THE ELECTRODE BEHAVIOR OF HEAT TREATED POLYACRYLONITRILE

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It has recently been shown [1, 2, 3] that organic semiconductors are catalysts for some oxidation-reduction reactions. It was a matter of interest to investigate what effect they have on the kinetics of electrochemical reactions, bearing in mind, in particular, that a well-known parallelism exists between the ability to take on an oxygen potential, and the activity with respect to the hydrogen peroxide decomposition reaction. In this connection we have studied the electrochemical behavior of heat-treated polyacrylonitrile, which, from the data of A. V. Topchiev, M. A. Geiderikh et al. [1], is a catalyst for the hydrogen peroxide decomposition reaction. All the electrochemical properties of polyacrylonitrile were compared with the properties of charcoal which had been prepared by carbonizing viscose.

The test samples were threads made up of several hundred filaments 2-3 μ thick. Especial attention was given to preventing the solution from falling on the contact between the polyacrylonitrile and the platinum wire to which the sample was fastened. To this end, the middle part of the sample was impregnated with paraffin. The potential in alkali was measured relative to a normal oxide-mercury electrode, and in acid relative to a normal sulfate electrode.

Figure 1 gives curves showing the potential change as a function of the logarithm of the current strength for samples of polymer and charcoal in hydrogen medium in 1 N H_2SO_4. As may be seen, the electrochemical activity of the material under test relative to the cathode and anode reactions is considerably less than the activity of charcoal. It remains unclear whether during anode polarization ionization of molecular hydrogen occurred at all or whether the current went into oxidation of the organic substance or of some residue of the hydrogen adsorbed during the cathode polarization which had preceded the anode process.

Another picture is found when the polymer is polarized in an atmosphere of air, as may be seen from Figs. 2 and 3, which give curves taken in 1 N H_2SO_4 and 1 N NaOH. In this case, the activity of the polymer and that of charcoal are quantities of the same order of magnitude.

It should be noted how fundamentally nonstationary all the processes are that occur on the polymer. With constant current, the potential changes continuously in the direction of increase in polarization. In order to lower the concentration polarization with respect to oxygen, volt-ampere curves were taken on a rotating electrode in 1 N NaOH, but a change in speed of rotation from several hundred to several thousand r.p.m. had no substantial effect on the form of the polarization curves. The nonstationary state observed in the experiments without mixing is not eliminated with a rotating electrode. Apparently, it has to do with depletion of the solution by oxygen in the micro-pores of the samples. The most interesting results were obtained from measuring the stationary potentials taken on by the polymers in an oxygen atmosphere in 1 N NaOH. With some samples, potentials of +0.280-0.285 were observed relative to a normal oxide-mercury electrode, which is only 25-30 mv more negative than the reversible oxygen potential for water formation. These potentials are considerably more positive than the oxygen potentials observed on electrodes made of active charcoal, or of smooth or platinized platinum. Only in super-pure solutions of H_2SO_4 were Bockris and Huq [4] apparently able to reach the values of the reversible oxygen potential on platinum. With the passage of time, the potential of the electrode made of polymer becomes more negative, shifting 90 mv in one hour, and 120 mv in thirty hours.

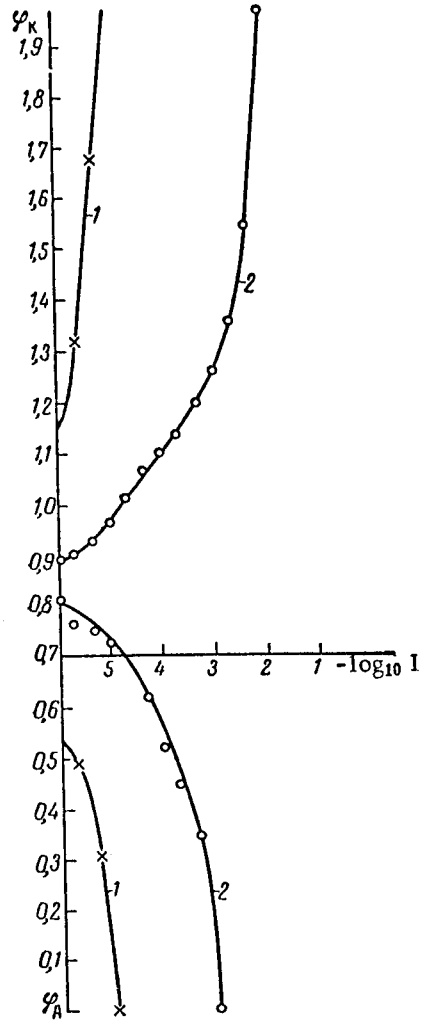

Fig. 1. Potential as a function of logarithm of current strength for samples of polymer and charcoal in hydrogen medium in 1 N H_2SO_4 during anode and cathode polarization.

