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Synthesis and characterization of conducting polymer composite (PAN/TiO₂) for cathode material in rechargeable battery

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Abstract

This paper deals with the preparation and characterization of polyaniline/TiO₂ composite by XRD, UV–VIS spectra, TGA/DTA and FTIR. The composite is used as a cathode material for rechargeable battery comprising of zinc container as the anode, cellulose acetate as the separator and polyvinyl sulfate and carboxy methyl cellulose as the solid polymer electrolytes (SPE). By using the PAN/TiO₂ composite as the cathode material, the cylindrical AA type rechargeable battery was fabricated and the following output was observed. The open circuit voltage (OCV) is 1.4 V and current is 250 mA to 1.0 A, 50 recharge cycles, power density is 350 A h/kg and power efficiency is 70%.

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1. Introduction

Conducting polymers are generally wide band gap semiconducting materials, which can be chemically doped, with resulting electronic properties ranging from insulating to near metallic [1]. Some of the polymers which have this exciting property are being developed for use in commercial and novel electrochemical applications such as battery materials, electro-optic devices, electrode coating and sensors. One of the most important energy storage applications of conducting polymers is their use as cathode material for rechargeable battery in view of associated reversible doping [2]. Polymer batteries play a crucial role in research towards developing new high energy

density batteries due to their certain unique properties such as easy thin film formation, processability, light weight, elasticity, etc. Solid state polymer batteries have proven to be feasible alternatives to the classical secondary battery systems.

Polyaniline is one of the most promising materials for electrochemical charge storage devices such as light weight batteries [3] and supercapacitors [4] essentially due to following properties.

- It is stable in air and has high conductivity under ambient conditions.
- It has very high energy density output under acidic condition because of continued protonation, thus it is always under charged condition.

In extensive studies, de Surville et al. [5] have shown that unspecified forms of polyaniline could be

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used both as the cathode and anode in a rechargeable battery in 6N aqueous H_2SO_4 . Kitani et al. [6] have described the use of polyaniline as a cathode material in rechargeable batteries in an aqueous ZnCl_2 or ZnSO_4 electrolyte in conjunction with a Zn anode. Tsutsumi et al. [7] reported that PANi-PSS composite can be used as a positive active material for a rechargeable lithium battery. Polyaniline is used as a cathode material in rechargeable batteries in aqueous electrolytes [8]. Li et al. [9] demonstrated that polyaniline and Nafion composite can be used as a rechargeable battery material. Polyaniline is also used as an electrode material for magnesium reserve battery [10]. Killian et al. [11] have used polypyrrole composite electrodes used in an all polymer battery systems. In our recent review, we have described the usage of electrochemically synthesized conducting polymeric materials used in electronics, optoelectronics and energy storage devices like rechargeable batteries and capacitors [12]. We have reported [13] that 80.6% of colloidal TiO_2 was incorporated in polyaniline matrix and the composite PAN/ TiO_2 has the thermal stability up to 265 °C. Polyaniline, when used as cathode material, has less rechargeable cycles in polymer battery [3]. In order to increase the recharge cycles, it should be in the form of composite with transparent conducting oxides (TCO). By attaining optimum level of incorporation of TCO in polyaniline matrix, the best cathode material for rechargeable battery has been obtained.

For the present study, various amounts of TiO_2 are incorporated in polyaniline matrix to form PAN/ TiO_2 composite by oxidative polymerization. The resulting composites are characterized by physicochemical techniques and the electrochemical properties of the material are determined. By using these composites as the cathode material, the cylindrical (AA) type rechargeable battery is also fabricated. The purpose of this paper is to furnish preliminary account of our research on use of polyaniline/ TiO_2 composite as a suitable cathode material for battery application.

2. Experimental

All chemicals used were of AnalaR grade. Aniline was used after double distillation. TiCl_4 was purchased from Johnson Matthey Chemicals, England.

The chemical oxidative polymerization of various amounts of TiO_2 incorporated in polyaniline matrix was carried out in H_2SO_4 medium at pH 2 and using 0.5 M ammonium persulfate (drop by drop addition) as an oxidising agent. The stirring of the reaction mixture was continued for 2 h to ensure the completion of the reaction which was indicated by stabilisation of temperature of the reaction mixture. The reaction mixture was filtered and washed repeatedly with distilled water and finally equilibrated in H_2SO_4 for 2 h to achieve uniform doping. The resulting polymer composite was dried under vacuum at 50 °C for 24 h. The ratios of dispersed TiO_2 to aniline were 0:7, 1:6, 1:3, 1:2, 1:1.5 and 1:1.4. However, the ratio 1:6 exhibits maximum yield and shows higher conductivity of the resulting composite.

