Percolation threshold potential of an electrochemically deposited poly(*ortho*-aminophenol) film

Kourosh Malek

Department of Chemical Technology, Delft University of Technology, 2628 BL, Delft, The Netherlands.
Fax: +31 15 27 88267; e-mail: K.Malek@tnw.tudelft.nl

The percolation threshold potential during the insulating/conducting transition of electrochemically deposited poly(*ortho*-aminophenol) films were found to lie in the range 0.15–0.17 V (Ag, AgCl).

The electrochemical conversion of potentially conducting electrodeposited polymeric films between conducting (C) and insulating (I) states finds application in energy storage, sensors and electrochromic display devices.[1] The rapidity of the conversion is ascribed to the propagation of conducting zones[2,3] rather than the diffusion-like hopping of charges. A required condition for the propagation is the electrical connection of the conducting zone to the electrode. Whether there is an electrical connection or not is the subject of electrical percolation.[4] A characteristic of the percolation is the presence of a threshold value of the molar fraction of conducting species. Let the molar fraction of the C species be p and its percolation threshold be p_C. When p is slightly larger than p_C, there is some possibility that at least one statistically aggregated C cluster spreads from the electrode surface up to the film/solution interface according to the percolation theory.[4] In contrast, most of the C clusters with $p < p_C$ have an average radius smaller than the film thickness. The size of the C cluster changes suddenly[5] at $p = p_C$. Since p in the vicinity of the electrode surface is controlled by the electrode potential E, a potential E_C may exist at which $p = p_C$, called percolation threshold potential.[2,5] This definition of E_C corresponds to an electrochemical interpretation of the percolation threshold.

In a thought experiment of a potential step from E_1 to E_2 in the positive direction ($E_1 < E_2$) three different phenomena can be observed. For $E_C < E_1 < E_2$, the C zone has already been developed before the potential step, because a number of C clusters at E_1 have sufficient electric connection to the electrode to work as a metal-like electrode for the I–C conversion. After the potential step, the concentration of the C species increases uniformly over the film. For $E_1 < E_C < E_2$, the film is almost in the I state initially, and C zones may grow from the electrode only after the potential step. No C zone develops from the inside of the I zone. Finally, when $E_1 < E_2 < E_C$, a large C cluster is rarely formed from the electrode; hence, the growth of the C zone is not expected. Indeed, careful control of the potential
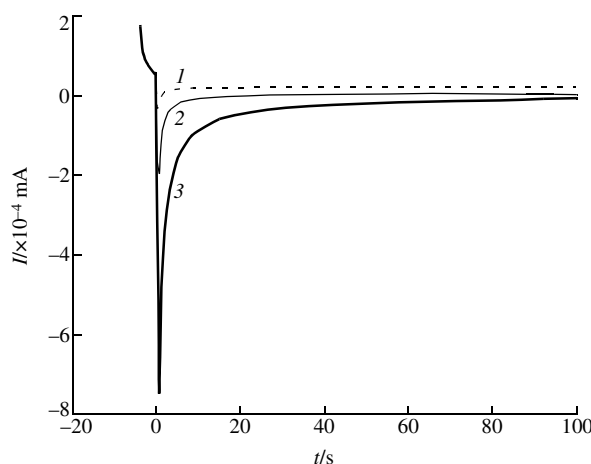

Figure 2 Chronoamperograms of the POAP-film/H$_2$SO$_4$ interface at various potential steps. $E_1 = -0.1$ V (Ag,AgCl). (*1*) $E_2 = 0.05$ V, (*2*) $E_2 = 0.10$ V, (*3*) $E_2 = 0.15$ V.

