BEHAVIOUR OF POLYANILINE ELECTRODES IN AQUEOUS AND ORGANIC SOLUTIONS

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Summary

Polyaniline (PAn) has been obtained in acidic solutions, chemically (by oxidation with $(NH_4)_2S_2O_8$), and electrochemically (by potential scans between -0.2 and 0.8 V *versus* a saturated calomel electrode), in order to determine its suitability as a cathode in rechargeable Li cells. It was ascertained that the loss of electrochemical activity observed during the cyclic voltammetry experiments depends on such factors as nature of the electrolyte, upper potential limit, nature of the substrate, and presence of substituents in the polyaniline rings.

The reduction/oxidation processes of PAn are basically the same in aqueous acidic solutions and in Li^+-containing organic solutions. The fully oxidized, anion-doped form of PAn is first reduced to an emeraldine-like, form, and the latter can be further reduced to an all-benzenoid rings form. Lithium cells based on PAn cathodes have been typically subjected to 100 cycles with average capacities of 0.1 A h g^{-1} (based on the weight of PAn)

Introduction

The attention of groups involved in the investigation of polymeric compounds for practical application has recently turned to polyaniline. This material has been shown to be suitable for a number of uses ranging from electrochromic displays [1], diodes and transistors [2], corrosion-resistant coatings for semiconductors [3], and cathodes for rechargeable Li batteries [4, 5]. Using polyaniline for such purposes is made easier by its outstanding stability in air and in many aqueous and nonaqueous solutions

On the other hand, the basic aspects of reactions governing the polymerization process and the redox behaviour of polyaniline are still a serious

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challenge [6 - 9]. In particular, the relationship between conductivity and oxidation level, and the number and pathways of oxidation steps have been the subject of dispute [2, 6, 10, 11] Also, the loss of the polymer's electrochemical activity, observed upon cycling, is still open to question

In the present work, to evaluate polyaniline positives for practical rechargeable Li cells, an effort has also been made to add to the understanding of some of the basic processes

Experimental

Polyaniline (PAn) was chemically synthesized by dissolving aniline hydrochloride in H_2O and oxidizing it with $(NH_4)_2S_2O_8$. The polymer was then refluxed with $LiAlH_4$ in dimethoxyethane (DME) at 85 °C for 1 h, followed by re-acidification with HCl This procedure affects the morphology of PAn (see Discussion), thus improving its performance as a positive in Li cells

PAn films were also obtained electrochemically on metallic substrates by repeated potential scans between −0.2 and 0 7 - 0.8 V *versus* a saturated calomel electrode (SCE) in a 0 1 M An, 0.1 M $H_2 SO_4$, 0 5 M $Na_2 SO_4$ solution. Platinum, Au, pyrolytic graphite or stainless steel were used as working electrodes Poly-*o*-phenylenediamine (PPD) was also obtained on a Pt electrode by cyclic voltammetry in acidic solutions.

The compositions of chemical and electrochemical PAn were checked by elemental analysis

The relevant technique for building and testing the Li cells containing PAn electrodes has been described elsewhere [12] Both chemical and electrochemical PAn were tested as a positive. The former was mixed with 10% of Teflonized acetylene black (TAB). The latter was mostly deposited on a stainless steel net and used without any further treatment Cell cycling in $LiClO_4/PC$–DME was performed between 2.3 and 4 0 V. A recent investigation has shown that anodic decomposition of the electrolyte used is not significant in this potential range [13]

Results and discussion

Infrared (IR) spectra of the chemical and electrochemical PAn obtained in this work show that both forms possess the basic emeraldine structure [14, 15]. The latter is an octamer with 2 quinoid and 6 benzenoid rings. The absence of the peak at 1625 cm^{-1}, corresponding to the stretching of the C=N bond, however, is remarkable

Elemental analysis of electrochemical PAn has shown that it contains 3 sulfuric groups per emeraldine unit This result is in agreement with that reported for PAn prepared under potentiostatic conditions in 1 M HCl, *i e*, ∼3 Cl⁻ in the same unit [6]

For chemical PAn, elemental analysis and acid-base titrations have demonstrated the presence of 4 Cl⁻ per emeraldine unit.

Both forms were shown to be completely amorphous by X-ray diffractometry.

