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Preparation of dry cells using polypyrrole and polyaniline composites

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Composite conducting materials, consisting of polypyrrole and polyaniline incorporated into an inorganic or polymer matrix have been produced. Low-cost, easily fabricated dry cells were constructed by gluing the composite conducting membrane on magnesium or aluminium foils. The efficiency and e.m.f. values of the cells were in the range 0.5–13.8 mWh cm^{-3} and 0.5–2.0 V, respectively.

1. Introduction

Conducting polymers are attracting research interest due to their wide range of current and potential applications. Polypyrrole and polyaniline, are among polymers possessing high conductivity [1, 2] and unusually good chemical stability, properties which suggest that these polymers may be useful as microelectronic elements [3] for the development of photovoltaic elements [4], as chemical sensors [5], as photochromic material [6] and for the development of rechargeable cells [7–9]. However, making composite polymers from conducting polymers may produce polymers with improved mechanical properties such as processability and atmospheric stability [10–12].

The introduction of $-SO_3H$ groups in polyaniline polymers would make possible new materials to be used in photocells [13]. $-SO_3H$ groups containing polyaniline have been found to be effective substrates for the removal of heavy metals in the form of the respective sulphides [14]. Moreover, sulphonated polymers may be useful for the development of polymer batteries.

The aim of this work is the preparation of conducting composite materials, consisting of polypyrrole and polyaniline, incorporated into an inorganic or polymer matrix; the investigation of the electrical properties of these preparations; and their application for the development of new dry cells.

2. Experimental procedure

2.1. Composite membrane preparation

Commercially available membranes, such as Millipore (USA) 0.22 μm membrane filters (cellulose nitrate), paper filters (Schleicher & Schuell, Germany), polyvinyl alcohol (PVA, BDH, England) membrane obtained in our laboratory by partial drying under reduced pressure, and Y-alumina (Houdry HO415, Germany), were used as carriers for the development of conducting polymer composites. Millipore membrane, paper filters and Y-alumina were submitted to dry impregnation with 29% $Fe(NO_3)_3$ (Ferrak, AR, Germany) solution in 2 N HCl. PVA membrane was made from mixtures of 10 wt % PVA solution in triple distilled water and 29 wt % $Fe(NO_3)_3$ in 3 M KCl aqueous solution. The preparation of conducting polymers was carried out by polymerization under reduced pressure in a vacuum reactor [15] as shown in Fig. 1. Pyrrole (Merck, Germany) and aniline (Merck), freshly distilled, were used as solution (10 vol %) in 2 N HCl. The temperature was maintained at 20 °C and the reaction time was 5 for the polypyrrole (PPY) composites and 24 h for the polyaniline (PA) composites. The composites were dried under vacuum overnight.

2.2. Conducting polymers in pellet form

Polyaniline and polypyrrole conducting polymers were prepared by polymerization at room temperature in the presence of $Fe(NO_3)_3$ aqueous solution (monomer: oxidant = 1:1 mol %) followed by soxhlet extraction for 36 h. The polymers were obtained as a black powder. The introduction of $-SO_3H$ groups was effected through the reaction of the $-NH$ groups of the polymers with freshly distilled chlorosulphonic acid at 5 °C. The sulphonated conducting polymers as well as mixtures of conducting polyaniline and polypyrrole powder with sulphonated polystyrene [16] or sulphonated polystyrene divinylbenzene (1.5%, 80–100 mesh) [17] were subsequently made into pellets using an infrared KBr pellet die. The pellets ($\approx$ 1-mm thickness, 13-mm diameter) were made by applying a pressure of 1400 MPa. The extent of sulphonation was estimated to be 10% for the non-conductive polymers and 50% for the conducting polymers.

