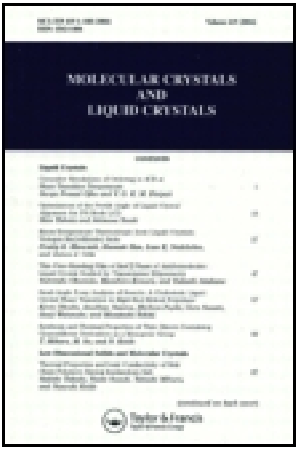

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Polypyrrole Patterns Formed During Electropolymerization of Pyrrole at Gold Surfaces in Potassium Chloride Electrolyte Solutions

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To cite this article: Sang-Eun Bae, Se-Hwan Paek, Young-Sang Kim & Chi-Woo Lee (2000): Polypyrrole Patterns Formed During Electropolymerization of Pyrrole at Gold Surfaces in Potassium Chloride Electrolyte Solutions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 359-362

To link to this article: http://dx.doi.org/10.1080/10587250008024938

Mol. Cryst. and Liq. Cryst., 2000, Vol. 349, pp. 359-362
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Printed in Malaysia

Polypyrrole Patterns Formed During Electropolymerization of Pyrrole at Gold Surfaces in Potassium Chloride Electrolyte Solutions

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Electropolymerization of pyrrole in the aqueous electrolyte solutions of potassium chloride was investigated by means of chronoamperometric, *in situ* electrochemical quartz crystal oscillator and optical microscopic methods. Polypyrrole patterns of one dot, two dots and three dots of triangle were successfully formed at gold electrode surfaces in aqueous solutions of pyrrole and were confirmed *ex situ* by optical microscopy. Further development of the technique and possible applications are discussed.

Keywords: pyrrole; polypyrrole; pattern; quartz crystal oscillator

INTRODUCTION

It has been known long time that pyrrole can be electropolymerized at conducting substrate under ambient laboratory conditions.[1-5] Electrodeposition of polypyrrole is believed to undergo the nucleation and growth processes to produce highly conductive free-standing materials. Electrochemical methods, compared to chemical ones, of polymerization of pyrrole offer materials with better conducting properties, and for some applications such as the construction and repair of electronic devices, electrochemical polymerization offers the possibility of *in-situ* formation.

We have been interested in investigating changes in microrheological property of polypyrrole during electrochemical growth.[6,7] *In situ* electrochemical quartz crystal oscillator (EQCO) method could be successfully applied to monitor films developed at the interface between the electrode and electrolyte solutions, when polypyrrole grew homogeneously on the substrate electrode. In potassium chloride electrolyte solution, however, polypyrrole did not grow homogeneously on gold electrode surfaces. It follows that EQCO was not applicable to probe the viscoelasticity of film grown over the whole surface of electrode. We investigated the phenomenon of inhomogeneous growth of polypyrrole and were able to control the electrochemical growth of polypyrrole to produce polypyrrole patterns on gold electrode surface in the aqueous electrolyte solutions of potassium chloride.

EXPERIMENTAL

All chemicals used in this work were of the best quality available from Aldrich and were used without further purification except pyrrole, which was purified by distilling under reduced pressure to produce colorless liquid. Solutions were made up with Milli-Q grade water.

Polypyrrole was grown by sweeping the potential applied to the electrode from 0 to + 900 mV versus potassium chloride saturated calomel electrode (SCE) in solutions of 0.2 M pyrrole and 0.1 M potassium chloride unless described otherwise. All the experiments were performed under argon atmosphere at 23 (±2) ℃. An electrochemical set-up of three electrode cell was the same as before.[6,7]

RESULTS AND DISCUSSION

Decrease in resonant frequency with little change in resonant resistance observed above + 800 mV when potential was scanned from 0 to + 900

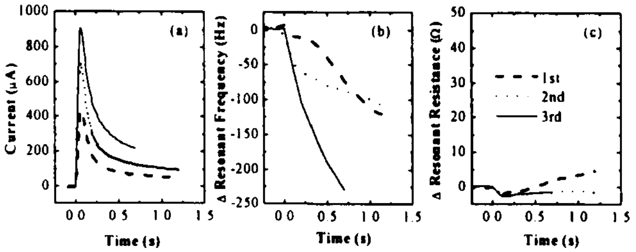

FIGURE 1 Chronoamperometric curves (a) and changes in resonant frequency (b) and resonant resistance (c) observed during electropolymerization of pyrrole at 0.65 V vs. SCE.