From scanning electron microscopy (SEM), morphological differences between chemical and electrochemical PAn were noticed. As-prepared chemical PAn has a rather coarse structure, formed by large and dense aggregates (Fig. 1(a)). This morphology is substantially altered by treatment with LiAlH₄. The aggregates are destroyed and small, large-area particles appear (Fig. 1(b)). The last configuration is best suited to electrode applications and, indeed, PAn treated with LiAlH₄ outperforms untreated PAn as a cathode in Li cells Electrochemical PAn has a fairly homogeneous structure formed by small granules (Fig. 1(c)) It is remarkable that under our experimental conditions such a structure is observed, even for relatively thick deposits (50 - 100 μm), while other authors have observed the growth of loosely-packed fibers superimposed to a dense layer, even for very thin films [16].

Smooth, strongly adherent, PAn deposits were obtained by cycling between −0.2 and 0.7 - 0.8 V *versus* SCE in acidic solutions. A typical initial polymer growth is shown in Fig 2. After a short induction period during which the peaks corresponding to the different reduction/oxidation
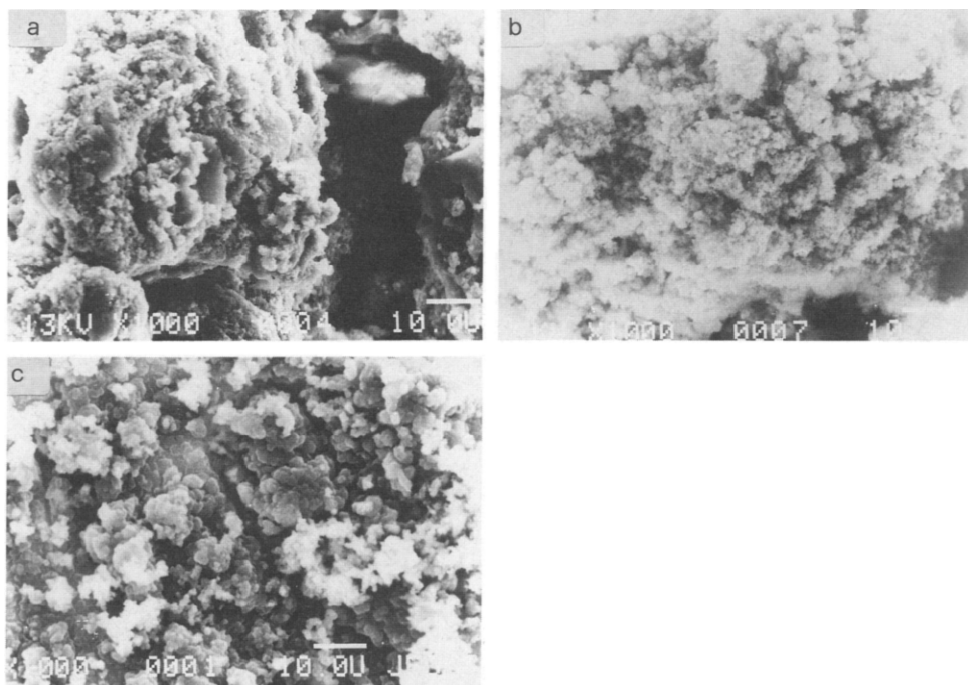

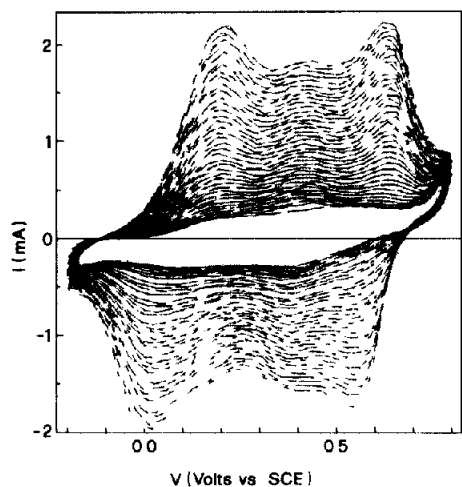Fig 1 SEM pictures of (a) as-prepared chemical P An, (b) chemical PAn treated with LiAlH₄, (c) electrochemical PAn.

Fig 2 Initial growth of a PAn film in 0 1 M aniline, 0 1 M H_2SO_4, 0 5 M Na_2SO_4. Pt electrode, 100 mV s^{-1}

steps were barely discernible, two major peaks were observed. The first of the two peaks corresponds to a protoelectronic equilibrium, while the second corresponds to anion doping/undoping (see Scheme 1) Between these two peaks, another flat peak has often been observed. According to Geniès [7] it may be attributed to the presence in the structure of monomer couplings other than the normal 1 - 4.

