SIMPLE MODEL FOR ELUCIDATION OF NATURE OF CURRENT-GENERATING PROCESSES IN POLYANILINE-TYPE CONDUCTIVE POLYMERS

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According to suggested simple model in the practically important potential range ($E \approx 0 \ldots + 0.6$ V against SHE) the nature of the electrochemical current-generating processes in conductive polymers of polyaniline type is not associated with a particular redox reaction, but it reduces to the charge/discharge of the double electric layer capacity, which is anomalously high ($300 \ldots 850$ F/g) in such systems due to structural peculiarities of these materials. The model gives a good fit to electrode behavior in this range.

1. Introduction

A typical cyclic voltammogram (CVA) of a polyaniline electrode (PANE) in acid and salt solutions has a high "ground" current and at least 3 peaks: coupled anodic and cathodic peaks (at an average potential of $E_1 \approx 0.4$ V against NHE) and an irreversible anodic peak (at $E_2 \geq 0.8$ V). All these peaks are usually comparable with the "ground" current. The potential values are somewhat shifted depending on the temperature and pH of the medium [1]. The peaks at E_1 are generally assumed to be due to the current-producing redox process occurring at the PANE. In the absence of current a stationary potential reaches a steady-state value close to E_1. Our recent studies, however, have shown [2–4] that the mechanism of the current-producing process in conductive polymers of the PAN type is not associated with a particular redox reaction, but it reduces to the charge/discharge of the double electric layer (DEL) capacity.

2. Results

2.1. Theoretical model

To understand the nature of current-producing process, let us take into consideration the structure of the materials under study, which are conductive polymeric molecule chains surrounded by doping ions (Fig. 1). We suppose that each of such polymeric chains can be regarded as a microelectrode with own DEL. In this case the total effective DEL capacity per polymer unit weight must be many times higher than, for instance, in metal electrodes (Fig. 2). Analysis of the model leads to an expression for capacity per polymer unit weight, $C_m^{theor} = kL^2 C_s N_A / M$. Here k is the number of atoms in a unit which take part in the formation of a poly-π-conjugated bond system ($k = 7$ for PAN), $C_s \approx 15$–$30\ \mu F/cm^2$ is the DEL capacity per metal electrode unit surface area, $L \approx 3 \times 10^{-8}$ cm is the linear atomic dimension, N_A is the Avogadro number, M is the PAN weight with allowance for doping ion weight. It is the estimation of the DEL capacity from the above relation that leads to the 300–850 F/g values depending on anion type (Cl^-, SO_4^{2-}, BF_4^-, ClO_4^-, etc.).
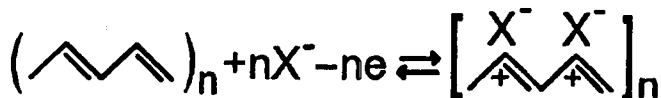
$$\left(\wedge\!\!\wedge\!\!\wedge \right)_n + nX^- - ne \rightleftharpoons \left[\overset{X^-}{\underset{+}{\wedge\!\!\wedge}}\; \overset{X^-}{\underset{+}{\wedge\!\!\wedge}} \right]_n$$

Fig. 1. Structure of the polymeric chain of a PANE. X^- is the corresponding anion.

$$C_S \sim 15\text{–}30\ \mu F/cm^2$$

$$C_m^{theor} \sim kL^2 C_s N_a / M_{p+x}$$
$$\sim 300...850\ F/g \qquad X \equiv \begin{cases} Cl^-;\ SO_4^{2-} \\ BF_4^-;\ ClO_4^-... \end{cases}$$
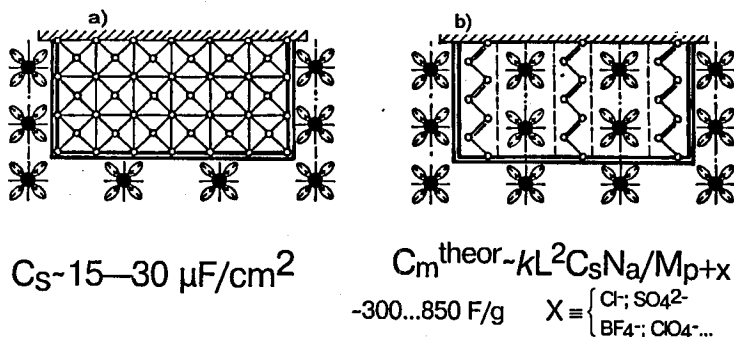
Fig. 2. Scheme of DEL formation on metal (a) and conductive polymer (b).