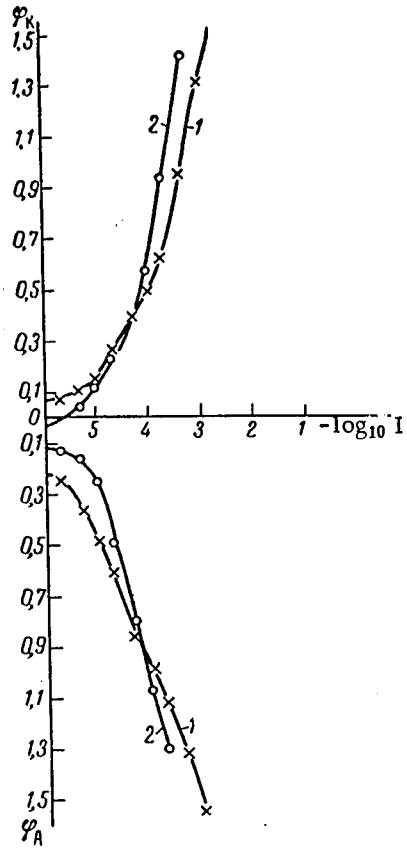

Fig. 2. Potential as a function of logarithm of current strength for samples of polymer and charcoal in air in 1 N H_2SO_4 during anode and cathode polarization.

It is obvious that for a reversible oxygen potential to be established one must assume reversibility of all stages of ionization of the oxygen, and above all of the stage where the O_2 molecule is adsorbed. Thus, the electrochemical behavior of the materials under test must be a matter not only of their ability to catalyze the transition from hydrogen peroxide to water, but also of the ability to form labile peroxides on the surface which easily split off oxygen, which is in fact characteristic of many polymers with conjugated double bonds. The constantly occurring transition from this primary oxidation stage to more stable forms of the oxygen bond may be one of the reasons for the incomplete reversibility of the electrode.

In view of the fact that O. V. Krylov and S. Z. Roginskii [5] have investigated the influence of the width of the forbidden zone on the decomposition rate of isopropyl alcohol in the ZnO–ZnTe series, and have observed a marked increase in the catalytic activity with decrease in width of the forbidden zone, we made a test on the filaments of a polymer with a smoothly varying conductivity activation energy, determined from the relation between the conductivity and the reciprocal temperature. The values of the activation energy were measured in the Semiconductor Institute of the Academy of Sciences, USSR, in L. S. Stilbans' laboratory. The potential which is established on the polymer in 1 N NaOH in an atmosphere of air depends on the magnitude of the activation energy as is shown in Fig. 4.

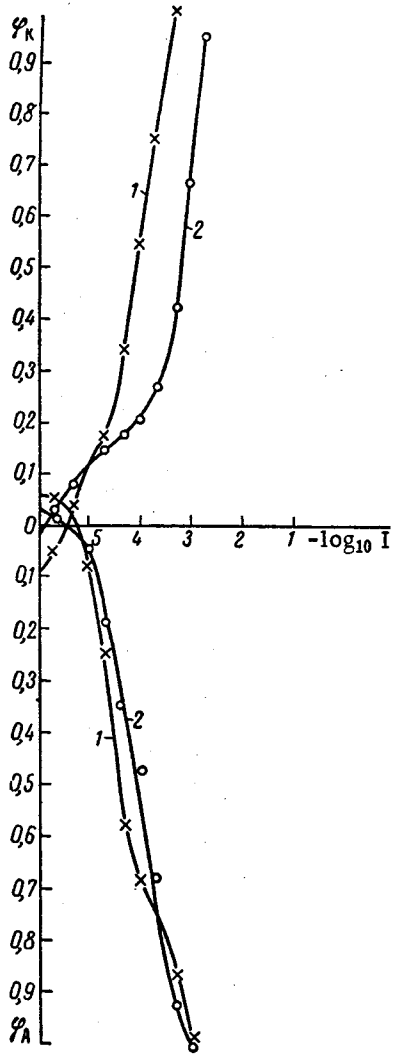

Fig. 3. Potential as a function of logarithm of current strength for samples of polymer and charcoal in air in 1 N NaOH during anode and cathode polarization. 1) Polymer 2) charcoal.

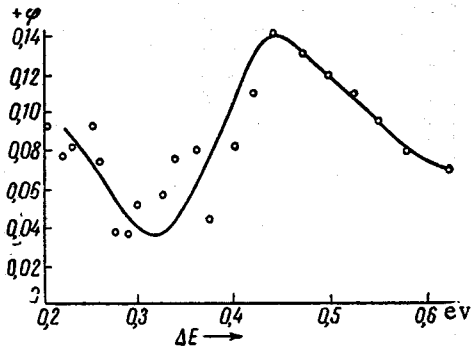

Fig. 4. Potential as a function of conductivity activation energy, ΔE.

It turned out that the value of the potential maximum differs from the minimum value by about 100 mv, which corresponds with a change in reaction rate of three orders of magnitude, although there is a considerable spread in the experimental values. The maximum observed in the catalytic activity may bear some relation to the specificity of the organic catalysts in biochemical systems.

LITERATURE CITED

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4. J. O'M. Bockris and A. K. Shamshul Huq, Proc. Roy Soc. A237, 277 (1956).
5. O. V. Krylov and S. Z. Roginskii, DAN 118, 523 (1958).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