(X = H or Li)
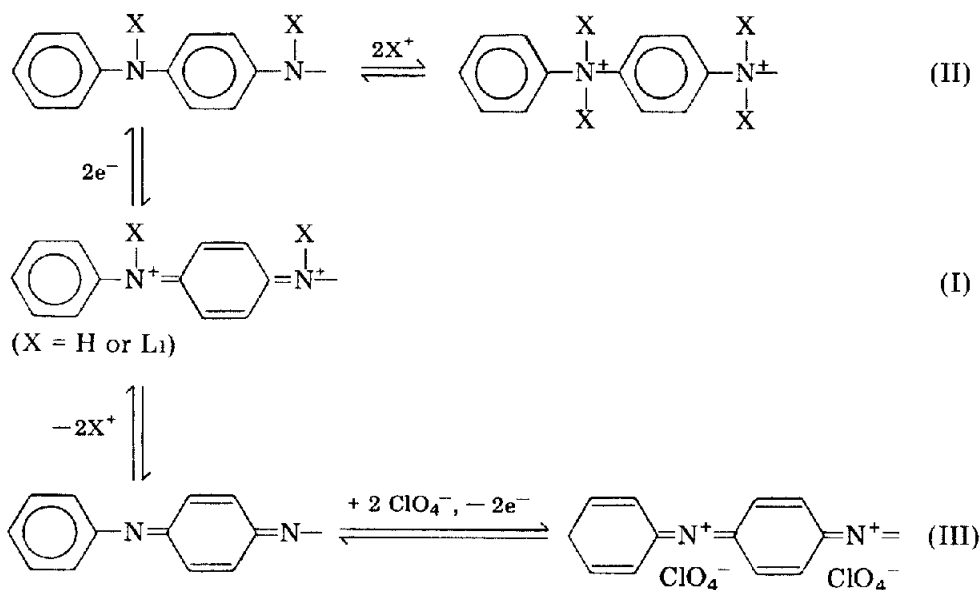
Scheme 1

Attempts were made to unravel possible electrocatalytic effects brought about by different substrates. The shapes of the cyclic voltammetries obtained with Pt, Au, C or stainless steel did show some differences, and the loss of PAn electrochemical activity (see below) was observed at different cycle numbers for the different substrates. Furthermore, the average polymer yield, although similar for Pt, C and stainless steel (~ 8 mg cm^{-2} after 200 cycles at 25 mV s^{-1}), was much lower for Au (~ 1 mg cm^{-2}) More work is in progress in this direction, especially in view of the need for plating PAn films onto very thin metal or semiconductor substrates for the practical applications mentioned in the Introduction.

The peak heights vary linearly with the scan rate, as shown in Fig. 3. This behaviour is typical of a thin film attached to a substrate where diffusion plays a minor role and, instead, electron transfer may be the rate-determining step. A similar relation between i_p and V was observed for the single peak couple of PPD films.
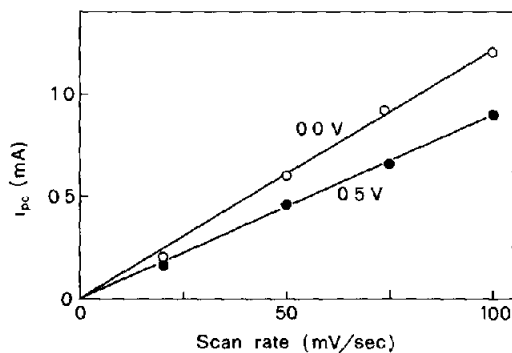

Fig. 3 Relationship between height of the two main cathodic peaks and scan rate

PAn loses its electrochemical activity after a number of cycles, as monitored by the disappearance of the peaks. This is certainly one of the most intriguing and controversial aspects of the electrochemistry of this material. It is commonly accepted that deactivation is a function of the potential and takes place above 0.7 V versus SCE [10, 17] We are reconsidering this assessment and have run tests with upper limits of 0.7 and 0.8 V (Fig. 4) and have shown that deactivation does occur even when the scan is stopped at 0 7 V. It has to be remarked, however, that with this limit the onset of the phenomenon is delayed. For instance, in Fig. 4(b) (upper limit, 0.7 V) the 320th cycle still shows the typical peaks, whilst the 315th cycle of Fig. 4(a) (upper limit, 0.8 V) is spindle-shaped.

