JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 283–287

Direct electrodeposition of poly(pyrrole) on continuous carbon-loaded microporous membrane films

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Received 13 May 1993; revised 15 September 1993

Ultrasonication helps direct electrodeposition of inherently conducting polymers (ICPs) into the pores of microporous membranes. Use of microporous membranes in conjunction with a partially immersed cylindrical horizontally revolving electrode (PICHRE) permits the production of conducting films on a continuous basis. Production and electrical and mechanical characteristics are described.

1. Introduction

Inherently conducting polymers are currently used in capacitors, corrosion protection and charge dissipation [1] and can be used in electromagnetic shielding [2–4], electroluminescent devices [5, 6], catalysis [7], electrochromism [8, 9], sensors [10–12] etc. Electrical signal and communication cables are currently shielded by either metal braids and/or aluminium laminated polyester, μ-metal (for low frequency magnetic shielding), carbon-loaded polyester tapes etc. Carbon filled semiconductive (10^{-3}–$10^{-4}\,\mathrm{S\,cm^{-1}}$) microporous polyurethanes are commercially available from Porvair plc (Norwich). Chemical oxidative polymerization of pyrrole with concommitant impregnation has been described [3, 4, 13, 14]. However, chemical oxidative preparation of inherently conducting polymers does not always produce the most conductive form [15], nor is it environmentally friendly because of large quantities of effluents. If a direct electrochemical polymerization were possible, a conducting material can be produced in a single step. Partially immersed cylindrical horizontally revolving electrode (PICHRE) enables the electrodeposition on a continuous basis (Fig. 1).

Normal direct electrodeposition using carbon-loaded polyurethane (C-PU) as anode led only to the deposition of the polymer on the surface. To increase the bulk conductivity (useful in reducing the skin depth $\delta = 1/\sqrt{(\pi f \mu \sigma)}$, where σ is the conductivity, μ is the permeability and f the frequency of the electromagnetic radiation) it would be necessary to impregnate the microporous porous material with ICPs. This was achieved by impregnating the membrane with the electrolyte by ultrasonication prior to electrolysis.

2. Experimental details

Carbon-loaded polyurethane films (CPU) of two thicknesses 150 μm (hereinafter referred to as CPU-150) and 510 μm (hereinafter referred to as CPU-510) of various lengths (8–10 m) and 11 cm width were employed in the study. The films were immersed in a beaker of electrolyte solution (0.2 M pyrrole, 0.2 M sodium p-toluene sulphonate) with an intervening layer of nonwoven polyester to allow even wetting and placed in an ultrasonic bath for 10 min at a power of $40\,\mathrm{W\,cm^{-2}}$ and a frequency of 20 kHz. The tape was then separated from the nonwoven and impregnated with poly(pyrrole) electrochemically, using a partially immersed cylindrical horizontally revolving electrode (PICHRE) assembly. Angular velocities from 1.7×10^{-2} to $1.67\,\mathrm{cm\,s^{-1}}$ and current densities from 60 to $230\,\mathrm{mA\,cm^{-2}}$ have been employed to optimize conditions for the polymerization. The electrolyte solution was changed at intervals depending on the current density employed as the pyrrole and the p-toluene sulphonate were depleted: $60\,\mathrm{mA\,cm^{-2}}$, twice hourly; $230\,\mathrm{mA\,cm^{-2}}$, every 30 min. Most of the experiments were carried out at room temperature ($20 \pm 1\,^{\circ}\mathrm{C}$). One experiment was performed at $-5\,^{\circ}\mathrm{C}$ to examine the temperature effect.

Electrical conductivity was measured using four probe (linear and square) and sandwich cell (two electrodes). Conductivity (four probe) against strain characteristics was measured using a home made tensometer fitted with a four probe apparatus. The tensometer can take film thicknesses ranging

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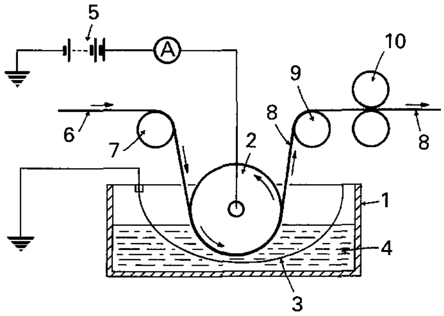

Fig. 1. Partially immersed cylindrical horizontally and revolving electrode. Key: (1) electrochemical cell, (2) working electrode, (3) counter electrode, (4) electrolyte, (5) power supply, (6) microporous membrane, (7) roller, (8) poly(pyrrole) impregnated film, (9) roller, (10) squeezing rollers.

from 25 μm to 3 mm. The effect of aging, humidity (50 °C/50%RH), thermal degradation kinetics (at 80 °C in air) and UV stability (by exposing the sample to a fluorescent lamp and at a power density 400 W m^{-2}) were monitored over a period of ten weeks.

