymers respectively. That means there is no spontaneous difference in current with time which may be caused by the chemical structure, physical conditions of the environment etc. These measurements also showed that for the same bias, the current passing through the gold thiol nanoparticle film is higher than the current passing through the C1216 and C16 polymers.

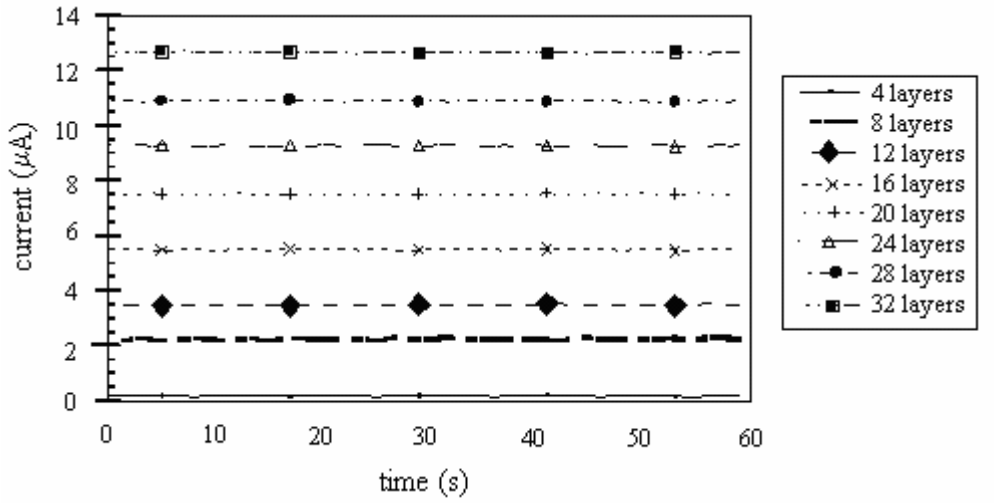

Fig 3: I-t graphs of gold thiol nanoparticle LB films for different numbers of layers (4 to 32).

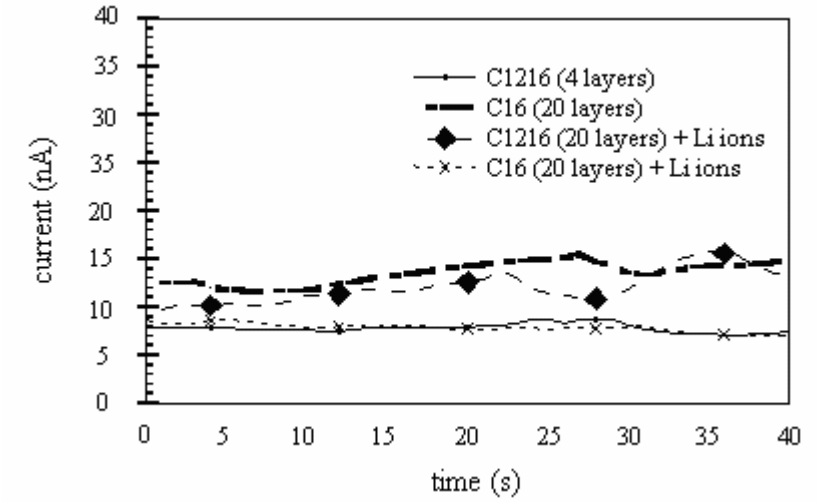

Fig. 4: I-t graphs of C1216 and C16 polymers different number of transferred layers with and without incorporated lithium ions.

The results of I-V measurements for gold thiol nanoparticles as a function of number of layers (from 4 to 32) are given in Figure 5. There is a regular increase in current with increasing applied voltage across the electrodes. However for C1216 and C16 such regular increase could not be observed. Figure 6 and Figure 7 show the dependence of current against applied voltage across the electrodes for C1216 and C16 respectively. For both materials there is an increase in current with voltage but the increase is not as regular as the gold thiol nanoparticle film. Additionally, the Langmuir-Blodgett films of polymer C1216 consisting 4 and 20 layers possess lower current than the Langmuir-Blodgett films of lithium ions incorporated of C1216 with the same number of layers. However, Langmuir-Blodgett films of C16 with incorporated lithium ions yields a smaller current than the Langmuir-Blodgett films of C16 without incorporated lithium ions. (Figure 7)

