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In the process of charging (or oxidizing) conducting polymers, e.g., polypyrrole, polythiophene, polyaniline, it has been common to assume that exclusively anions can compensate the excess charge of the radical cation sites of polypyrrole in the oxidized state. Very recently, however, cation insertion has also been indicated by some workers (1-8). In this short note, the authors report strong evidence of cation/release in polypyrrole film and the dependence of the proportion of anion and cation charge compensation on film thickness during the oxidation process. Keywords;

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Quartz Crystal Microbalace Analysis:
Partial Cation Release During Oxidation of Conducting Polymers

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In the process of charging (or oxidizing) conducting polymers, e.g., polypyrrole, polythiophene, polyaniline, it has been common to assume that exclusively anions can compensate the excess charge of the radical cation sites of polypyrrole in the oxidized state. Very recently however, cation insertion has also been indicated by some workers(1-8). In this short note, the authors report strong evidence of cation incorporation/release in polypyrrole film and the dependence of the proportion of anion and cation charge compensation on film thickness during the oxidation process.

Experimental

Shear mode 6MHz AT-cut quartz crystals obtained from Inficon (East Syracuse, NY) were used for this investigation. The crystals had vacuum deposited gold electrodes on both sides. The total projected area exposed to the solution was 0.33 cm^2. The crystal oscillator circuit included a power source and an oscillator (Inficon XTC). The frequency was measured with a frequency counter (HP5384A) and measurements were sent to and stored in a personal computer (HP9816). The details of the QCM instrumentation are described elsewhere(6-9).

Polypyrrole films were grown on quartz crystals at a constant potential(0.75 V vs. $Ag/AgNO_3$(0.01 mol dm^{-3})) by passing a known amount of charge(50, 200, 300 mC cm^{-2}) in acetonitrile solution containing 0.2 mol dm^{-3} pyrrole and 0.2 mol dm-3 $TBAClO_4$. The frequency shifts of doped dry films on the quartz crystal were used to calculate the weights and thicknesses of 50, 200 and 300 mC cm^{-2} charged films which were 3.8 μg; 780Å, 14.0μg; 2800Å, and 18.6μg; 3800Å, respectively. The mass change(Δm) of the films was measured under in-situ conditions and the charge(Q), current and potential were also monitored against time during cyclic voltammetry at 1 mV s^{-1}. Doping level(y) was estimated from the Q values according to equation[1].

$$y = \frac{100Q/F}{m_f/M} \qquad [1]$$

where F, m_f and M represent the Faraday constant, the mass of film and the molecular weight of pyrrole, respectively.

Results and Discussion

Figure 1 shows the mass change vs. doping level for polypyrrole films of three different thicknesses. The mass change was estimated in two different ways; one is based on charge(Eq.[2]), where only anions were assumed to incorporate in order to compensate the charge in the oxidized state($M_{ClO_4^-}$ is the molecular weight of the perchlorate anion). The other is based on Sauerbrey's equation(Eq.[3]) where C(0.24 Hz ng^{-1}) is the absolute mass sensitivity(10).

$$\Delta m_Q = \frac{Q}{F} M_{ClO_4^-} \qquad [2]$$

$$\Delta m_{QCM} = -\frac{\Delta f}{C} \qquad [3]$$

In the case of the 780Å film, Δm_Q and Δm_{QCM} show a relatively good agreement. If the agreement were perfect, the two curves would coincide at all doping levels. However, at a low

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doping level(below ca. 25%), the Δm_{QCM} value is larger than Δm_Q, suggesting that solvent plus electrolyte incorporates into the film, and this may be associated with a volumetric increase of the film. At high doping levels(beyond 25%), Δm_{QCM} levels off so that the mass of incorporated anions(ClO_4^- : MW=99) and the releasing cations($(Bu)_4N^+$: MW= 66) is kept constant when the film is charged above the 25% doping level. For thicker films(2800Å), the deviation of the two mass changes becomes larger, indicating that the oxidized charge is compensated by the release of a larger number of cations compared to the 780Å film. The thickest film investigated (3800Å), showed the largest difference between Δm_{QCM} and Δm_Q. Anions doped deeply inside the film are trapped strongly and are less mobile than cations existing in the vicinity of electrode/electrolyte interface. The above results suggest that the charge compensating ions change from largely anions to largely cations as the film thickness increases. This can be extremely important for an application like a rechargeable battery where anion intercalation requires an excess of electrolyte in the external solution, but cation release from the cathode is more akin to the behavior of V_6O_{13} and TiS_2 cathode materials. In the latter case, the cation(usually Li^+) is also reversible at the anode and is recycled between the two electrodes. Thus, less excess electrolyte may be required for charge and discharge(6-7) of thick polymer cathode films. This finding will result in higher specific energy and power for polymer cathode rechargeable battery systems.

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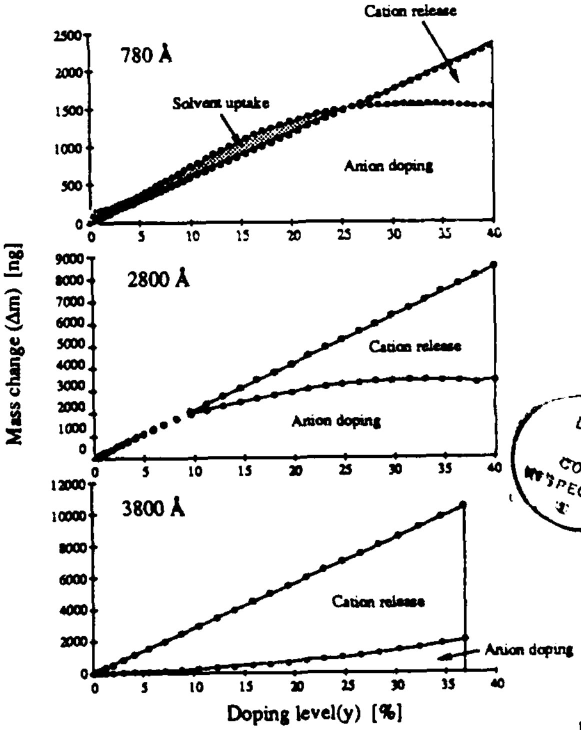

Fig.1 Mass change(Δm_Q(-o-); Δm_{QCM}(-•-)) vs. doping level plots for polypyrrole films with three different thicknesses.