

Short Communication

Improved conducting polymer cathodes for lithium batteries

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Abstract

This paper reports the preparation and characterization of some complex-ion (ferricyanide and nitroprusside) doped conducting polymers. The physical properties are evaluated by thermogravimetric and scanning electron microscopic techniques. Results show that doped polypyrrole (PPY) polymers are thermally stable up to 550 °C and have a certain degree of crystallinity with a globular (as opposed to a fibrous) structure. The electrical conductivity of the polymers is between 2 and 10 S cm⁻¹. The polymers can be deposited on iron (inner wall of an AA-size cylindrical vessel) for use as the cathode in the cell: Li|LiClO₄ (saturated) in propylene carbonate (PC) PC|PPY–Fe. The cell exhibits good performances in terms of open-circuit voltage, short-circuit current and discharge behaviour, especially when using a ferricyanide-doped polymer. The behaviour is explained in terms of the presence of transition metal ions inside the polymer matrix.

Introduction

Conducting polymers have been found [1–7] to be attractive cathode materials for lithium cells [1–3] and other batteries [4–7]. Among the conducting polymers, polypyrrole (PPY) is most promising [7] because of its thermal stability, resistance to dissolution in different solvents (particularly in mild-acid medium), and good electrical conductivity. Various types of Li/PPY batteries have been reported [2, 7].

In this paper, a report is given of the preparation and performance of Li/PPY batteries where the PPY has been doped with complex ions (ferricyanide and nitroprusside) and deposited on an iron sheet. The motivation comes from the fact that these complex-ion doped polymers are reported to have improved [8–11] physicochemical properties.

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Experimental

Materials

Pyrrole (Merck, Germany), potassium ferricyanide (Aldrich), sodium nitroprusside (Aldrich), lithium perchlorate (Aldrich) and lithium metal (Merck, Germany) were used as supplied. Propylene carbonate (PC) (Korch-Light, UK) was distilled using the procedure described in ref. 12.

Electropolymerization

Electrolytic solutions were prepared by dissolving an appropriate amount (10 g) of potassium ferricyanide or sodium nitroprusside in 100 ml of distilled water. After complete dissolution, 1 ml of pyrrole was added and stirred well to make a homogeneous solution. The solution was poured into an AA-type [13] cylindrical iron vessel that was previously etched with dilute HCl and thoroughly washed with distilled water. This vessel served as the anode for the electropolymerization of pyrrole. The cathode was a platinum wire electrode and a saturated calomel electrode (SCE) was used as the reference electrode to measure the potential of the working electrode. All potentials are reported with respect to the SCE. A current density of 5 mA cm^{-2} was passed for 1 h to deposit PPY smoothly at a potential of $\sim 1.25 \text{ V}$. Finally, the deposited complex-ion doped PPY on the inner side of the iron cylinder was washed with distilled water and dried under a controlled temperature of 80°C for 5 to 6 h. The film was removed by a sharp knife. Thickness (Mitutoyo), conductivity, thermogravimetric analysis (Perkin Elmer) and scanning electron micrographic (Hitachi) studies were carried out on this film. A notable feature was the brittle nature of the film. Film conductivities were in the order of 2 to 10 S cm^{-1} and the thickness was in the range 40 to $50 \text{ }\mu\text{m}$.

Cell fabrication

A lithium rod was used as the anode. This was treated to remove any oxide coatings and was degreased in dried distilled acetone. The electrolyte solution was

