

Adsorption force of polyaniline-coated polystyrene latex particles

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Received 22 August 2006; accepted 18 September 2006

Available online 24 October 2006

Abstract

Visible polyaniline–latex particles 13 μm in diameter were used for obtaining a quantitative relationship between the adsorption force and the electroactivity at a platinum electrode. An optical cell equipped with wire electrodes was filled with the suspension in hydrochloric acid. When electrode potential was switched between the oxidized and the reduced domains, some adsorbed particles showed color change owing to the electroactivity. The numbers of electroactive and the inactive particles in the suspension were counted, including poly(*N*-vinylpyrrolidone) (PVP). The ratio of the numbers was proportional to the concentration of PVP, as it was in equilibrium. The adsorbed particles were desorbed mechanically by forced flow. The numbers of the desorbed particles did not decrease with an increase in the flow velocity until threshold values. The threshold value for the electroactive particle was 10 times larger than that for the inactive ones, corresponding to 10 times larger adsorption energy of the electroactive particles than of the inactive ones. The adsorption stress was evaluated from the removal of the electropolymerized polyaniline film from the electrode. Then the adsorption area of the particle was estimated.

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Keywords: Polyaniline; Latex particles; Poly(*N*-vinylpyrrolidone); Adsorption force; Suspensions

1. Introduction

Electrochemically polymerized aromatic conducting films such as polyaniline are superior to chemically polymerized films in that films with (a) high cohesion to electrodes, (b) uniformity of film thickness, and (c) controlled thickness are obtained [1,2]. The electrochemical advantages are due to the decrease in the solubility of polyaniline near the electrode with an increase in the degree of polymerization, and hence polymers with large molecular weight are accumulated on an electrode. However, inhomogeneity has still been observed at large conducting films, exemplified by the appearance of a macroscopic pattern composed of oxidized and reduced species with different colors [3,4].

Adsorption onto an electrode occurs when a species has stronger interaction with the electrode than with the solvent. Consequently, the adsorbed redox species ought to bring about an electrode reaction from the thermodynamic point of view. If it does not, it may be located on inactive sites by keeping

the electroactive species away from the double layer, by blocking counterions, or by generating voids. For example, vinylferrocene films copolymerized with electroinactive polymers have lost electroactivity conditionally [5–7] because hydrophobic polymers block insertion of counterions. The blocking or void formation may be apparently removed by filling the voids with conducting polymers, as for adsorption of metal nanoparticles [8–10]. The blocking can be controlled by use of surfactants in that surfactants weaken the adsorption force. Surfactants cause also desorption of electroactive species to yield micellized form. Then, it is difficult to determine whether a reaction is due to the adsorbed species or the micellized ones. The difficulty is circumvented by using the optically detectable big redox particles [6–17]. If the particle contains polyaniline as a redox species, the electroactivity can readily be identified by the color change [18–20]. As for a surfactant, poly(*N*-vinylpyrrolidone) (PVP) works well not only as a steric stabilizer for polyaniline [21–23] but also to enhance the processability of polyaniline [24,25]. The combination of polyaniline latex with PVP may be suitable for the investigation of the relation between the adsorbability and the electrode reaction. We here use the monodisperse polyaniline-coated polystyrene latex (PANI-PS)

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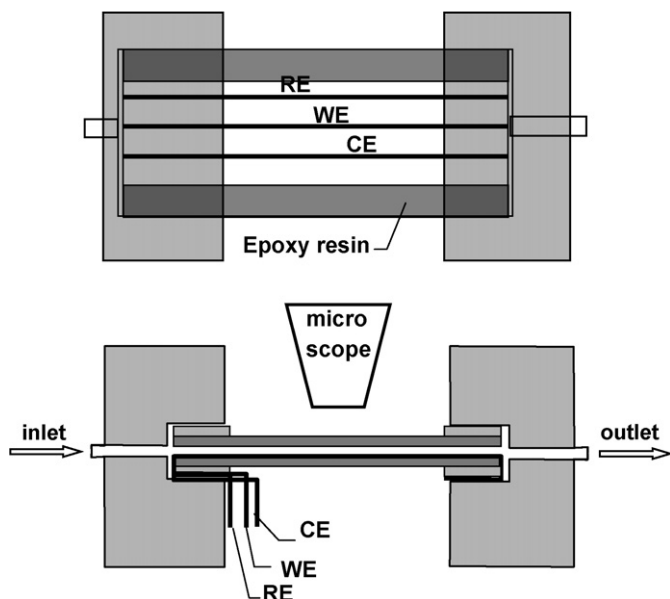


Fig. 1. Schematic diagram of the flow cell of used to measuring the flow velocity of PANI-PS particles during potential application.

as an optically detectable redox particle and obtain the relationship between the redox activity of the adsorbed particle and the adsorption force in the presence of PVP. We employ the forced flow of the solution for the estimation of the adsorption force, following image processing by an optical microscope under hydrodynamic control [26–30].