3. Results and discussion

The experimental conditions employed for the production of poly(pyrrole)-*p*-toluenesulphonate are summarized in Table 1 (note that runs 1–8 are for 150 μm CPU and 9 and 10 are for 510 μm CPU). It was found that lowering the temperature from 20 °C to −5 °C did not significantly alter the conductivity under revolving electrode conditions. The uptake of poly(pyrrole) (PPy) has not been altered either. Thus, it appears that the conductivity is directly dependent on the PPy content. Figure 2 shows the variation of conductivity of the PPy-impregnated poly(urethane) (150 μm) with the PPy content in the film. The plot (Fig. 2) indicates that the percolation threshold is reached at a loading level of 7% (m/m). Thus, any increase in pyrrole content above 8% (m/m) is unlikely to change the conductivity markedly.This is exemplified by runs 3 and 4 where the loading levels of PPy are 9 and 13% (m/m), respectively, but no significant differences in conductivity. On increasing the angular velocity from 1.67 × 10^{-2} cm s^{-1} to 5.01 × 10^{-2} cm s^{-1}, (threefold increase), a fourfold increase in current density (58 to 229 mA cm^{-2}) was required to produce comparable loading level of PPy, conductivity and uniform coating. This is explained on the basis of reduced resident time at high angular velocity. This has to be offset by increased rate of production of PPy requiring the need for increased current density. The other reason for increased current density requirement is because of the fact that the oligomers formed at the electrode would be lost owing to the fact that the forced convection is now considerably higher than the free convection. Further, it is intriguing to note that at an angular velocity of 1.67 × 10^{-1} cm s^{-1}, a current density of 371 mA cm^{-2} was adequate to provide a uniform deposition. However, the uptake of PPy is lower than the maximum possible (~ 13%) which in turn, has

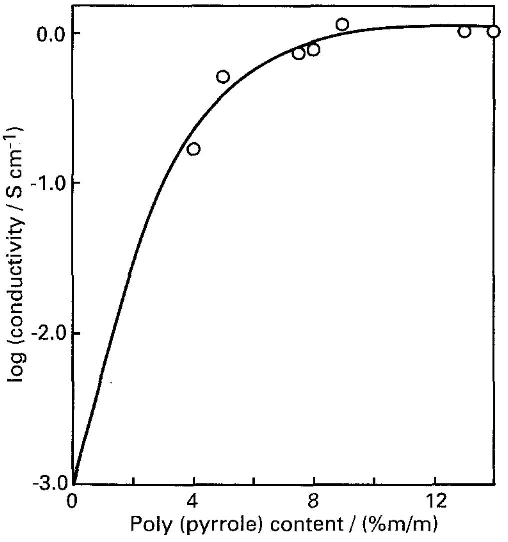

Fig. 2. Conductivity against poly(pyrrole) content in the microporous polyurethane (150 μm).

Table 1.

Run number	*Initial volume conductivity /S cm^{-1}*	*Angular velocity /cm s^{-1}*	*Current density /mA cm^{-2}*	*Uptake of poly(pyrrole) /% (m/m)*	*Conductivity /S cm^{-1}*	*Comments*
1	10^{-3}	1.67 × 10^{-2}	58	8.0 ± 0.1	0.79 ± 0.05	even coating at 20 °C
2	10^{-3}	1.67 × 10^{-2}	58	8.0 ± 0.1	0.88 ± 0.10	even coating at 5 °C
3	10^{-3}	1.67 × 10^{-2}	114	9.0 ± 0.1	1.15 ± 0.10	even coating at 20 °C
4	10^{-3}	1.67 × 10^{-2}	229	13.0 ± 0.1	1.01 ± 0.10	0.6 M pyrrole, −8 °C, patchy deposit
5	10^{-3}	5.01 × 10^{-2}	143	5.0 ± 0.1	0.53 ± 0.05	patchy deposit at 20 °C
6	10^{-3}	5.01 × 10^{-2}	229	7.5 ± 0.5	0.73 ± 0.05	even coating at 20 °C
7	10^{-3}	1.67 × 10^{-1}	286	8.0 ± 0.1	0.13 ± 0.05	patchy deposit at 20 °C
8	10^{-3}	1.67 × 10^{-1}	371	4.0 ± 0.1	0.17 ± 0.05	even coating at 20 °C
9	2 × 10^{-4}	1.67 × 10^{-2}	143	6.0 ± 0.5	0.19 ± 0.05	patchy deposit
10	2 × 10^{-4}	1.67 × 10^{-2}	229	7.0 ± 0.2	0.23 ± 0.05	uniform coating

Notes: 1. Samples 1–8: 150 μm sample; samples 9 and 10: 510 μm sample.