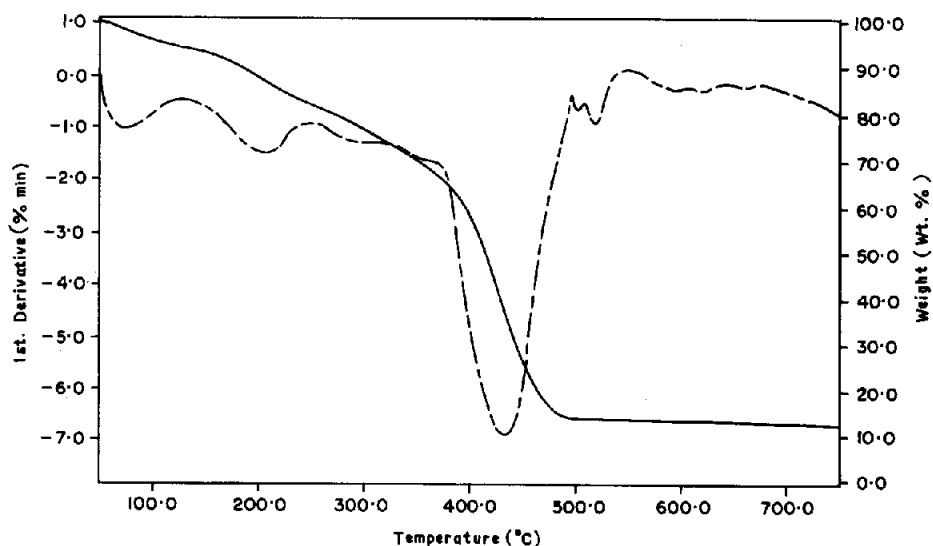


Fig. 1. Thermogravimetric analysis curve for nitroprusside-doped polypyrrole.

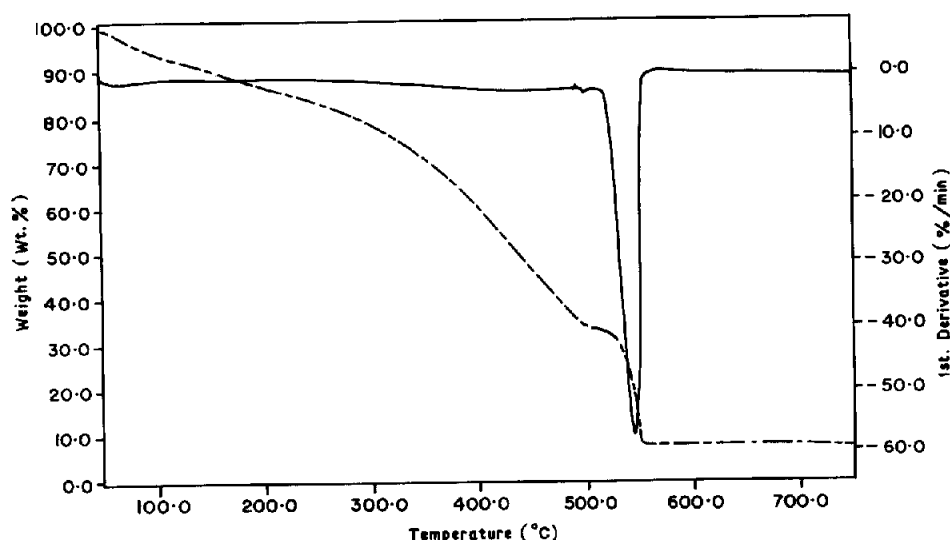


Fig. 2. Thermogravimetric analysis curve for ferricyanide-doped polypyrrole.

TABLE 1

Physicochemical properties of nitroprusside- and ferricyanide-doped polypyrrole (PPY)

Compound	Thermogravimetric analysis		Conductivity (S cm^{-1})	Film thickness (μm)
	%wt loss up to 700 °C	Temp. at sharp decomposition (°C)		
PPY-nitroprusside	88	390	2-8	40-50
PPY-ferricyanide	92	520	4-10	40-50

prepared by dissolving LiClO_4 in PC up to the saturation stage. The lithium rod was wrapped in a cotton separator and placed inside the polymer-coated iron vessel. The latter was charged with electrolytic solution and then sealed. The open-circuit voltage (OCV) and short-circuit current (SCC) were measured with a MIC-6000Z (Taiwan) multimeter.