mV versus SCE in the aqueous solution of 0.2 M pyrrole, 0.1 M potassium chloride, and 0.03 M phosphate (pH 7), because electropolymerized pyrrole was deposited on the electrode surface. Voltammogram simultaneously recorded agreed with those reported in the literature.[3,6] As the number of potential cycles increased, the potential where the resonant frequency drops decreased, indicating that the electropolymerization is easier at the surface of polypyrrole than that of bare goid electrode.

Electrochemically grown polypyrrole films were inhomogeneous in color as well as in thickness, when they were removed from electrochemical cells and inspected visually ; in the one part of the gold electrode surface, little film was formed, in the second some film with blue color and in the third thick film with black color. The deposition of polypyrrole was strongly dependent on the shape and location of counter electrode, potential imposed and the concentration of pyrrole and supporting electrolyte.

After some experimental trials, we found the conditions where a reliable growth of polypyrrole film can be made electrochemically. Figure 1 shows the chronoamperometric curves (a) and changes in resonant frequency (b) and resonant resistance (c) observed during the three different experiments of electropolymerization of pyrrole at + 0.65 V versus SCE in the aqueous solution of 0.2 M pyrrole, 0.1 M potassium chloride, and 0.03 M phosphate at pH 7. In all three experiments, chronoamperometric curves have similar features with the maximum current near 0.1 second after the potential applied. The rising and decaying transients are those expected for the nucleation and growth of a new conducting phase on an inert electrode surface.[8] Resonant frequency decreased monotonically with little change in resonant resistance, suggesting that polypyrrole film grew elastic. The dots of polypyrrole films formed in the above three chronoamperometric experiments are shown in Figure 2. All the optical microscopic images were taken *ex situ.*

Analysis of the above frequency data shows that the amount of pyrrole units of the first, second and third dots are 0.29, 0.18, 1.01 x 10^{-10} mole, respectively. Similar triangles of three dots were reproducibly produced in our laboratory. The size of each dot and of triangle can be controlled by change in electropolymerization time and mechanical movement, respectively. Thus, we successfully fabricated patterns with elastic polypyrrole film dots.

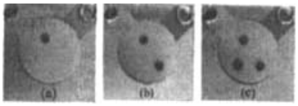

FIGURE 2. *Ex situ* optical microscopic images of polypyrrole patterns of one dot (a), two dots (b), and three dots of 0.33, 0.28, and 0.42 mm (c) formed in Figure 1.

ACKNOWLEDGEMENT
This work was supported by Korea Science and Engineering Foundation.

References

[1] A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc. Chem. Commun.*, **635** (1979).
[2] F. -R. F. Fan, and A. Bard, *J. Electrochem. Soc.*, **129,** 1009 (1982).
[3] S. Asavapiriyanont, G. K. Chandler, G. A. Gunawadena, and D. Pletcher, *J. Electroanal. Chem. Interfac. Electrochem,* **177,** 229 (1984).
[4] K. Naoi, Y. Oura, M. Maeda, and S. Nakamura, *J. Electrochem. Soc.*, **142,** 417 (1995).
[5] J. Rodriguez, H. J. Grande, and T. F. Otero, *Handbook of Organic Conductive Molecules and Polymers* ed. by H. S. Nalwa, Vol. 2, John Wiley & Sons Ltd., 415 (1997).
[6] S. -E Bae, and C. -W. Lee, *J. Korean Electrochem. Soc.*, **2,** 66 (1999).
[7] C. -W. Lee, S. -Y. Lee, S. -E Bae, G. -R Lee, D. -S. Shin, and S. -H. Paek, *Molecular Functions of Electroactive Thin Films* ed. by N. Oyama and V. Birss, Electrochemical Society PV **98–26,** 91 (1998).
[8] L. Heerman and A. Tarallo, *J. Electroanal. Chem.*, **470,** 70 (1999).