2. Condition of electrolysis unless otherwise mentioned: pyrrole 0.2 M; sodium *p*-toluenesulphonate 0.2 M.

3. The current densities were chosen so that a uniform deposit is obtained.

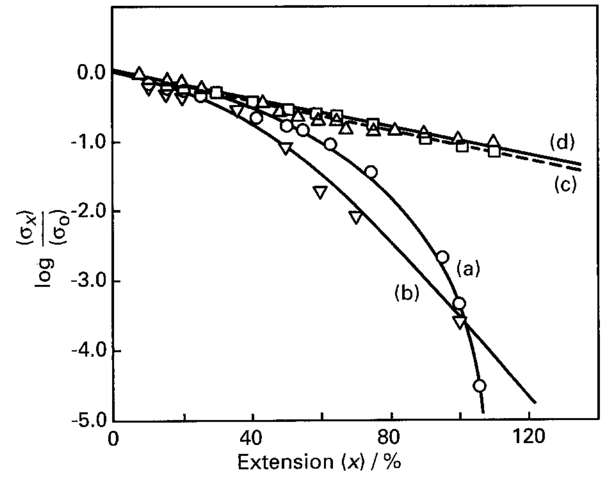

Fig. 3. Ratio of conductivity at extension to original conductivity against extension. Carbon-loaded polyurethane: (a) 150 μm, and (b) 510 μm. Poly(pyrrole)-impregnated carbon-loaded polyurethane: (c) 150 μm and (d) 510 μm.

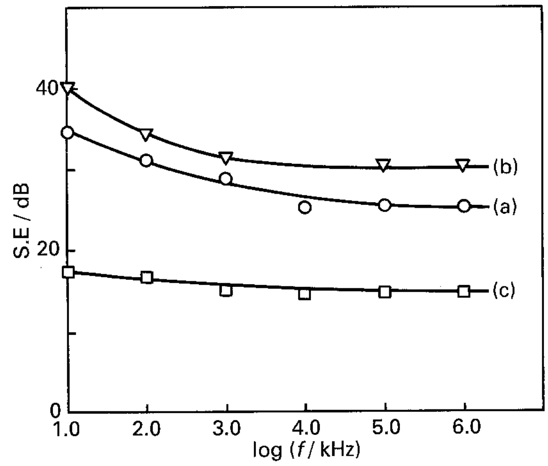

Fig. 4. Shielding efficiency (SE/dB) against frequency. Poly(pyrrole)-impregnated polyurethane: (a) 150 μm and (b) 510 μm. (c) Poly(aniline)-impregnated polyurethane (150 μm).

been reflected in the lower conductivity of $0.17 \pm 0.05\,\mathrm{A\,cm^{-1}}$.

The 510 μm poly(urethane) film was impregnated at a higher current density of $229\,\mathrm{mA\,cm^{-2}}$ at an angular velocity of $1.67 \times 10^{-2}\,\mathrm{cm\,s^{-1}}$. This is expected in view of the larger volume that PPy needs to fill.

An important question is whether the PPy deposited is really impregnated into the matrix of the microporous membrane. The density of PPy is $1.45\,\mathrm{g\,cm^{-3}}$. On the basis of weight gain in run 1, and the density for poly(urethane) of $1\,\mathrm{g\,cm^{-3}}$, a thickness increase of 7.42 μm is predicted. But, no measurable increase in thickness was observed.

Figure 3 shows the variation of conductivity with strain. Curves (a) and (b) represent the carbon-loaded starting materials, 150 μm and 510 μm, respectively. The loss in conductivity on extension to 100% is dramatic as expected and of the order of 3100 fold. Curves (c) and (d) represent PPy impregnated 150 μm and 510 μm poly(urethane) films, respectively. These samples undergo a loss of conductivity of only tenfold. This suggests that the conductivity is due to the matrix of PPy rather than just a surface film. Were the conductivity due only to a surface film, a large decrease in conductivity would be expected, since the film would lose its coherence as the tape was extended.