2.1. Characterization of the sample

The TiO_2 -incorporated polyaniline was characterised by UV–VIS absorption spectroscopy using Hitachi U 3400 UV–VIS–NIR spectrophotometer. Diffuse spectra have been recorded using an integrating sphere and BaSO_4 as a white standard. The spectra were recorded as $R_{\text{stand}}/R_{\text{sample}}$ vs. the wavelength, R being the absolute reflection intensity. X-ray diffraction patterns were recorded with a computer-controlled X-ray diffractometer (Model JEOL JDX 30) using $\text{CuK } \alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Thermal analysis of

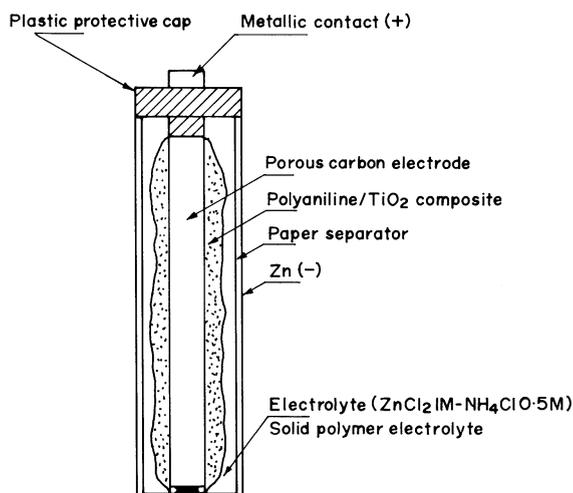


Fig. 1. Battery cell fabrication by using PAN/ TiO_2 composite as the cathode material.

polyaniline and TiO₂-incorporated polyaniline was carried out by using the thermal analyser (STA 1500, PL Thermal Sciences) in dynamic nitrogen atmosphere. Infrared spectroscopic analysis was carried out by Fourier transform infrared spectrometer (FTIR, Perkin-Elmer, Model SPECTRUM 2000, USA) by making the pellet of samples in KBr medium.

2.2. Fabrication of battery

The fabrication of dry cell using PAN/TiO₂ composite is quite easy by replacing MnO₂ in a dry cell by chemically synthesized PAN/TiO₂ composite and solid polymer electrolytes (SPE).

The configuration of the battery is

Zn/Electrolyte/PAn–TiO ₂ composite	
Electrolyte	1 M ZnCl ₂ –0.5 M NH ₄ Cl and SPE
SPE	Carboxy methyl cellulose and polyvinyl sulfate (1:1 ratio)
Composite	PAn/TiO ₂

This battery uses SPE composed of carboxy methyl cellulose and polyvinyl sulfate with a cellulose sheet as a separator.

Five grams of PAN/TiO₂ composite, acetylene black and electrolyte were grounded to fine powder

and loaded in a zinc container which is coated inside with cellulose paper as a separator. The cellulose paper is soaked in PVA solution. The mixture of PAN/TiO₂ and electrolyte was thickly loaded and graphite (porous carbon rod) was inserted in the zinc container to establish contact with PAN/TiO₂ composite and electrolyte and subsequently sealed with epoxy resin. The cell fabrication is shown in Fig. 1.

3. Results and discussion

3.1. Characterization

The diffuse reflectance spectra of polyaniline, TiO₂, PAN/TiO₂ composite containing various amounts of TiO₂ and deprotonated polyaniline powders prepared in sulfosalicylic acid (SSA) medium are shown in Fig. 2. The dark green-coloured powder of polyaniline exhibits peaks at 440 and 650 nm, whereas electronic spectra PAN/TiO₂ composites exhibited bands at 440 and 640–710 nm presumably due to the formation of new composite.

X-ray diffractograms of pure polyaniline, PAN/TiO₂ composites and deprotonated polyaniline are presented in Fig. 3. From the analysis of resultant XRD data, it is inferred that experimentally observed lattice parameters of polyaniline, TiO₂ and deprotonated polyaniline are in good agreement with the