Although no direct conductivity measurements were taken at the various stages of the potential scan, deactivation seems to be connected with loss of electronic conductance. The shifting of the anodic peaks to high V values and featureless voltammograms is typical of the loss, or absence, of conductivity. Very recently, the conductivity of PAn films has been correlated with the oxidation level by impedance measurements [10] In this latter
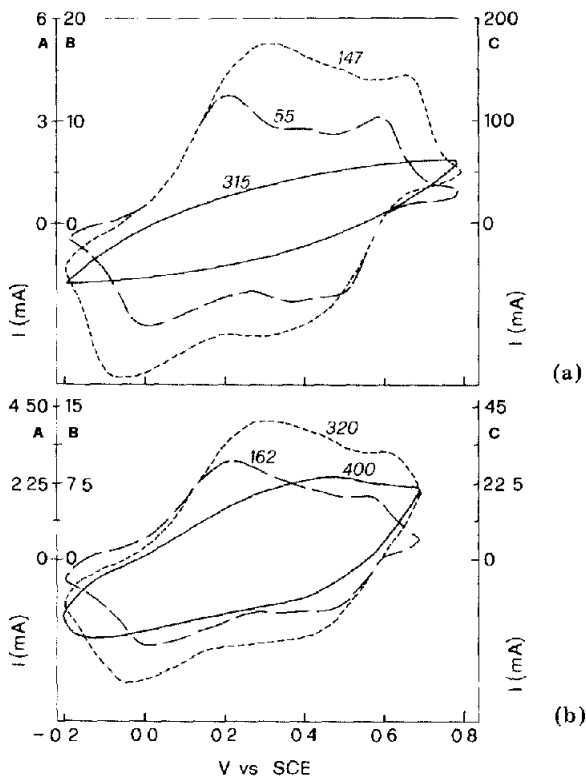
Fig 4 Variation of the cyclic voltammetry profiles as a function of the cycle number (indicated on each cycle) (a) upper limit 0 8 V, (b) upper limit 0.7 V Scales A, B, and C on ordinates refer to the lower, medium, and higher cycle number, respectively

investigation, the conclusion was also reached that the major influence of deactivation is a decrease in electronic conductivity. Why this occurs upon cycling, however, is still unaccounted for.

Meanwhile, we have observed that deactivation is influenced by a number of factors. As previously mentioned, the onset of the deactivation process depends on the metal substrate and on the upper potential limit. The solution, too, seems to play a role, since in 0.2 M $HClO_4$ the peaks are still present after 1000 cycles The use of substituted anilines further affects the deactivation Indeed, when polymerizing o-phenylenediamine, we were able to reach several thousands of cycles without loss of activity (Fig 5) The behaviour of this polymer gives rise to comment. The redox couple corresponding to the anion doping/undoping is absent here, as also observed by others [18]. It is our opinion that the presence of two protonated amino groups in the polymer rings prevents anion uptake. Indeed, polymer deprotonation, which is a necessary step towards full oxidation (see Scheme 1), would be more difficult in this case since H^+ may shift between the two nitrogen atoms Partly protonated PAn would then be stabilized by the resonance
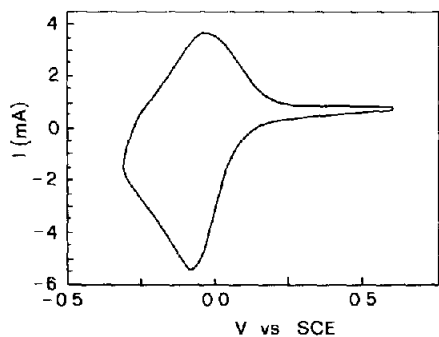
Fig. 5. Cyclic voltammetry of PPD in a sulfuric solution Pt electrode, 100 mV s^{-1}. 5000th cycle
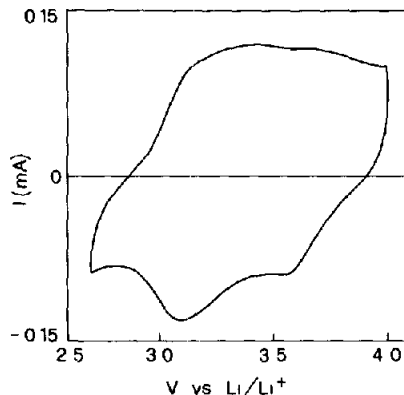
Fig. 6. Cyclic voltammetry in LiClO$_4$/PC–DME of a PAn film prepared in a sulfuric solution. Scan rate, 20 mV s^{-1}.

Preliminary tests on a PAn film containing —SO$_3$H groups instead of —NH$_2$ show that the peaks related to anion doping/undoping are still present and deactivation occurs — although at later cycling stages with regard to nonsubstituted PAn. More work is in progress in this direction.