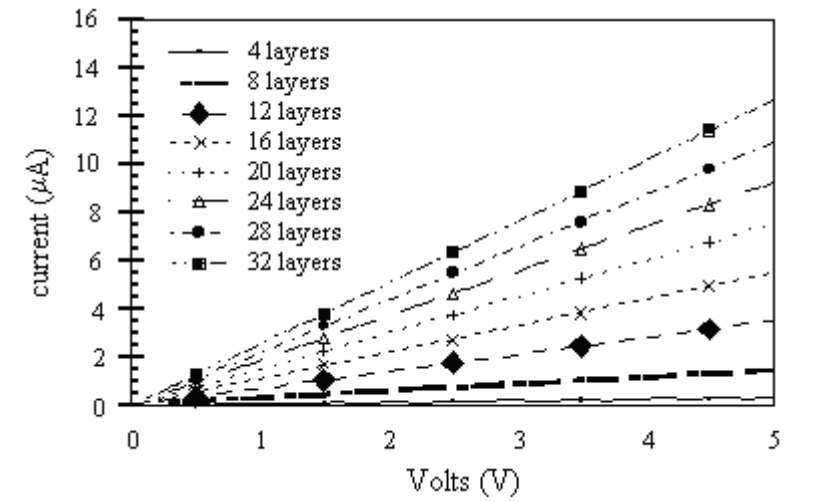

Fig. 5: I-V graphs of gold thiol nanoparticle LB films for different numbers of layers (4 to 32).

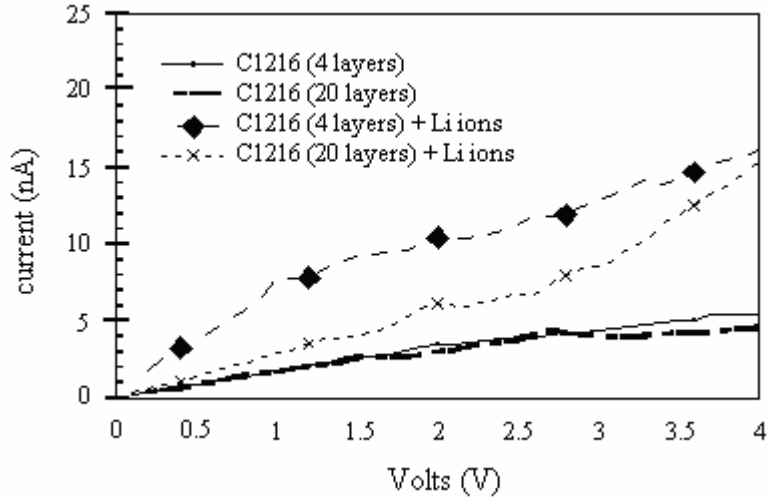

Fig. 6: I-V graphs of C1216 polymer LB films for 4 and 20 layers with and without incorporated lithium ions.

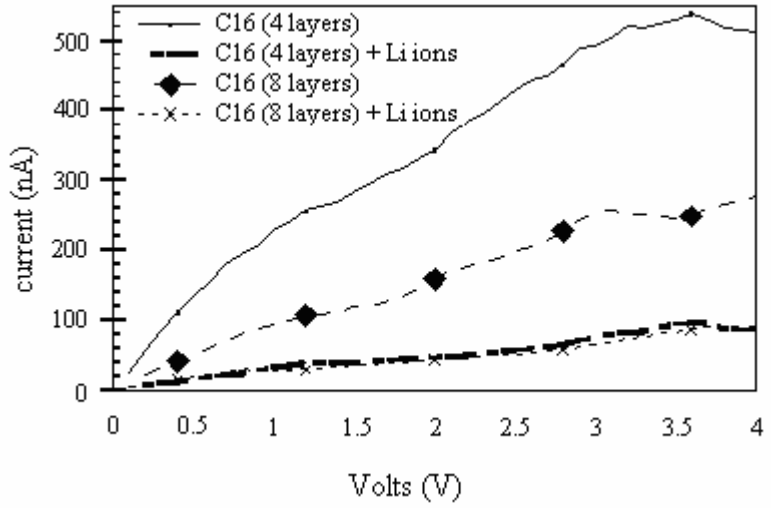

Fig. 7: I-V graphs of C16 polymer LB films for 4 and 8 layers with and without incorporated lithium ions.