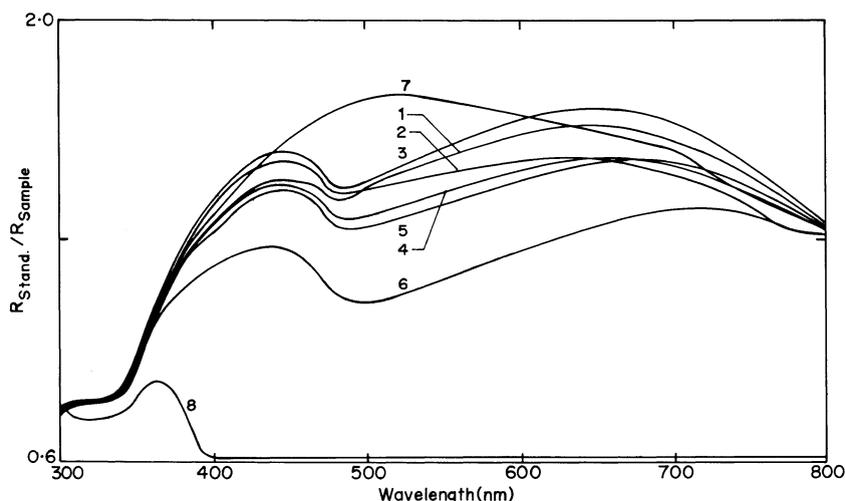


Fig. 2. Diffuse reflectance spectra of (1) polyaniline (PAN)/SSA, (2) PAN/TiO₂ (1:6), (3) PAN/TiO₂ (1:3), (4) PAN/TiO₂ (1:2), (5) PAN/TiO₂ (1:1.5), (6) undoped PAN, (7) TiO₂.

value of 48° in addition to 'd' spacings of TiO_2 and polyaniline.

Typical thermogram (TG) curves of TiO_2 powder, polyaniline and PAn/TiO_2 composite are shown in Fig. 4. From these figures, it is evident that the dehydration of the material occurs from 80 to 100°C , and thereafter exists a plateau up to 245°C . A mass loss of 28% occurred between 245 and 305°C with an exothermic peak probably due to the expulsion of the dopant. From 305°C , the decomposition of polyaniline starts.

The main FTIR characteristic bands observed in KBr medium of polyaniline, TiO_2 , deprotonated polyaniline and PAn/TiO_2 composite are shown in Fig. 5. The bands at 2343 cm^{-1} is assigned to O–H stretching, 1581 cm^{-1} to nitrogen benzenoid–quinoid, 1474 cm^{-1} to N–H stretching, 1124 cm^{-1} to C–H band, 1022 cm^{-1} to SO_3^- , 803 cm^{-1} to C–H out of plane and 667 cm^{-1} for Ti–O stretching.

3.2. Conductivity studies

The pellets of polyaniline, $\text{PAn/acetylene black}$, PAn/TiO_2 composite and PAn/TiO_2 composite/acetylene black were prepared and four probe conductivity was measured. The values of the conductivity are presented in Table 1. In order to improve current

Table 1

Four probe conductivity of polyaniline and PAn/TiO_2 composite

Sample	Conductivity (S/cm^2)
Polyaniline (PAn)	0.10
$\text{PAn/acetylene mixture}$	10.00
PAn/TiO_2 composite	0.04
PAn/TiO_2 composite/acetylene black	4.00

carrying capacity of a composite, acetylene black was added.

3.3. Studies on battery application

A conducting polymer battery system having a configuration of a dry cell (Leclanche type) which can be discharged with a cyclability of >50 cycles would be the preferred choice. The redox properties of conducting polymers have been utilized in charge storage devices such as super capacitors and batteries.

The Leclanche cell is irreversible and therefore is not capable of recharging. The emf of above system is above 1.6 V, but the cathode potential is a function of pH. This value falls rapidly on continuous discharge, whereas in secondary cells, such as lead accumulators (lead acid battery), electrode processes are reversible and the cell is based upon pre-electrolysis of an

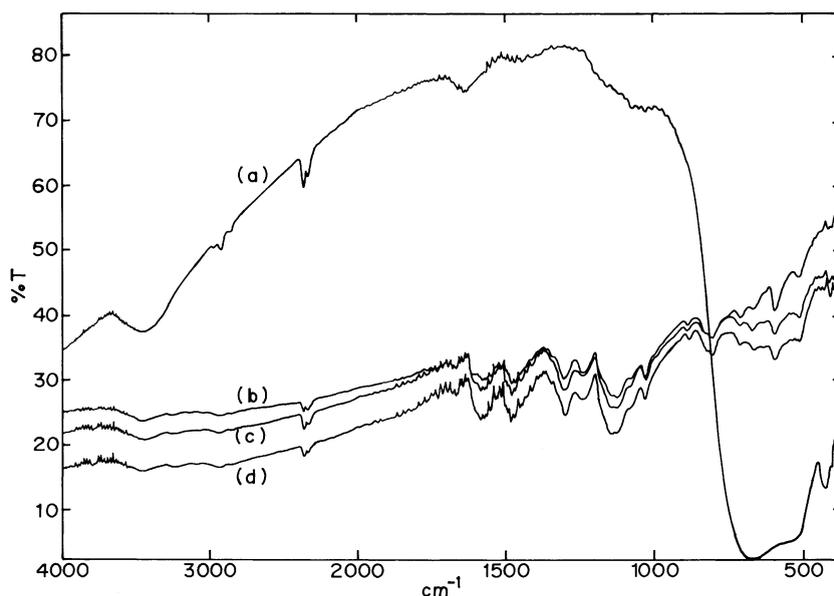


Fig. 5. FTIR spectra of (a) TiO_2 , (b) polyaniline, (c) PAn/TiO_2 , (d) PAn/TiO_2 .

