A Conductive and Electroactive Elastomer: A Polyaniline–Nitrilic Rubber Composite

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A conductive and electroactive elastomeric material has been obtained by the electrochemical polymerization of aniline on a nitrilic rubber-coated platinum working electrode.

After the initial discovery that conductive composites could be prepared by the electrochemical polymerization of pyrrole onto a poly(vinyl chloride)-coated platinum working electrode[1,2] many researchers have prepared different conductive composite materials.[3] The technique used consisted of combining a polymer which could be swollen in the electrolyte solvent under the necessary polymerization conditions. The materials obtained usually possessed the mechanical properties of the insulating polymer host and the electrical properties of the conductive polymer guest.

Polyaniline can be prepared in organic solvents (*viz.* acetonitrile) using an appropriate acid and an electrolyte. For the composite, the host polymer must be able to withstand the acid medium and be swollen by the solvent used. Nitrilic rubber (NBR) is a copolymer of butadiene and acrylonitrile and is produced commercially with different comonomer proportions. It is known to be acid resistant and can be vulcanized.

We prepared films of NBR–polyaniline composites by the potentiodynamic polymerization (0—2.0 V *vs.* Ag/AgCl, 50 mV s^{-1}) of aniline on a NBR-coated platinum working electrode using an acetonitrile solution containing trifluoroacetic acid and tetrabutylammonium tetrafluoroborate as electrolyte. NBR samples with different acrylonitrile contents (29, 32, 39, and 45%) were tested. With 45% NBR no composite was obtained. The other NBRs showed composite formation with the 29% acrylonitrile content NBR furnishing the most homogeneous product, in the form of a rubber which was light green in its oxidized form. Figure 1 shows the cyclic voltammograms (CVs) recorded during the potentiodynamic polymerization of aniline on a bare Pt working electrode using the above-mentioned conditions at 50 mV s^{-1}. The first cycle corresponds to the monomer oxidation with E_{pa} = 1.400 V. After the first cycle the intensity of this peak decreases and other oxidation peaks at lower potentials start to grow. The increase in the anodic and cathodic peak currents is proportional to the increase in film thickness. After the third cycle, three oxidation processes are observed with E_{pa} of 0.456, 0.824, and 1.000 V; the corresponding reduction peaks having E_{pc} of 0.430, 0.686, and 0.905 V. After the fourth cycle the third wave coalesces into the main peak at 0.830 V and after the twelfth cycle the aniline oxidation peak almost disappears. On repeating the same experiment with a NBR-coated Pt working electrode very similar CV curves are observed, Figure 2. In the first cycle the E_{pa} of aniline is lower (1.280 V) and in the three subsequent cycles anodic peaks with E_{pa} of

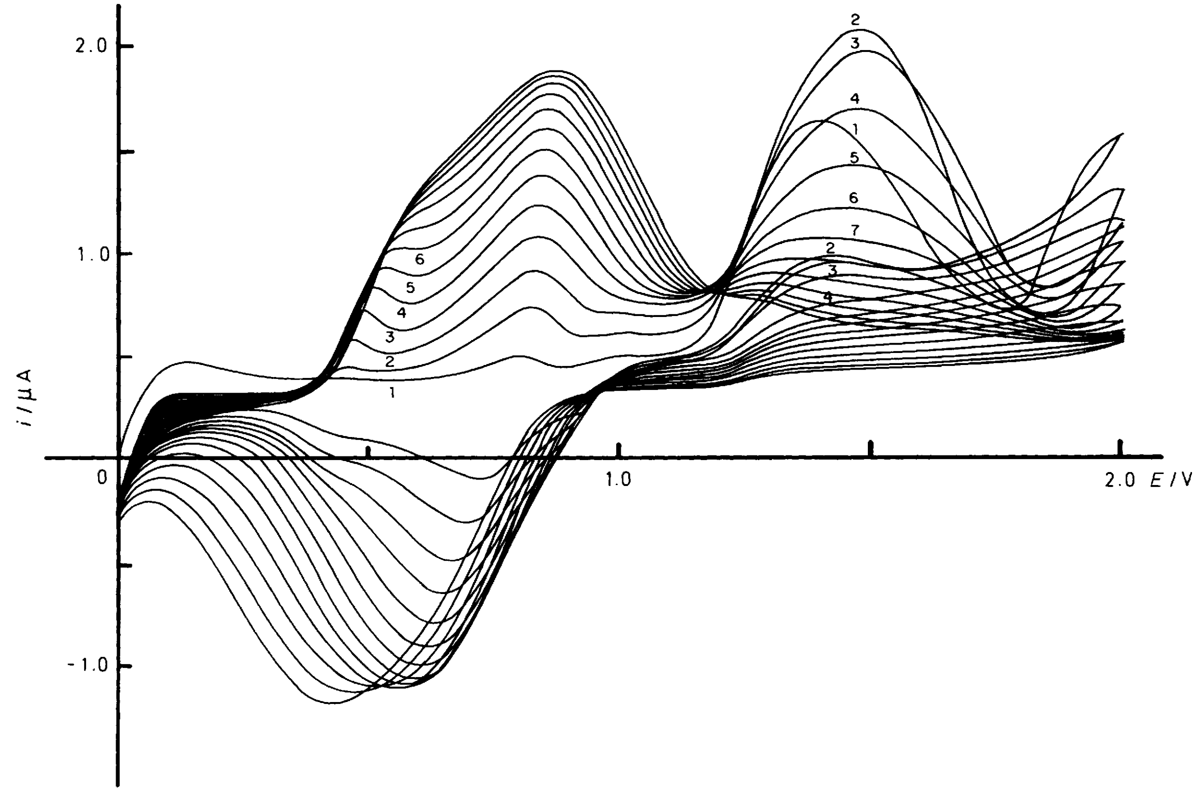

Figure 1. CV curves recorded during potentiodynamic aniline polymerization on a bare Pt working electrode; 0—2.0 V, 50 mV s^{-1}.

