Electropolymerisation of Benzene to a Poly(*p*-phenylene) Film for Use as a Rechargeable Battery Electrode

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Benzene can be polymerised to a rechargeable polymer film with a formation potential of 2.3 V in highly purified SO_2; the charging–discharging capacity amounts to 85 A h kg^{-1}.

Amongst the conducting polymers poly(*p*-phenylene), PPP, has been known for many years. Its synthesis is normally achieved using the method of Kovacic *et al.*[1,2] which involves the reaction of benzene with $AlCl_3$–$CuCl_2$ or other Friedel–Crafts catalysts; a non-melting insoluble dark brown powder is obtained as product. For electrochemical applications, *e.g.* as an active battery electrode, the powder must be pressed with graphite to a solid pellet in order to obtain a stable and conducting solid material.[3]

Recently, the anodic electropolymerisation of benzene was described in several independent[3—9] publications. The electropolymerisation is more advantageous than the conventional chemical synthesis, in as much as it produces directly conducting polymer films, which can be used without further changes as active material. In the case of benzene the electropolymerisation is not as simple as for pyrrole or thiophene,[10,11] because it is oxidized at the very positive potential of +2.4 V (*vs.* Ag/AgCl), as already reported by Osa *et al.*[12] Therefore, it is obvious that the number of solvents which are stable at this potential and exhibit a low nucleophilicity is small. For example acetonitrile, which is very common in anodic oxidation and which was used in the studies of Osa *et al.*, reacts nucleophilicly with 'hot' cations. To avoid such complications the electropolymerisation of benzene was attempted in HF,[5—7] SO_2,[4] and nitrobenzene.[8,9] In every case the formation of a growing polymeric film was observed, whose quality varies with the different experimental conditions. Obviously, from an electrochemical point of view the best results were obtained with HF as solvent. But as HF is corrosive and hazardous a ready application is ruled out. Attempts to polymerise benzene in SO_2 yielded different results. While Tinker and Bard[13] obtained a blocking film, Dubois *et al.*[4] succeeded in preparing a dendrite-forming conductive deposit, which showed reversible behaviour.

As our own experiments show, the varying results obtained by electrochemical oxidation in SO_2 strongly depend on the purity of the solvent. In our experience H_2SO_4 as well as P_2O_5 are excellent drying agents but they produce unknown

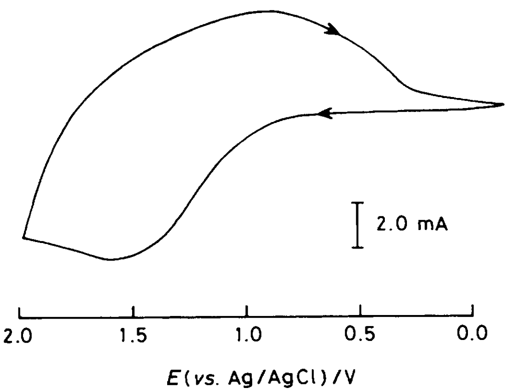

Figure 1. Slow sweep (1 mV/s) voltammogram of the oxidation of PPP in SO_2 at −40 °C.

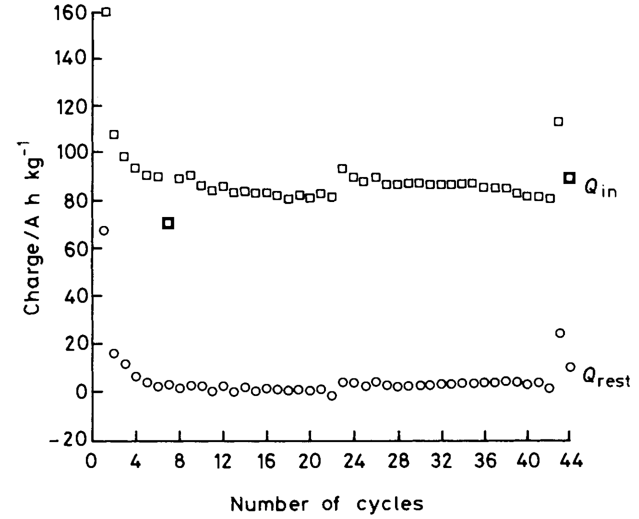

Figure 2. Coulometric analysis (potentiostatic) of the anodic charging–discharging capacity of PPP in SO_2 at −40 °C during continuous cycling; Q_{in} gives the amount of charging in A h kg^{-1}, Q_{rest} the remaining charge after discharging.

nucleophilic impurities which decrease the stability of highly reactive cations. Therefore, we have modified the purification technique for SO_2 by employing superactive alumina. So we were able to generate for the first time the tetracation of 9,9′-bianthryl.[14] Under these circumstances it was reasonable to use SO_2 again for the electropolymerisation of benzene. During the cyclic voltammetry of a diluted benzene solution [10^{-3} M, $TBA^+PF_6^-$, 0.1 M (TBA = tetrabutylammonium)] one observes at +2.4 V an irreversible anodic wave, which in multisweep experiments is accompanied by a rapidly increasing reversible wave in the range between 0.5 and 2.0 V. Simultaneously the electrode is covered by a brown-red film which changes to a black colour during further cycles. However, electropolymerisation occurs only when the potential scan reaches the foot of the benzene oxidation wave. This provides a clear indication of the validity of a radical–radical ion association mechanism which includes a redox disproportionation.[15]

The preparative formation of a PPP film is achieved using a 2×10^{-2} molar solution of benzene in SO_2 with $TBAPF_6$ as supporting electrolyte (T = −40 °C). At a working potential of +2.3 V *vs.* Ag/AgCl a smooth dark brown film is rapidly formed. The coulometric analysis indicates that 2.25—2.40 electrons per phenylene ring are consumed during electrolysis. Two electrons are needed for the coupling reaction while the remaining part is involved in the charging of the polymer. The results clearly show that every third to fourth phenylene unit is charged during the electropolymerisation. The films which we have obtained up to now are mechanically brittle but further optimization experiments are in progress.

Conducting polymers are candidates for rechargeable battery electrodes. Therefore, the reversibility of the charging–discharging process is an important criterion of the quality of such materials. To test these properties we have used slow sweep voltammetry. Figure 1 shows the cyclic voltammetric response in SO_2–$TBAPF_6$ of a electrochemically generated PPP film obtained with a scan rate of 1 mV s^{-1}. In the forward scan, which corresponds to the charging of the polymer, the current maximum is observed at +1.6 V while the current maximum in the reverse scan is at +0.8 V *vs.* Ag/AgCl. The total amount of charge acquired in this battery cycle is 90 A h kg^{-1}, whereas 87 A h kg^{-1} are regained during discharging. During 44 battery cycles the average charging–discharging capacity reaches 85 A h kg^{-1} (Figure 2). In agreement with the results from the electropolymerisation this corresponds to reversible charging of every fourth phenylene unit in the polymer. Surprisingly, overoxidations with values more than 90 A h kg^{-1} do not lead to a marked decrease in the charging capacity. As the overoxidation only becomes a significant pathway when the potential exceeds +2.0 V, we presume that, similar to the electropolymerisation, coupling reactions between phenylene units of different chains followed by deprotonation steps take place. To generate an additional C–C bond between two phenylene units a charge of 357 A h kg^{-1} is consumed. This means that overoxidation does not influence the charging–discharging quality of the polymer electrode over a great number of battery cycles.

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