2.3. Further characterization of polymers

In all cases the sulphonated polymers exhibited the characteristic infrared adsorption band at 1335 cm^{-1} (Perkin-Elmer 577 infrared spectrometer). The extent of polymer sulphonation was verified by elemental analysis for C, H and N (Hewlett Packard 185 CHN

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TABLE I Conducting composites and their characteristics

Sample No.	Carrier/support (dimensions)	Conducting polymer (wt %)	Conductivity (s cm^{-1})
1	–	PPY(100)	30.6
6	–	PA(100)	7
2	Y-alumina (1/8″pellets)	PPY(5)	2×10^{-5}
7	Y-alumina (1/8″pellets)	PA(25)	6×10^{-4}
3	PVA (0.05 cm thick)	PPY(50)	3×10^{-5}
8	PVA (0.05 cm thick)	PA(50)	6×10^{-6}
4	Millipore (0.027 cm thick)	PPY(50)	0.15
9	Millipore (0.027 cm thick)	PA(50)	0.02
5	Paper filter (0.032 cm thick)	PPY(50)	0.7
10	Paper filter (0.032 cm thick)	PA(50)	0.03
11	Millipore (0.02 cm thick)	PPY(50)/0.1[a]	0.29
12	Millipore (0.027 cm thick)	PA(50)/0.1[a]	0.1
13	–	PPY-SO_3H(50%)	10.2
14	–	PA-SO_3H(50%)	25.4
15	Sulphonated polystyrene	PPY(60)	1.2
16	Sulphonated polystyrene	PA(60)	0.09
17	Sulphonated polystyrene–DVB	PPY(60)	3.2
18	Sulphonated polystyrene–DVB	PA(60)	0.2

All preparations were carried out at reduced pressure (20 mm Hg).
[a] Preparations at reduced pressure (0.1 mm Hg).

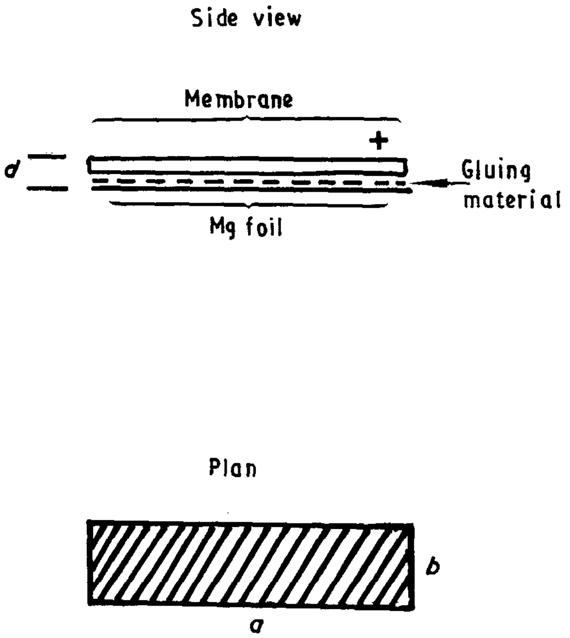

Figure 1 Construction of the cells presented in Table II, weight ~ 0.3 g, $a = 2.5$ cm, $b = 0.9$ cm, $d = 0.04$–0.052 cm.

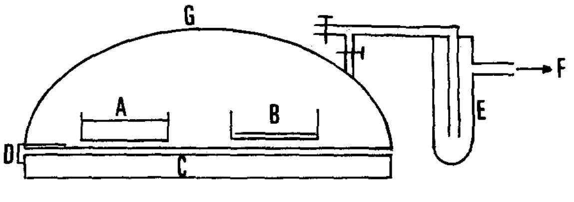

Figure 2 Vacuum reactor for composite membrane preparations. A, pyrrole or aniline solution; B, impregnated matrix; C, heating device; D, thermocouple; E, trap (– 30 °C); F, to vacuum pump; G, glass reactor.

analyser). For the conductivity measurements, a centred square four-probe array of the electrical contacts, made by pressing tungsten wires against the specimen, was employed [18]. The conducting polymers obtained and their properties are summarized in Table I.

2.4. Construction of cells

The composite polymeric membranes were stuck on a magnesium or aluminium foil (Merck 99.9%), using as gluing material a thin film of 10% PVA in 2 M KCl aqueous solution, as shown schematically in Fig. 2. A number of dry cells were obtained just by swelling the polyaniline membrane and the composite pellets with dimethyl sulphoxide (DMSO) and then by overlying on a magnesium foil. The e.m.f. of the batteries was measured by a high input impedance voltmeter (10^{11} Ω). The cells obtained had the shape of a thin film, which would be folded and given a cylindrical or any other shape. The electrical properties of the preparations are summarized in Tables II and III.