Table 2 summarizes the mechanical properties obtained for the films produced in this work. The tensile strength and elongation at break are not altered by direct electrodeposition of PPy.

Electromagnetic shielding efficiency (measured according to ASTM ES 7/83) of PPy impregnated carbon-loaded microporous membrane (150 μm; (a) in Fig. 4) and 510 μm ((b) in Fig. 4) and poly(aniline) (deposited from a solution of aniline (0.1 M), methane sulphonic acid (0.2 M) (c) in Fig. 4) indicate that the shielding efficiencies simply follow the thickness and conductivity law as expected (conductivity of (a) $= 1.0 \pm 0.1\,\mathrm{S\,cm^{-1}}$, 150 μm; (b) $= 0.23 \pm 0.05\,\mathrm{S\,cm^{-1}}$ 510 μm; (c) $= 0.02 \pm 0.01\,\mathrm{S\,cm^{-1}}$, 150 μm).

Although the conductivity of (a) is fourfold higher than that of (b), the thickness of (a) is approximately fourfold less than that of (b), thus compensating each other as far as the shielding efficiency is concerned. Thus, the SE of (a) and (b) are comparable. As the poly(aniline) impregnated material has 50 fold lower conductivity than (a), the SE efficiency is significantly lower than (a) as expected [3].

Figure 5 shows the ageing characteristics (curve (a)) of PPy impregnated carbon-loaded material,

Table 2. Mechanical properties of poly(pyrrole)-impregnated polyurethane films

No.	*Material*	*Tensile strength*/$\mathrm{N\,mm^{-2}}$	*Elongation at break*/%
1	carbon-loaded polyurethane (150 μm)	2.9 ± 0.1	100 ± 7
2	as in 1, but poly(pyrrole) impregnated	3.0 ± 0.1	100 ± 10
3	carbon-loaded polyurethane (510 μm)	4.3 ± 0.4	106 ± 4
4	as in 3, but poly(pyrrole) impregnated	3.6 ± 0.4	108 ± 2

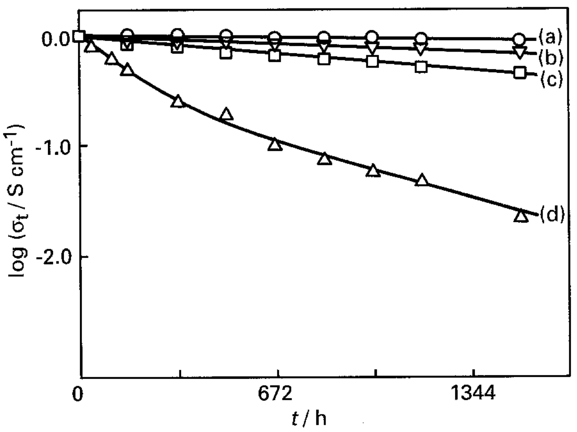

Fig. 5. Conductivity against time plots for (a) ageing, (b) u.v. effect, (c) 50 °C/50% r.h. and (d) 80 °C in air.

ultraviolet stability (curve (b)) humidity effect (curve (c)) at 50 °C/50% r.h. and thermal effect (curve (d)) at 80 °C in air. The rate of loss of conductivity, a reflection of the rate of degradation of the substrate, is Rate (80 °C) $>$ Rate (50 °C/50% r.h) $>$ rate (u.v) $>$ rate (ageing). This was expected, as it is well known that PPy is unstable towards moisture and oxygen in particular at elevated temperature. However, the rate of drop in conductivity under normal conditions required for signal cable shielding is not severe and therefore these materials are eminently suitable.

Scanning electron microscopy (SEM) of the microporous membranes prior to and after impregnation with PPy *p*-toluenensulphonate is shown in Fig. 6. Figures 6(a) and (b) show the surface morphology of the starting and impregnated materials, respectively. It is clear that there is a thin deposit of fibrous network of PPy on the surface. Figures 6(c) and (d) compare the SEMs of the cross sections of the membrane prior to and after impregnation, respectively. Figure 6(d) clearly indicates the presence of PPy in fibrous forms. This type of structure has also been observed when PPy is impregnated into microporous poly(ethylene)(s) by the author.