2.2. Trend of galvanostatic curve

If the charge/discharge of a PANE is considered by analogy with the charge/discharge of a capacitor, its capacitance $C = Q/E$. As follows from literature data (e.g., [1, 5]) and our measurement (Fig. 3), when potential is changing by 600 mV, the electrochemical electrode capacity is usually 100–130 mA·h/g. Then

the specific capacity estimated from experimental data is $C_m \approx 780$ F/g, which is in good agreement with the theoretical estimate. In terms of the known relation

$$I(t) = C dE(t)/dt, \tag{1}$$

which relates the current across the capacitor to the dependence of voltage on time, it is easy to understand that for galvanostatic conditions ($I(t) = \text{const}$) the functions $E(t)$ and $E(Q = It)$ must be linear, which is observed experimentally (Fig. 3).
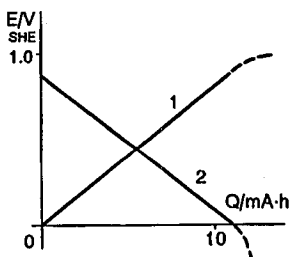

Fig. 3. Typical experimental galvanostatic charge (1) and discharge (2) curves on a PANE.

2.3. Trend of CVA

If a PANE is regarded as an ideal capacitor (without allowance for the drop of ohmic voltage — IR-drop), then as follows from the same relation (1), when potential variation is linear, CVA must be of a rectangular form (Fig. 4, curve 3). When IR-drop is taken into account, the rectangle must change to a parallelogram. Such a form of CVA is in fact observed in experiment (curve 2, Fig. 4) if it is taken
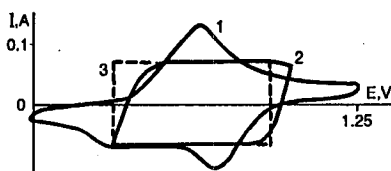

Fig. 4. CVA on a PANE. Conditions: $V_s = 12$ mV/s; (1) $E_s = -0.05$ to $+1.25$ V (SHE); (2) $E_s = +0.25$ to 0.95 V (SHE); $E_s = +0.25$ to 0.95 V (theory).

in somewhat narrower potential range ($E = +0.25...+0.95$ V). It should be noted that this range is wide enough to overlap peak position in CVA's taken over the complete possible stability range of the material ($E \approx -0.05...+1.25$ V, curve 1 in Fig. 4). At the same time, there are some side factors responsible for the appearance of peaks in CVA's taken over the complete E_{max} range. These factors are:

1) sharp change in PAN conductivity when passing from the fully oxidized state to the fully reduced state (and vice versa);

2) reversible reaction of reduction of air oxygen to H_2O_2 proceeding on the effective PANE surface (the potential of this reaction is close to E_1 at the conditions under consideration); the catalytic activity of PANE towards oxygen reduction found by us allowed us even to develop on this principle a mockup of air-zinc battery with a PAN catalyst [6].

3. Conclusion

Thus, in the absence of side effects, the CVA of a PANE is the form of parallelogram. This form is in good agreement with the model concepts of PANE, which consider the electrode as a capacitor of super high capacity (with allowance for IR-drop). The so-called "ground" current in the given system appears to be the charge/discharge current of effective double-layer capacitor. As to equilibrium potential, it appears to be not applicable to this system (due to the absence cf redox reaction). The stationary PANE potential is determined from the quantity of electricity taken by the electrode during charge/discharge.

References

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