3. Results and discussion

As shown in Table I, the development of conductors with desirable shapes and sizes is feasible using inorganic or polymeric porous materials as carriers for the polymerization of aniline and pyrrole monomers. The construction process is easy and safe as polymerization proceeds at low pressure and at room temperature, and may be regulated through the control of pressure and polymerization time.

Magnesium dry cells were the most efficient, yielding the highest e.m.f. values. These findings can be explained by the standard electrode potential of the metals, – 2.34 V and – 1.67 V for magnesium and aluminium, respectively, in aqueous solution against standard hydrogen electrode (SHE) [19].

The electrochemical reaction, which offers the energy, is the cathodic dissolution of the metal M ($M = M^{+x} + x e^{-}$). In other words, the metal works as an energy source. If the cathodic reaction takes place spontaneously, the chemical energy of the metal

TABLE II Dry cells containing PVA/KCl electrolyte and their characteristics

Cell No.	Metal cathode	e.m.f (V)	Discharge time (h)	Conducting polymer anode No.[a]	Efficiency (mWh cm^{-3})
1	Mg	1.6	700	5	8.9
2	Mg	1.4	700	10	6.8
3	Mg	1.9	700	4	12.5
4	Mg	1.4	300	9	2.9
5	Mg	1.55	100	3	1.2
6	Mg	1.5	100	8	1.1
7	Al	1.1	600	9	3.6
8	Al	0.9	600	4	2.4
9	Al	0.5	500	11	0.6
10	Al	0.6	600	12	1.0
11	Al	0.7	500	6	1.2

[a] Taken from Table I.

Foil thickness: Mg, 0.02; Al, 0.04 cm; total cell thickness 0.04–0.072 cm; external load, 2 MΩ; surface area, 2.25 cm^2.

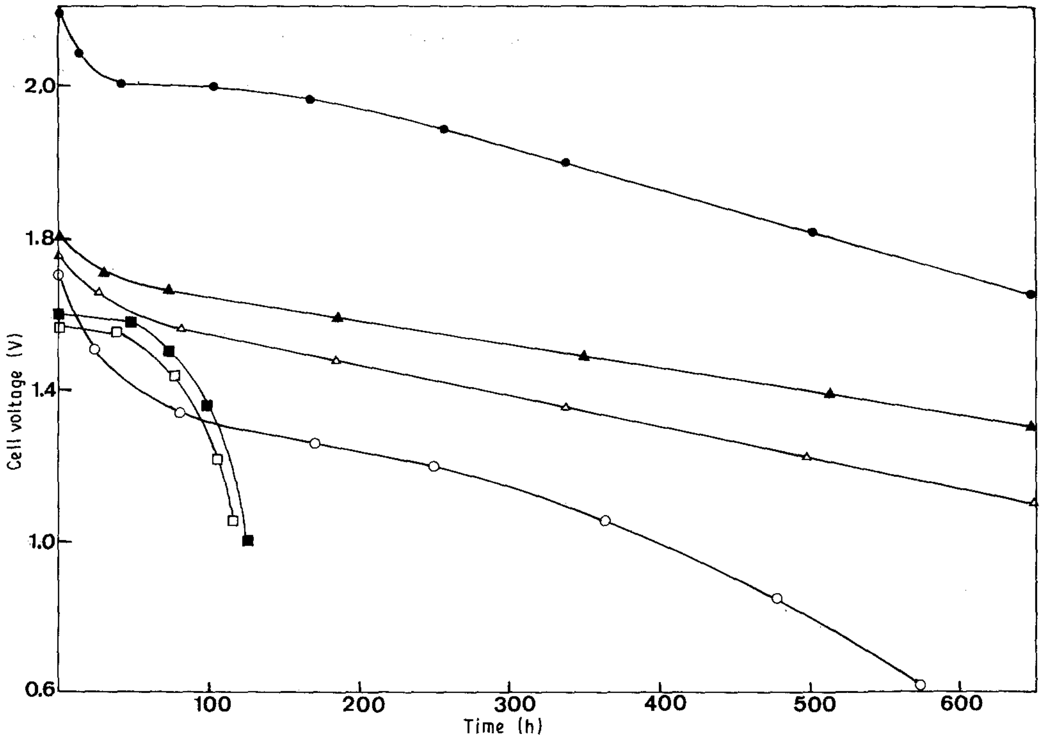

Figure 3 Discharge curves for the Mg/PVA–KCl/composite membrane primary batteries, under a load resistance of 2 MΩ. Cell No.: ▲, 1; △, 2; ●, 3; ○, 4; ■, 5; □, 6.

