Electrochemically Controlled Release of Adenosine 5′-Triphosphate from Polypyrrole Film

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Polypyrrole (PPy) film is synthesized by anodic polymerization of pyrrole onto the surface of a platinum electrode in the presence of toluene-*p*-sulfonate and the film is used for the controlled release of the neurotransmitter, adenosine 5′-triphosphate (ATP).

It is well known that an electric pulse (impulse) generates at nerve ending, transfer through the axon and reaches the presynaptic membrane to release the neurotransmitter. The presynaptic membrane thus transmits the electric pulse into chemical information.[1] Different neurotransmitters can influence a variety of tissues and physiological processes; they can influence mood and behaviour.

Previous studies have reported that PPy film has redox properties.[2,3] It can be switched from the oxidized state to the reduced state. In the oxidized state anions must be incorporated into the film to neutralize the positive charge of the polymer backbone; the incorporated anions can be released from the film when the film is in the reduced state. This property has been applied to the study of the controlled release of chemicals, especially neurotransmitters such as glutamate and dopamine.[4,5]

In the present communication, we report a study on the electrochemically controlled release of ATP from the PPy film. ATP was chosen because of the important role it plays in numerous biological energy conversion phenomena and in the conduction of electrical signals *in vivo* between neurons as a neurotransmitter. The purpose of the study was to demonstrate the method of making a device for electrochemically controlled release of drugs based on electrochemical principles.

PPy films were prepared on a Pt plate (1×4 cm^2) by electrochemical oxidative polymerization of pyrrole in aqueous electrolyte solution which contained 0.1 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} sodium toluene-*p*-sulfonate (NaTos). A Pt plate and Ag/AgCl were used as the counter electrode and reference electrode, respectively. The electrolyte solution was bubbled with pure nitrogen for 20 min before each electrochemical experiment. The polymerization was carried out at constant potential of 0.8 V (*vs.* Ag/AgCl) with a Model CV-47 Voltammograph (BAS). The thickness of the resulting film was calculated to be 0.8 μm from the charge consumed during the polymerization (24 mC cm^{-2} gives a 0.1 μm thick PPy film).[6] After polymerization the resulting film was preconditioned by cyclic voltammetry in 0.1 mol dm^{-3} NaCl solution from -1.0 to $+0.6$ V to replace the Tos$^-$ anions in the film by Cl$^-$ anions. Electrochemical binding of ATP in the film was then performed in potential steps from -0.6 to

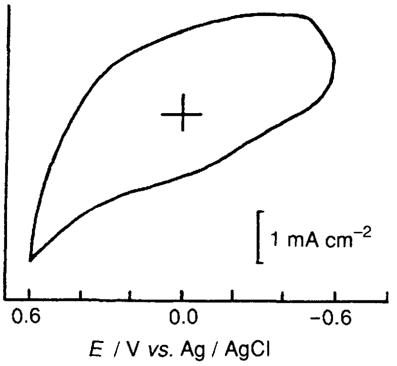

Fig. 1 Cyclic voltammogram of PPy film in 0.1 mol dm^{-3} ATP solution (pH 6.8). Scan rate: 100 mV s^{-1}.

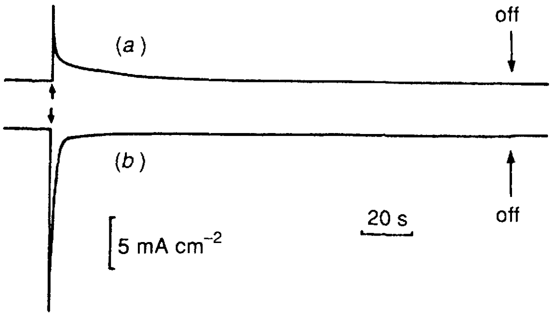

Fig. 2 Incorporation and release of ATP by PPy film: (*a*) electrode potential step from −0.6 to +0.6 V in 0.1 mol dm^{-3} ATP solution to incorporate ATP; (*b*) electrode potential step from +0.6 to −0.6 V in 0.1 mol dm^{-3} NaCl solution to release ATP

+0.6 V in 0.1 mol dm^{-3} disodium salt of ATP solution (pH 6.8, adjusted by dilute NaOH). Compared with the ATP anions the Cl$^-$ anions were very small in the solution, so the competititve doping process of Cl$^-$ anions was ignored. Electrochemical release of ATP from the film was performed in potential steps from +0.6 to −0.6 V in 0.1 mol dm^{-3} NaCl. The release of ATP into the electrolyte solution was monitored by the UV spectroscopic method using a DMS 90 UV–VIS Spectrophotometer (Varian).

Fig. 1 shows the cyclic voltammogram of the PPy film deposited on the Pt surface in the 0.1 mol dm^{-3} ATP solution; PPy was oxidized at positive potential which was accompanied by the incorporation of ATP anions into the film matrix to compensate the net charge. The reverse scanning resulted in the reduction of the oxidized PPy into the neutral state which was followed by the release of the incorporated ATP anions. Because the ATP anions are very large, a clear redox peak was not observed.

The potential of the film was set at +0.6 V in 0.1 mol dm^{-3} ATP solution to incorporate ATP anions into the film. The anodic current–time curve is shown in Fig. 2(*a*). Electrochemical incorporation was continued until the current decayed to background level. The electrode surface bound with ATP was then rinsed thoroughly with water and then immersed in the 0.1 mol dm^{-3} NaCl solution. The potential was set at +0.6 V again. In this case no release of ATP occurred. When the potential was stepped to −0.6 V, the ATP anions were released out of the PPy membrane. The cathodic current–time curve, which is attributed to the reduction of the PPy film and the release of the incorporated ATP anions, is shown in Fig. 2(*b*). The charge of the electrochemical oxidation and reduction were almost the same at about 50 mC cm^{-2}. The electrolyte solution was assayed in quartz cuvette to detect the amount of ATP released from the film before and after the electrochemical release. It indicated that 1.7×10^{-7} mol of ATP was released from the PPy film, which means that 8.5×10^{-7} mol of ATP was released from the PPy film per coulomb of charge passed. The conditions of the polymerization of PPy film and the incorporation of ATP play important roles in the amount of ATP released.

From these results we can conclude that ATP can be incorporated into a PPy film and released from it using electrochemical control.

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