Further evidence of impregnation comes from simple experiment of flow rate of water through the membrane before and after impregnation. For example, water can be sucked through the starting material using a rotary pump at a rate of $1\,\mathrm{dm}^3\,\mathrm{h}^{-1}$ whereas only 10 ml of water can be sucked through the impregnated film. Dynamic wetting characteristics of the membrane were determined by Wilhelmy technique using a Cahn Instrument (DCA 322, Cahn Instruments Inc, 16207 Carmenta Road, USA) as described in [17]. The advancing and receding contact angles were 97 ° and 21 ° for the starting membrane and 54 ° and 24 ° for the impregnated membrane. This demonstrates that the impregnated membranes have become hydrophilic. This is expected as poly(pyrrole) *p*-toluenesulphonate is of the structure [(pyrrole)$_3$ PTS] and should interact with water.

4. Conclusion

It has been shown that ultrasound can be used for direct electrochemical impregnation of poly(pyrrole)

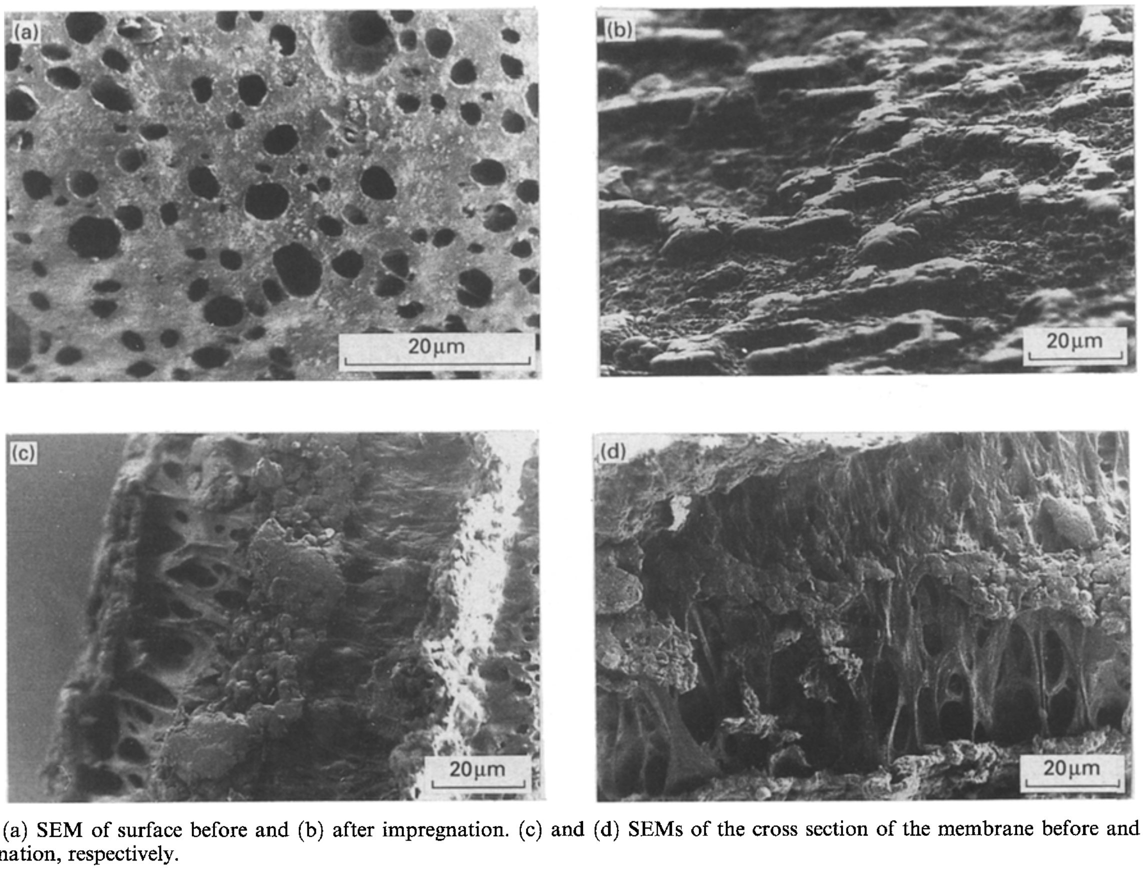

Fig. 6. (a) SEM of surface before and (b) after impregnation. (c) and (d) SEMs of the cross section of the membrane before and after impregnation, respectively.

and poly(aniline) into microporous membranes of polyurethane. This method can be applied to any membrane with sufficient conductivity (at least $10^{-4}\,\mathrm{S\,cm^{-1}}$) and thus the method is of general applicability [18]. Monomers such as poly(thiophen)(s), poly(isothianaphthene) are being impregnated.

Acknowledgement

The author thanks Dr D. R. Rosseinsky and Professor D. E. Williams for their encouragement.

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