applied to the film can, in principle, lead to the observation of a definite potential,[5] the percolation threshold potential E_c. Percolation is a(n) (electrochemical) phase transition and, consequently, the current–potential relationship should exhibit a sharp change at E_C. In this work, a new method is proposed to determine the percolation threshold potential of a conductive polymer [poly(*ortho*-aminophenol), POAP] film through the chronoamperometric behaviour of the electrodeposited polymeric film. The electropolymerization and relevant aspects were described previously.[7–10] The POAP films were electrochemically deposited on glassy carbon electrodes by multiply cycling potential between –0.2 and 0.9 V (Ag,AgCl) at a 50 mV s^{-1} sweep rate in a sulfuric acid solution (pH 0.5) containing *ortho*-aminophenol at a concentration of 0.1 M (Figure 1). The films were subsequently reduced exhaustively by dipping the electrode in an aqueous hydrazine solution and further rinsing in 1.0 M sulfuric acid solutions before use. All the materials were of Analar grade (Merck). The electrochemistry was conducted in a conventional three-electrode cell powered by an EG&G model 273A potentiostat/galvanostat. The film potential was measured against an Ag/AgCl reference electrode and a large Pt plate formed the counter electrode. Figure 2 represents the chronoamperograms of the film/H$_2$SO$_4$ interface recorded at pH 0.5 at various potential steps in the range 0.01–0.2 V (Ag,AgCl). Below 0.01 V (Ag, AgCl) only small capacitive currents, which decay quickly to zero, have been observed. The electrochemical activity begins at ~0.15 V (Ag,AgCl), as indicated by the sharply rising initial current and its relatively slow decay with time. To unequivocally assign the nature of the electrode processes involved in the relevant regime, the plots of current (I) against the inverse of both the square root of time ($t^{-1/2}$) and time (t^{-1}) at various potential steps are presented in Figure 3. Below 0.15 V (Ag, AgCl), linear relationship between I and $t^{-1/2}$ was observed, pointing to the dominance of diffusion-controlled processes giving rise to the development of the conducting (C) zone.[11] Above 0.15 V (Ag,AgCl), no linearity of I *vs.* $t^{-1/2}$ was observed
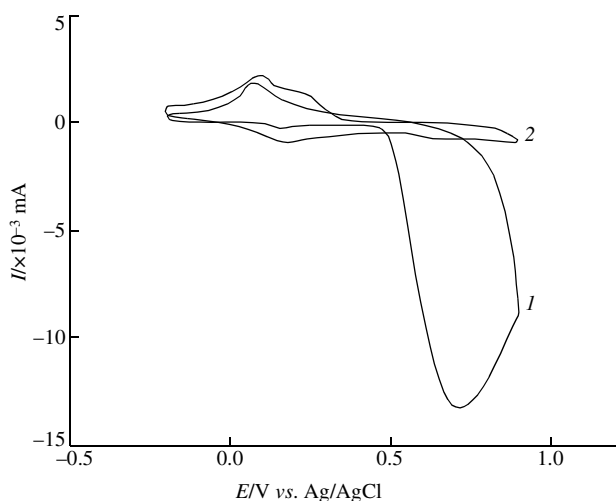

Figure 1 Electrochemical deposition of a POAP film under conditions of cyclic voltammetry, (*1*) first scan, (*2*) after 25 scans. 0.1 M OAP; pH 0.5; scan rate, 50 mV s^{-1}.
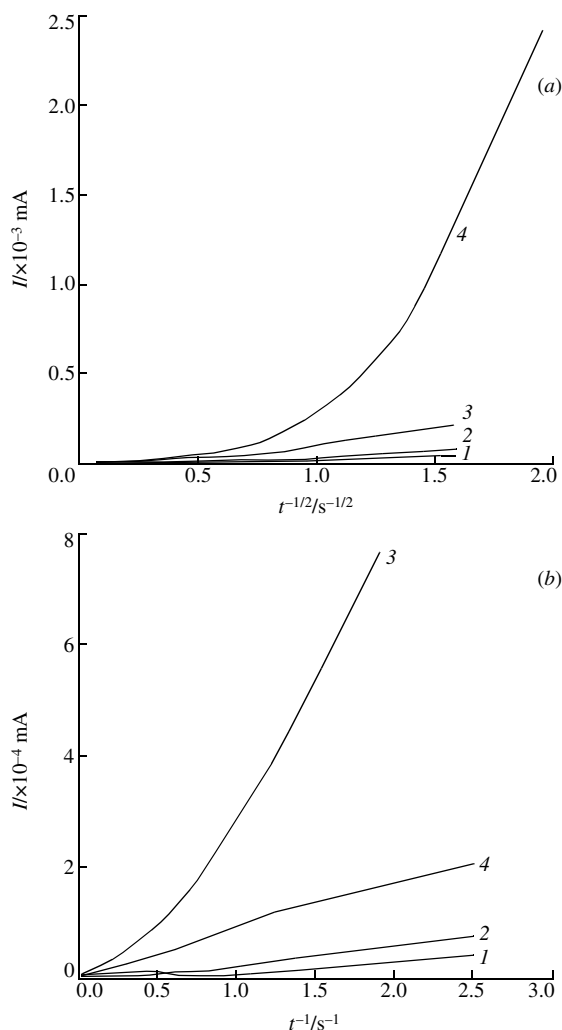
Figure 3 Plots of chronoamperometric current against $t^{-1/2}$ and t^{-1} when the potential was stepped from $E_1 = -0.1$ V (Ag,AgCl) to E_2. (*a*) (*1*) $E_2 = 0.10$ V, (*2*) $E_2 = 0.12$ V, (*3*) $E_2 = 0.14$ V, (*4*) $E_2 = 0.15$ V. (*b*) (*1*) $E_2 = 0.10$ V, (*2*) $E_2 = 0.15$ V, (*3*) $E_2 = 0.17$ V, (*4*) $E_2 = 0.20$ V.