The results of the investigation of the dependence of the current as a function of the number of layers are indicated in Figure 8 for gold thiol nanoparticles and in Figure 9 for C1216 and C16 polymers. For gold thiol nanoparticles, the dependence of the current on the number of layers is linear. However for C1216 and C16 polymers, the dependence of the current is nonlinear. That result may have a number of causes. The deposition conditions are important in determining the deposition of homogeneous layers. The dependence of current on the number of layers may be a result of deposited layer quality.

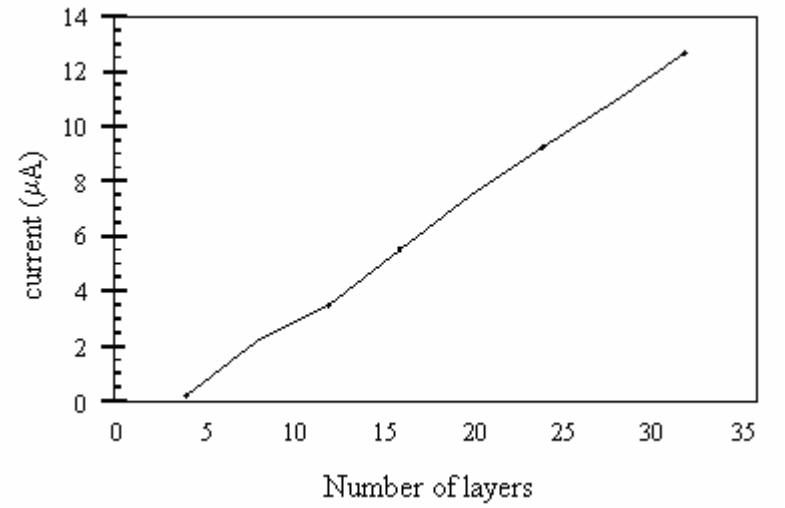

Fig. 8: Dependence of current through gold thiol nanoparticle LB film versus number of layers.

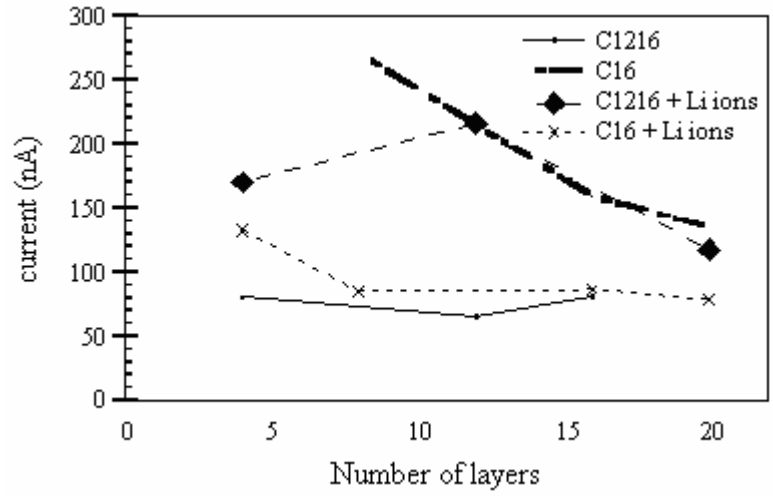

Fig. 9: Dependence of current for C1216 and C16 polymers against number of layers

4. SUMMARY

It is found that the current passing through the Langmuir—Blodgett films is stable with time. For gold thiol nanoparticles there is a regular increase in current with increasing applied voltage across the electrodes. For polymer C1216 incorporating lithium ions into the films causes an increase in current passing through the LB films; however for polymer C16 incorporating lithium ions into the films causes a decrease in current passing through the LB films.

Future studies will concentrate on the conducting behavior of the systems made of poly (ethylene oxide) derivatives and gold thiol nanoparticles mixed together for a possible application of lithium-ion batteries.

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