Results and discussion

Thermogravimetric analysis (TGA) graphs of nitroprusside- and ferricyanide-doped PPY are shown in Figs. 1 and 2, respectively. The important TGA parameters are listed in Table 1.

It is interesting to note that the complex-ion doped PPY exhibited a lower decomposition temperature (below 550 °C) than the ordinary ion-doped PPY (around 600 °C, [14]). Nitroprusside-based PPY decomposes 32% at 390 °C, but above 390 and below 485 °C the decomposition rate sharply decreases.

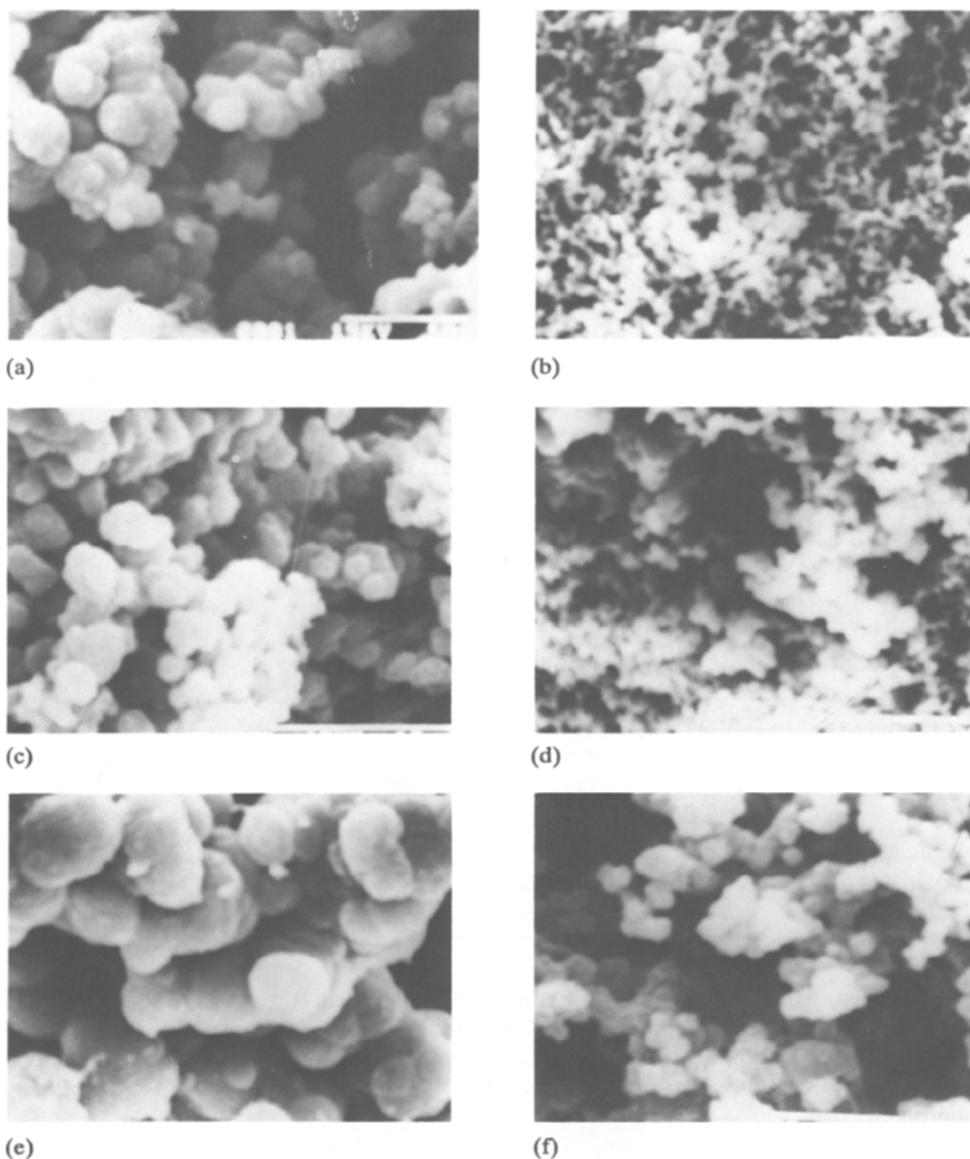


Fig. 3. Electron micrographs of nitroprusside- and ferricyanide-doped polypyrrole: (a, b) $\times 3000$; (c, d) $\times 4000$, and (e, f) $\times 5000$; (a, c, e) nitroprusside-doped and (b, d, f) ferricyanide-doped polypyrrole, respectively.

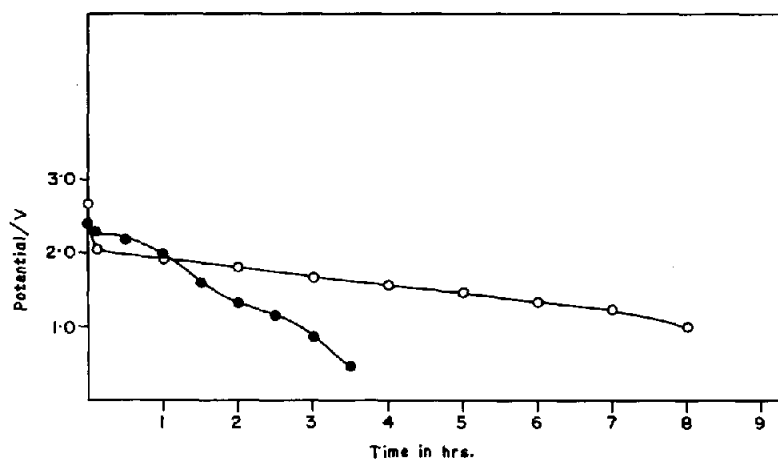
With ferricyanide-based PPY, 70% decomposes at 500 °C. The decomposition rate is slow. Above 520 °C, the decomposition rate is fast and 92% decomposes at above 540 °C.

Scanning electron micrographs, taken at different magnifications, are shown in Fig. 3. Both the polymers have a certain degree of crystallinity with a nonfibrous

TABLE 2

Electrochemical parameters of cells^a comprising a PPY-coated iron cathode and a lithium anode

	Open-circuit voltage (V)	Short-circuit current (mA)	Capacity (mWh)
Cell I	2.43	15	7.5
Cell II	2.69	16	24.5