TABLE III Dry cells without electrolytes and their characteristics

Cell No.	e.m.f (V)	Discharge time (h)	Conducting polymer anode No[a]	Efficiency (mWh cm^{-3})
12	2	700	13	13.8
13	2	250	14	4.9
14	1.95	700	16	13.2
15	1.8	500	15	8.0
16	1.85	700	18	11.8
17	1.9	700	17	12.5
18[b]	1.7	300	11	4.3
19[b]	0.7	200	[c]	0.5

[a] Taken from Table I.

[b] Total cell thickness, 0.05 cm.

[c] Polymer film prepared by drying a PPY (16%) paint on Mg foil.

Mg foil thickness, 0.02 cm; total cell thickness, 0.12 cm; external load, 2 MΩ; surface area, 1.33 cm^2.

converts to thermal rather than electrical energy. This problem can be solved by an appropriate combination of the anode and the presence or absence of an electrolyte. From Table II, it may be concluded that PPY/millipore membrane 4 yielded the Mg cell with the best electrical characteristics (Fig. 3). For Al cells, PA/millipore membrane leads to the construction of the most efficient cell (Fig. 4). The above conclusions are valid when the electrolyte PVA/KCl is used between the anode and the cathode.

In Table III the cells shown were prepared without any electrolyte, but the anode, swollen with DMSO, was stuck on the Mg cathode. Cell No. 18, prepared without any electrolyte, shows higher efficiency and e.m.f. value than cell No. 4, probably due to the absence of any electrolyte or to the preparation of the anode at 0.1 mm Hg. Cells 12 and 14, constructed

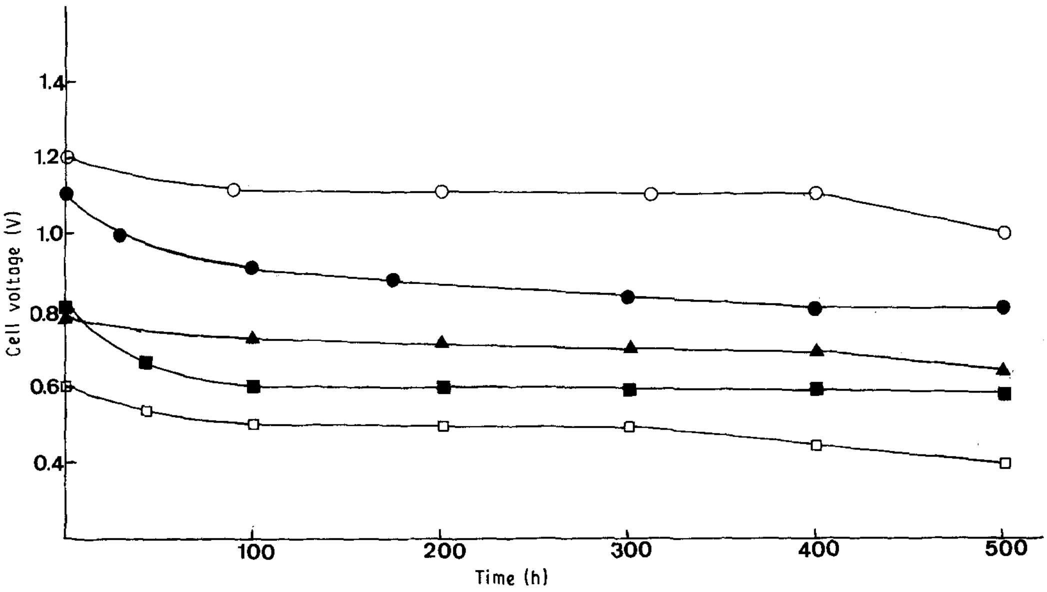

Figure 4 Discharge curves for the Al/PVA–KCl/composite membrane primary batteries, under a load resistance of 2 MΩ. Cell No. ○, 7; ●, 8; ■, 9; □, 10; ▲, 11.