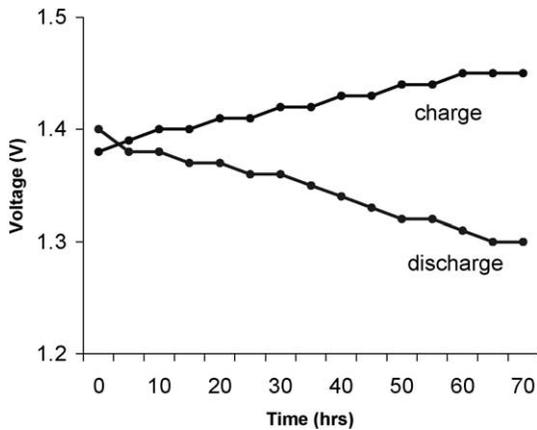


Fig. 6. Charge–discharge characteristics of PAN/TiO₂ composite at constant current.

aqueous solution of H₂SO₄ saturated with lead sulfate between lead electrodes.

3.4. Advantages of conducting polymer composite battery

Assembly of PAN/TiO₂-based dry cell battery is advantageous over the above-mentioned batteries (Leclanche) on the following market grounds:

- rechargeable at at least 50 cycles
- 25% less weight
- low production cost.

I–*V* characteristics (cyclic voltammetry) of TiO₂, polyaniline and polyaniline/TiO₂ composite are re-

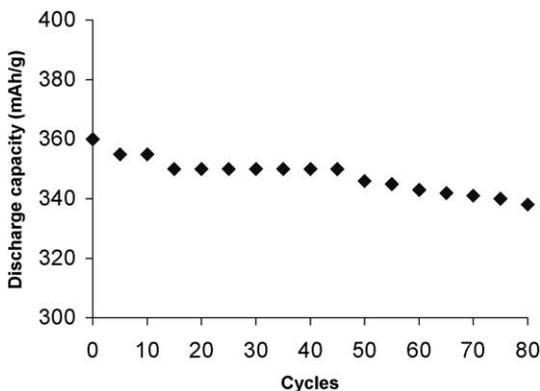


Fig. 7. Capacity as a function of cycles.

Table 2
Electrochemical parameter for battery application

Parameter	Value	
	Polyaniline	PAN/TiO ₂ composite
Open circuit voltage	1.4 V	1.4 V
Short circuit current	250 mA–1.0 A	250–500 mA
Operating voltage	0.8–1.4 V	0.7–1.4 V
Number of recharge cycles	30	50
Power density	350 h/kg	350 h/kg
Power efficiency	70%	70%

ported by us [13]. The charge–discharge characteristics of polyaniline/TiO₂ composite as a cathode material assembled in zinc container as the anode at constant current of 8 mA is presented in Fig. 6. Fig. 7 presents the discharge capacity as a function of cycles. From Fig. 7, we inferred that up to 50 cycles, there is no capacity fading, and after that, there is a capacity fading. This may be due to the conducting polymer decomposition while charging

Table 3
Brief product specifications for the conducting polymer composite rechargeable battery

Parameter	Value
Type	AA cylindrical and button types
Cell case	zinc container
Case thickness	0.5 mm
Diameter	10 mm
Internal lines	PVA soaked cellulose acetate paper
Terminal seal	Cu cap
Terminals	Cu cap and zinc plate
Cathode (+)ive electrode	PAN/TiO ₂ powder with acetylene black and graphite rod as current collector. Graphite rod soaked in carboxy methyl cellulose (CMC).
Loading level	0.5 g
Negative electrode	zinc container
Separator	PVA or CMC soaked cellulose acetate paper
Electrolyte	1 M ZnCl ₂ and 0.5 M NH ₄ Cl and SPE (PVS or PVA and CMC)
Stack configuration	AA type
Stack to wall gap	0.2 mm
End plates	flattened
Central core	cylindrical
Electrode configuration	cylindrical sealed with PVC sheet and epoxy
Operating pressure	100–500 psi
Operating temperature	10–50 °C

and discharging. The various electrochemical parameters are presented in Table 2. From Table 2, we inferred that the recharge cycles are increased in PAn/TiO₂ composite as a cathode material than the polyaniline. This can be attributed to the fact that transparent conducting oxide TiO₂ has a multiple role in charge–discharge reactions, which also acts as an oxidising agent. The brief product specifications are presented in Table 3.

4. Conclusion

From the above study, it is inferred that the conducting polymer composite has better charge–discharge characteristics up to 50 cycles than conducting polymer alone and has better cyclability. Further research on battery work on the above composite is on progress.

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