^aCell I: Li|LiClO₄(saturated)|PPY-nitroprusside-iron, in PC.^aCell II: Li|LiClO₄(saturated)|PPY-ferricyanide-iron, in PC.Fig. 4. Discharge Li|LiClO₄(saturated)|PPY-Fe cell at 2 mA drain; (—●—) nitroprusside-doped polypyrrole, and (—○—) ferricyanide-doped polypyrrole.

structure. Compared with ferricyanide-doped PPY, the nitroprusside-doped counterpart is well arranged with large voids [15].

The OCV and SCC of the lithium cell with ferricyanide-doped PPY are both slightly greater than the values obtained for the corresponding nitroprusside-doped cell (Table 2). The magnitude of each of these parameters is slightly better than that obtained with a simple ion-doped polymer battery.

The cells have been discharged under 2 mA drain, the discharge profiles are presented in Fig. 4. The observed superior performance of the ferricyanide-doped cell is probably due to the fact that ferricyanide may take part in the electronation reaction to form ferrocyanide. A similar reduction is not possible with the nitroprusside ion.

Conclusions

The results of these preliminary investigations suggest that the conducting-polymer doped with complex ions exhibits slightly different physicochemical properties compared with simple ion-doped PPY. The former are better cathode materials for lithium batteries, particularly in the presence of easily reducible complex ions.

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