2. Experiment

2.1. Chemicals and synthesis

Styrene (Wako) was purified by distillation under vacuum at 60 °C and stored in a refrigerator until use. Poly(*N*-vinylpyrrolidone) (PVP) (Wako) with 360 kg mol⁻¹ was used as a surfactant for the dispersion-polymerization of styrene. 2,2'-Azobisisobutyronitrile (AIBN) (Kanto) was used as an initiator of polymerization for latex seeds. Ethanol (99.5%, Wako), 2-methoxyethanol (Wako), ammonium peroxydisulfate (Kanto), aniline hydrochloride (Kanto), and 2-propanol were used as received. All aqueous solutions were prepared with deionized water.

The synthetic procedure for the PANI-PS latex has been described in Ref. [20]. The size and morphology were examined with an S2400 scanning electron microscope (Hitachi).

2.2. Electrochemical flow cell

The electrochemical flow cell consisted of two glass plates for a flowing space 15 mm wide and 0.05 mm thick, which led to an inlet and an outlet, as is shown in Fig. 1. The two plates sandwiched three platinum wire electrodes 0.03 mm in diameter, and were fixed to the plastic block by epoxy resin. The flow cell was mounted horizontally in a VMS-1900 digital microscope (Scalar). The cell was filled with the PANI-PS aqueous suspension containing 0.5 M HCl. Video of PANI-PS

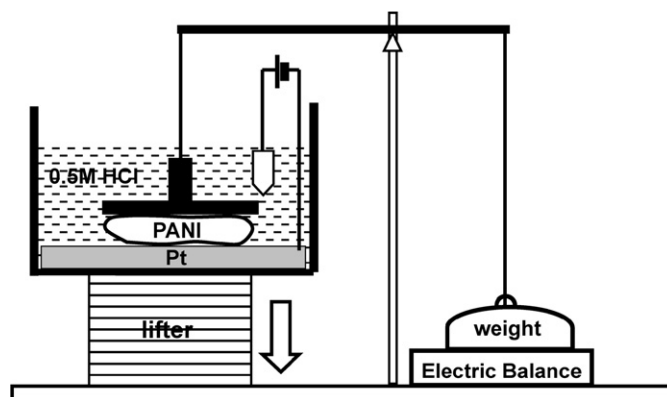


Fig. 2. Schematic diagram of the balance of used to measuring the adsorption force of the polyaniline film on the platinum electrode.

particles close to the Pt working electrode was recorded during the square-wave potential application between 0.5 and -0.2 V by use of an HECS-1112 potentiostat (Fuso, Kawasaki). A further amount of the suspension was injected into the flow cell at various flow rates. A series of time-varying images of the video were saved in mpg files, which were decomposed into 30 frames a second in jpg files. Each frame of an image had 720 × 480 pixels.

2.3. Measurement of adsorption force of polyaniline film

Adsorption force of a polyaniline film was obtained with a homemade apparatus equipped with a GX-200 balance (A & D Comp.) and an electrochemical cell, as is shown in Fig. 2. The cell was supported with a controllable lifter. The platinum plate leading to a copper wire was coated with epoxy resin so that a given area (typically 4 × 12 mm) was exposed to the solution. The polyaniline film was electrochemically deposited onto the exposed area by means of a cyclic potential scan between 0 and 0.9 V vs Ag|AgCl.

The face of the platinum plate opposite to the polyaniline film electrode was fixed onto the bottom of the cell with double-sided adhesive tape. The stripped area of the polyaniline film was controlled by a given area of the adhesive tape. The polyaniline film was connected to a string with adhesive tape. The string reached the arm of the balance, which led to a weight on the electronic balance. A potential of 0.5 V vs Ag|AgCl was applied to the electrode and then the lifter was lowered at a given speed until the polyaniline film was detached from the platinum plate. A reading of the balance just before the detachment was recorded.

3. Results and discussion

3.1. Electroactivity of adsorbed PANI-PS particles

The polyaniline-coated polystyrene latex (PANI-PS) particles, appearing dark green, were almost spherical. The average diameter was $2a = 13.03 \pm 0.12 \mu\text{m}$, evaluated from SEM. Although the polystyrene core was synthesized by growing it from seed iteratively, it was kept nearly monodisperse, as shown in

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