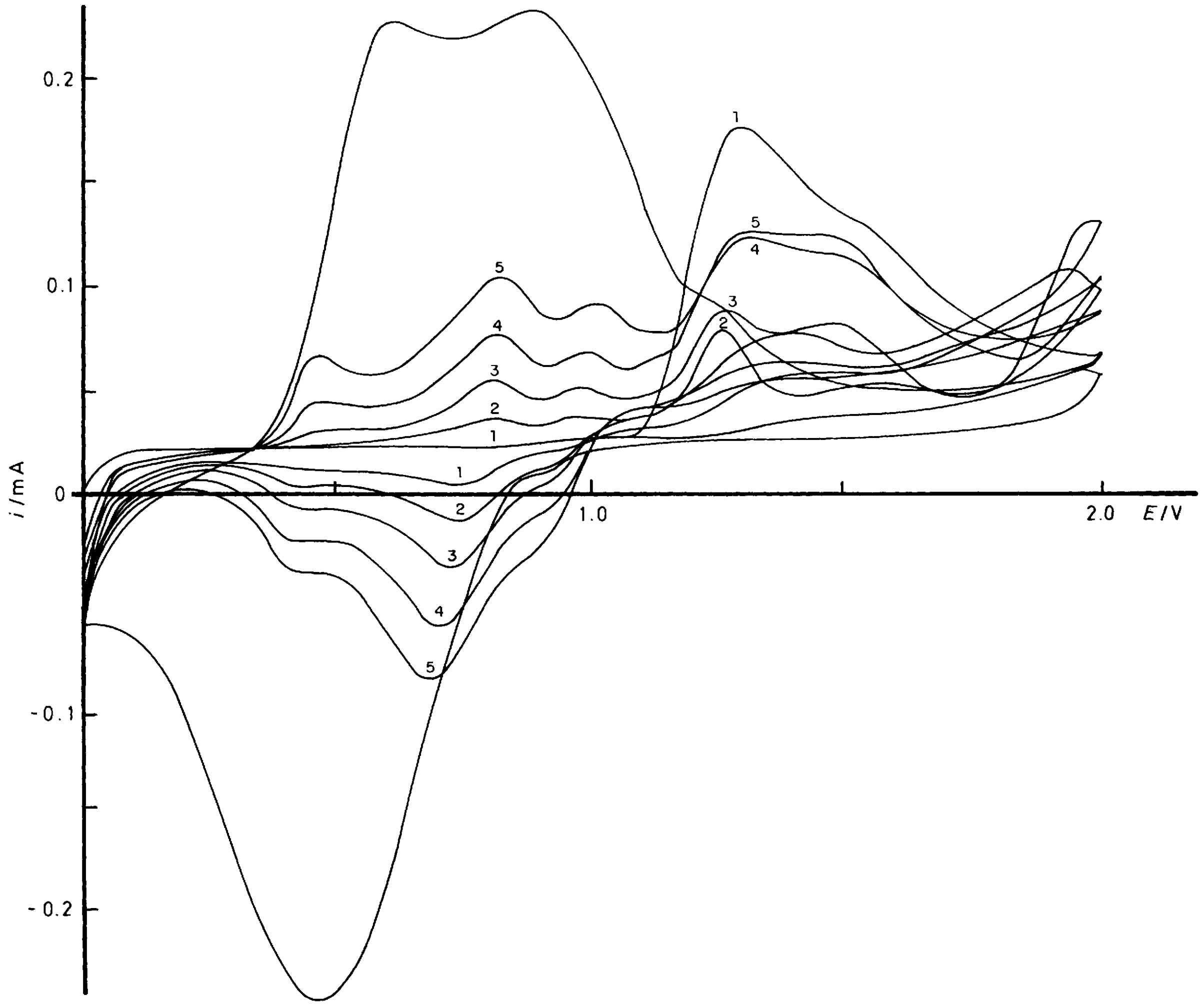

Figure 2. CV curves recorded during potentiodynamic aniline polymerization on a NBR-coated Pt working electrode; 0—2.0 V, 20 mV s^{-1}.

0.460, 0.825, and 0.995 V and cathodic peaks with E_{pc} of 0.410, 0.705, and 0.920 V are obtained. As the number of cycles increases [*i.e.* as the amount of polyaniline (PANI) in the composite increases] the high potential oxidation systems fuse into two peaks and the reduction peaks fuse into one. After 2 h (36 cycles) there is no further increase in the peak currents, indicating a saturation of the rubber with PANI. The characteristic colour change of PANI is observed in the composite during cycling. The rubbery composite can be peeled easily from the electrode and handled as a rubber film. After exposure to the atmosphere for several months the material retains its electroactivity.

Comparison of the CVs for pure polyaniline and the composite (Figures 1 and 2, respectively) reveals that, under our experimental conditions, coating the working electrode with nitrilic rubber does not affect the electrochemical properties of polyaniline. The peak potentials and the peak currents observed for the composite and for pure polyaniline are shifted in relation to previously reported data for polyaniline in acetonitrile–$HClO_4$, also the lower potential redox couple shows a much lower peak current. According to published data, the electrochemical properties of this polymer are affected strongly by the acid and the electrolyte used.[4] In our case the main changes observed are in the lowest potential redox peaks, assigned to the proto-electronic process,[5] these are caused by using a different acid, *viz.* CF_3CO_2H.

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