PAn films deposited in acidic solutions were transferred, after a quick wash in water and drying, into organic solutions, and cyclic voltammetry tests were run Figure 6 shows a typical voltammogram in LiClO$_4$/PC–DME at 20 mV s^{-1}. The two major peaks observed in aqueous solutions are still evident here, although they tend to merge into a large capacitive current The cathodic peaks are more distinguishable and occur at ~3.1 and ~3.6 V *versus* Li/Li$^+$. By taking into account that the latter electrode has a potential of 3 18 V *versus* SCE, one could transform the cathodic peak values obtained in acidic solutions (see Fig. 2) into 3.2 and 3.7 V *versus* Li/Li$^+$ There is good agreement, therefore, between values measured in H$^+$-containing aqueous solutions and Li$^+$-containing nonaqueous solutions.

This evidence permits the conclusion that Li$^+$ may replace H$^+$ in the redox equilibria. Indeed, the proton-like character of Li$^+$ is well known in organic electrochemistry.

The importance of the presence of H$^+$, or Li$^+$, in the equilibria of the polymer is confirmed by the fact that PAn is only active in aqueous solutions at pH < ~ 4 [14] or in Li$^+$-containing organic solutions. We propose Scheme 1 to account for the two main steps of the reduction/oxidation process, as evidenced by the cyclic voltammetries (Figs. 2 and 6).

In Scheme 1 we have adopted the dimeric symbol formed by a benzenoid and a quinoid ring. Form (I) may be either a protonated or a neutral one and two such dimers are contained in the emeraldine octamer. Form (II) is expected to be highly protonated, thus justifying the protoelectronic term used for equilibrium (I) → (II).

As observed by others [7], and in the present work, using protonated PAn in organic solutions does not result in the release of protons in solution and Li attack. The protons remain permanently bound to the polymer and grant it a sufficiently high electronic conductivity.

The formation of the two dications (bipolarons) in Scheme 1 is preceded by the formation of radical cations (polarons) Geniès has proved this using *in situ* optical and ESR measurements [8, 9]

Figure 7 shows typical discharge curves of protonated chemical Pan in an organic solution Curve 1 corresponds to the reduction (I) → (II) in Scheme 1, whereas curve 2 corresponds to the reduction (III) → (I) → (II) In the range 4 - 3 V, curve 2 tends to approach a straight line, thus being similar to a capacitor discharge curve ($Q = CV$)

With neutral PAn (+20% TAB) we obtained a capacity of 0.14 A h g^{-1} (based on the polymer weight only). This represents about 50% of the theoretical value based on the reduction (III) → (I). On the other hand, according to Geniès [19], in the fully oxidized state only 20% of form (III) should be present

Lithium cells containing PAn cathodes (both chemically and electrochemically prepared) were extensively cycled at 0 5 mA cm^{-2} between 2.3 and 4 0 V Average capacities of 0.1 A h g^{-1} were obtained with protonated chemical PAn (treated with LiAlH$_4$) mixed with 10% TAB (Fig. 8) Electrochemical PAn showed a somewhat inferior performance because of the less favourable morphology, the absence of conducting additives, and the lower content of pure PAn base (due to the presence of the sulfuric groups) Tests to obtain the highest capacity output are in progress with different cathode formulations.

As the average voltage on load is very high ($\sim$3.4 V), gravimetric energy densities are also high, but the volumetric energy densities compare poorly with those of inorganic materials. From SEM experiments using electrochemical PAn, we obtained an apparent density of about 0.2 g cm^{-3}, which is not too different from the 0.3 g cm^{-3} reported by others [20]. These values are more than one order of magnitude lower than those of the inorganic salts (MoS$_2$, TiS$_2$, V$_6$O$_{13}$) used in lithium cells, and could limit appli-
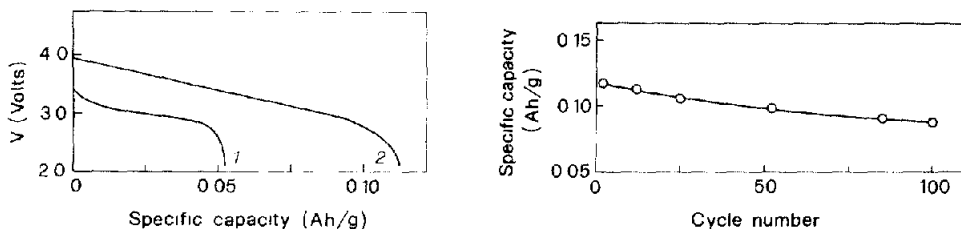

Fig 7 Discharge profiles of Li/PAn cells 1, first discharge, 2, discharge after 20 cycles (between 2 3 and 4 0 V) Protonated PAn (+10% TAB)

Fig 8 Variation of the specific capacity of an Li/PAn cell with cycle number

cations of PAn in practical rechargeable batteries. On the other hand, the possibility of growing extremely thin, very adherent, stable films on different substrates may be advantageous for special applications.

Acknowledgements

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