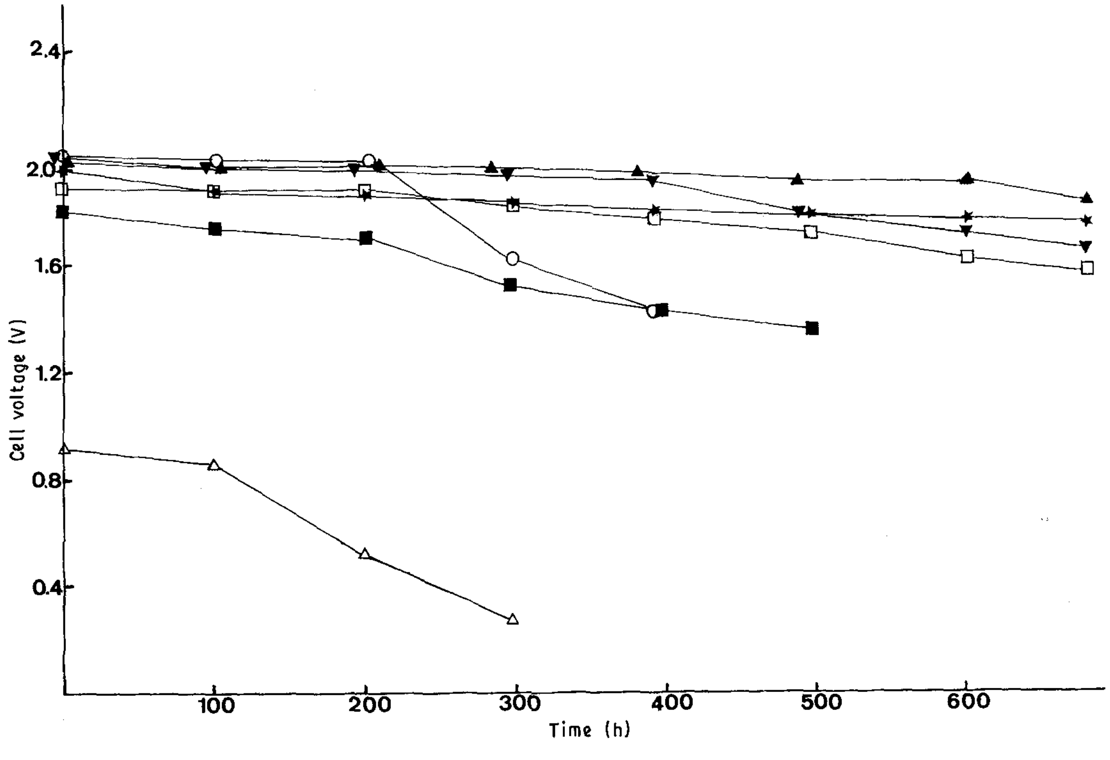

Figure 5 Discharge curves for the Mg/composite conducting polymer primary batteries under a load resistance of 2 MΩ. Cell No. ○, 12; ●, 13; ▲, 14; □, 15; ★, 16; ▼, 17; ■, 18; △, 19.

from PPY 50% sulphonated or from a mixture of PA(60%)/sulphonated polystyrene, showed the highest e.m.f. and efficiency values. The introduction of $-SO_3H$ groups resulted not only in an increase of polyaniline conductivity [13] but also in an increase of the primary battery efficiency. It should be noted that the primary batteries constructed from an anode which contains $-SO_3H$ groups (Table III) gave higher e.m.f. values and the higher efficiencies as compared to those shown in Table II. The discharge behaviour of the cells presented in Table III under a load resistance of 2 MΩ is shown in Fig. 5.

Finally, the efficiency of the cells ranging from 0.5–13.8 mWh cm^{-3} is comparable to other commercial cells [20] constructed from polyaniline as a cathode and Li/Al as an anode (Bridgestone & Seiko, Japan). The energy density of the cell with the best characteristics shown in Table III (cell No. 12) was 2.2 mWh g^{-1}, ten times less than the energy density of the PbO_2–H_2SO_4–Pb multiple charge–discharge system (20 mWh g^{-1} [21]).

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