



Electropolymerization of polypyrrole at the three-phase interline: Influence of polymerization conditions

Min Li, Hua Zhu, Xuhui Mao, Wei Xiao, Dihua Wang*

School of Resource and Environmental Science, Wuhan University, Wuhan 430072, PR China

ARTICLE INFO

Article history:

Received 30 November 2012

Received in revised form 1 January 2013

Accepted 3 January 2013

Available online 11 January 2013

Keywords:

Electropolymerization

Polypyrrole film

Three-phase junction

Supercapacitor

Three-phase electrochemistry

ABSTRACT

Free-standing polypyrrole film was electrosynthesized at the interface between an HClO_4 aqueous solution and a pyrrole chloroform solution through a dynamic three-phase interline electropolymerization (D3PIE) process. The cyclic voltammetry measurements showed that the onset potential for the oxidation of pyrrole monomers was $\sim 0.2\text{ V}$ vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$, and the radial expansion of conductive polymer film gradually increased the reaction currents. Under potentiostatic conditions, higher potentials, higher counterion (perchlorate) concentrations and higher monomer concentrations all caused a faster growth of polymer, and the aqueous perchlorate ions appeared the most sensitive factor for the reaction currents. In the initial stage of electropolymerization, the reaction currents and the diameters of polymer films increased linearly with the operating times, and a simple model can be used to describe the growth behavior of the circular polymer film. However, several factors can cause the deviation from an ideal linear relation in the later stage of electropolymerization. Higher aqueous perchlorate concentration increased the penetration amount of perchlorate ions to organic solvent phase, resulting in the longitudinal growth of PPy polymers. In addition, the prepared PPy films exhibited significantly different microstructures between the side toward water and the side toward organic solvent, and the aqueous perchlorate concentration and monomer concentration both affect the morphologies of films greatly. In order to observe a well-defined expansion of three-phase interline, lower concentrations of aqueous perchlorate ions and monomers are preferable.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Many electrochemical processes involve three phases, such as the intercalation of lithium ions into cathode materials [1–4], the electrochemical conversion of AgCl to Ag in KCl aqueous solution [5,6], and the electrochemical reduction of oxygen gas in solid oxide fuel cells [7–10]. Three-phase electrode or three-phase electrochemistry is used to describe the electrochemical process involving a solid electrode in contact with two other phases, such as gas/liquid, liquid/liquid and solid/liquid. A typical three-phase electrochemical system can be constructed with one solid phase (electron conductor) and two liquid phases (a polar solvent and an apolar solvent). The two immiscible liquids were separated, but also connected by their interface, while the three phases were only connected by the one dimensional interline (or a junction point). Due to its unique structure and easy assembly, this facile solid/liquid/liquid three-phase system was initially

employed for investigating the thermodynamics and kinetics of ion transport from water to organic solvent [11,12]. Scholz et al. [11–14] proposed a three-phase electrode for determining the Gibbs energy of ion transfer across water–organic liquid interfaces. In this exquisite method, a graphite electrode (electron conductor), an organic solvent droplet and the aqueous electrolyte formed a three-phase interline. The electrochemical reaction can only proceed and advance into the organic solvent droplet along the circumference of the droplet, thus the correlation between ions transfer rate and redox current can be built. Marken et al. [15,16] utilized the microdroplet three-phase electrode to investigate the effect of molecular structure of organic precursors on the anions insertion and the formation of electroactive polymeric compounds. Gergely [17] demonstrated the electropolymerization of 3-methylthiophene at liquid/liquid/solid three-phase junction using a pyrolytic graphite electrode with an organic solvent droplet.

Due to the irreproducibility of the droplet size and the need of using the graphite substrate, the aforesaid system is further developed for evaluating the lipophilicity of different anions: graphite rod was replaced with a thin gold or platinum wire, and it was placed in a mixture of two immiscible liquids in such a way that the upper part of the wire remained in the aqueous phase and its lower part was immersed in a dense organic liquid, forming a

* Corresponding author at: School of Resource and Environmental Sciences, Wuhan University, Wuhan 430072, PR China. Tel.: +86 27 68775799; fax: +86 27 68775799.

E-mail address: wangdh@whu.edu.cn (D.H. Wang).

circular solid/liquid/liquid three-phase junction. Bak et al. [18–21] investigated the electropolymerization of *N*-vinylcarbazole at the nitrobenzene/water/platinum three-phase boundary. The results showed that a 100 μm thickness poly(*N*-vinylcarbazole) film was obtained, and the polymerization current and the width of obtained polymer films were dependent on the types of anions presented in the aqueous phase. Moreover, the polymerization process is characteristic of separated monomers and counterions, namely the monomers and counterions existed in the organic solvent and aqueous solution, respectively. Likewise, Niedziolka [22] synthesized a silicate stripe at a solid electrode/organic phase/aqueous three-phase junction via an electrochemically assisted sol–gel process: the sulfite protons, which generated in the aqueous solution by electrochemical oxidation, can catalyze the sol–gel process of the precursor dissolved in the organic phase.