over an appreciable period of time. On the other hand, good to fair linear plots of *I* vs. t^{-1} were obtained over a large period of time (Figure 3). Interestingly, the slope of the plot increases as the magnitude of the potential step increases to 0.17 V (Ag,AgCl) and decreases upon a further increase of the potential step. This finding resembles slow relaxation with the logarithmic dependence of the faradaic reduced charge q:[12]

$$q = a \ln t + b \tag{1a}$$

or

$$I = \frac{\mathrm{d}q}{\mathrm{d}t} = \frac{a}{t} \tag{1b}$$

According to the percolation theory,[4] there are some small clusters even before the percolation threshold ($p < p_C$). Small C clusters then electrochemically form near the electrode. Some C clusters may keep growing on the electrode and some may be transported through the film by diffusion. If the depletion of C clusters for the C–I conversion is substituted for the enhancement of C clusters in the I–C conversion, it can explain the experimental linearity of *I versus* t^{-1}. The polymeric film is initially in the insulating mode. Upon stepping the potential into the electrochemically active region, the polymer immediately adjacent to the metallic back contact is oxidised and converted to the conducting mode while the rest is still insulating. Further conversion has to continue at the partially metal-like progressive conducting zone. It is believed[11] that the rate of enlargement of the conducting cluster is slowed down by the depletion of the wandering (migration off the metallic back contact) of the already existing small conducting clusters giving rise to the t^{-1} dependence of the current (rate).[12] The linearity was found to be limited to the potential range $0.15 < E_2 < 0.17$, beyond which the graphs have similar slopes. The current at $E_2 < 0.15$ V (Ag,AgCl) was controlled by the diffusion of reduced species. Although the estimation involved some ambiguity, E_C was estimated between $0.15 < E_C < 0.17$.

References

1 G. P. Evans, *Advances in Electrochemical Science and Engineering*, eds. H. Gerischer and C. W. Tobias, VCH, New York, 1996, vol. 1.
2 K. Aoki, *J. Electroanal. Chem.*, 1991, **300**, 13.
3 K. Aoki and Y. Tezuka, *J. Electroanal. Chem.*, 1989, **267**, 55.
4 M. Sahimi, *Application of Percolation Theory*, Taylor & Francis, London, 1994.
5 K. Aoki and Y. Teragishi, *J. Electroanal. Chem.*, 1998, **441**, 25.
6 J. Cao and K. Aoki, *Electrochim. Acta*, 1996, **41**, 1787.
7 M. G. Mahjani, F. Gobal and M. Jafarian, *Indian J. Chem.*, 1997, **36A**, 177.
8 F. Gobal, K. Malek, M. G. Mahjani, M. Jafarian and V. Safarnavadeh, *Synth. Met.*, 2000, **108**, 15.
9 K. Malek and F. Gobal, *Synth. Met.*, 2000, **113**, 167.
10 C. Barbero, J. J. Silber and L. Sereno, *J. Electroanal. Chem.*, 1990, **291**, 81.
11 Y. Tezeka, T. Ishii and K. Aoki, *J. Electroanal. Chem.*, 1996, **402**, 161.
12 K. Aoki, J. Cao and Y. Yoshino, *Electrochim. Acta*, 1994, **39**, 2291.