Recently Zhu et al. reported a dynamic three-phase interline electropolymerization (D3PIE) process for the fabrication of free-standing conductive polymer films in an aqueous solution/organic solvent/platinum metal three-phase system [23]. As overpotential was applied to the platinum electrode, the electron transfer, ion transfer and monomer oxidation simultaneously occurred at the three-phase interline, promoting the growth of polymeric film. Because the resultant polymer, e.g. 3,4-polyethylene dioxythiophene (PEDOT), is of good electronic conductivity, the radial frontier of the formed polymerized film acted as the subsequent working electrode, resulting in a radial spread of polymer at the liquid/liquid interface. Our previous studies demonstrated the interesting aspects of a dynamic three-phase electrode process and the validity of the D3PIE method for fabricating free standing conductive polymer film, however, the understanding on the growth mechanisms of polymer film at a three-phase interline is still limited. In order to determine the extent to which a uniform polymeric film can be obtained at a solid/liquid/liquid three-phase interline, and to explore the feasibility of controlling the microstructure of the polymeric films, some experimental variables for electropolymerization are investigated in the present study. The effects of electrochemical oxidation potential, monomer concentration and counterions concentration on the growing kinetics and the morphologies of polymers are discussed. Pyrrole is chosen for electropolymerization experiments due to its high electronic conductivity, low-cost, long-term environmental stability, and extensive prospect for applications [24–27].

2. Experimental

2.1. Chemicals

Perchloric acid (HClO_4 , 99% purity), pyrrole and chloroform (99.5% purity) were purchased from Tianjin Chemical Reagent Company of China. Pyrrole was purified by distillation prior to use. All other chemicals were used as received without further purification. Chloroform was used as the solvent for dissolving pyrrole. Aqueous solutions were prepared using double distilled water.

2.2. Electrode preparation and experimental setup

A three-electrode configuration was employed for all experiments. A platinum wire electrode with 0.5 mm diameter was used as a working electrode, a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode and a ring shape Pt wire (20 mm ring diameter) served as reference and counter electrode, respectively. The platinum wire working electrode was vertically immersed into aqueous solution (HClO_4 electrolyte solution)/chloroform solution (containing pyrrole monomer), as depicted in Fig. 1. The exposed length of Pt wire electrode in the chloroform solvent was approximately 5 mm. The reference

electrode and counter electrode were placed in the upper aqueous solution, but close to the interface of two liquids. Electrochemical measurements, including cyclic voltammetry and chronoamperometry, were performed using a computer-controlled CHI 440 electrochemical workstation. The mass of the polymer film was measured when it had been dried in a desiccator overnight. The average diameter of the PPy film was measured by ex situ or in situ methods. The prepared film after each experiment was taken from the system and its diameter was directly measured using a vernier caliper (ex situ method). The in situ method was performed with the assist of an optical image scanner: the experimental device was placed on top of an optical image scanner which was used to record the growth of the PPy film during electrochemical measurements. The microstructure of the film was characterized using a JSM 6700F scanning electron microscope (Japan Electron Company, Japan). XPS analysis was performed on a XSAM800 X-ray photoelectron spectroscopy (KRATOS Company).

3. Results and discussion

3.1. Cyclic voltammetry at three-phase interline

Fig. 2a–d presents the initial four consecutive cyclic voltammograms of the Pt electrode at the water/chloroform interface under different concentrations of Py monomer and perchlorate. As can be observed, oxidation current for electropolymerization rose when the potentials were positive of 0.2 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$. This potential basically accords with the reported values from other scholars who conducted the electropolymerization of Py in aqueous solution [28], suggesting that same chemical reactions proceeded at the solid/liquid/liquid interline. Comparing the CV profiles in Fig. 2a–d, we can observe very different relations between sweep number and reaction current. In Fig. 2a, with the increasing of sweep number, the current gradually decreased and the current of reverse scan was lower than that of forward scan, suggesting the electropolymerization process was limited by the mass transfer of reactants, namely Py monomer or perchlorate counterions. In contrast, when the concentration of perchlorate increased to 0.5 M in the aqueous solution, an increasing trend of reaction currents can be clearly observed (Fig. 2c), and the current of reverse scan was constantly higher than that of forward scan. At the potential of 0.7 V, the current of the 4th cycle was 3 mA, which was 10 times of the value of the 1st cycle. Without the limitation of mass transfer of reactants, the remarkable increase of currents is obviously due to the growth of the conductive polymer at three-phase interline: expanded reaction region (length of 3PI), namely the growing circumference of the conductive polymer film, resulted in the rising of current. Same phenomena were also observed in the electropolymerization of PEDOT at three-phase interline [23]. It is also noted that the current values in Fig. 2c are much higher than those in Fig. 2a, implying that the concentration of perchlorate plays an important role for the electropolymerization process.

Comparing the CVs in Fig. 2a–d, the effect of the concentration of Py monomer also can be assessed. When the aqueous perchlorate is fixed at 0.1 M, the current of the first forward scan can reach 0.4 mA for the 0.5 M Py (Fig. 2b), being higher than the corresponding current of 0.1 M Py in Fig. 2a. Moreover, at higher perchlorate concentration of 0.5 M, increased Py concentration in chloroform (from 0.1 M to 0.2 M) almost doubles the electrochemical oxidation current in terms of the current values at 0.7 V. This observation suggests that both the diffusion of Py monomers and penetrating of perchlorate ions affect the electropolymerization of PPy at the three-phase interline. Moreover, the electrochemical oxidation current basically exhibits a positive correlation with Py monomer and aqueous perchlorate concentration.

Download English Version:

<https://daneshyari.com/en/article/6618166>

Download Persian Version:

<https://daneshyari.com/article/6618166>

[Daneshyari.com](https://daneshyari.com)