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# Synthesis and characterization of conducting polymer composite (PAN/TiO<sub>2</sub>) for cathode material in rechargeable battery

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## Abstract

This paper deals with the preparation and characterization of polyaniline/TiO<sub>2</sub> 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/TiO<sub>2</sub> 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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*Keywords:* Conducting polyaniline; TiO<sub>2</sub>; Composite; Solid polymer electrolyte battery

## 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  $\text{H}_2\text{SO}_4$ . Kitani et al. [6] have described the use of polyaniline as a cathode material in rechargeable batteries in an aqueous  $\text{ZnCl}_2$  or  $\text{ZnSO}_4$  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  $\text{TiO}_2$  was incorporated in polyaniline matrix and the composite PAN/ $\text{TiO}_2$  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  $\text{TiO}_2$  are incorporated in polyaniline matrix to form PAN/ $\text{TiO}_2$  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/ $\text{TiO}_2$  composite as a suitable cathode material for battery application.

## 2. Experimental

All chemicals used were of AnalaR grade. Aniline was used after double distillation.  $\text{TiCl}_4$  was purchased from Johnson Matthey Chemicals, England.

The chemical oxidative polymerization of various amounts of  $\text{TiO}_2$  incorporated in polyaniline matrix was carried out in  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  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  $\text{TiO}_2$  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  $\text{TiO}_2$ -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  $\text{BaSO}_4$  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

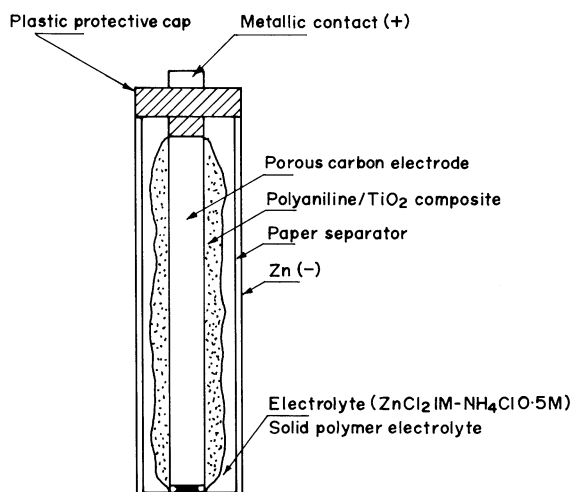


Fig. 1. Battery cell fabrication by using PAN/ $\text{TiO}_2$  composite as the cathode material.

polyaniline and TiO<sub>2</sub>-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/TiO<sub>2</sub> composite is quite easy by replacing MnO<sub>2</sub> in a dry cell by chemically synthesized PAN/TiO<sub>2</sub> composite and solid polymer electrolytes (SPE).

The configuration of the battery is

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

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

Five grams of PAN/TiO<sub>2</sub> 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/TiO<sub>2</sub> and electrolyte was thickly loaded and graphite (porous carbon rod) was inserted in the zinc container to establish contact with PAN/TiO<sub>2</sub> 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, TiO<sub>2</sub>, PAN/TiO<sub>2</sub> composite containing various amounts of TiO<sub>2</sub> 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/TiO<sub>2</sub> composites exhibited bands at 440 and 640–710 nm presumably due to the formation of new composite.

X-ray diffractograms of pure polyaniline, PAN/TiO<sub>2</sub> 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, TiO<sub>2</sub> and deprotonated polyaniline are in good agreement with the

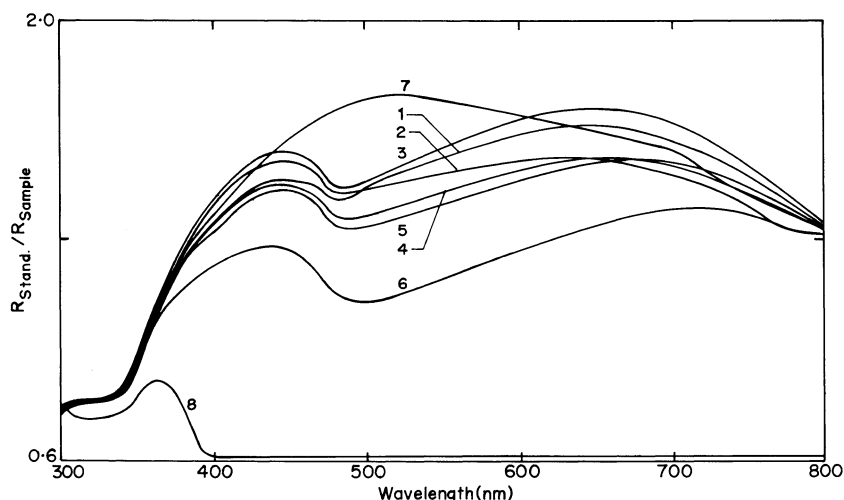


Fig. 2. Diffuse reflectance spectra of (1) polyaniline (PAN)/SSA, (2) PAN/TiO<sub>2</sub> (1:6), (3) PAN/TiO<sub>2</sub> (1:3), (4) PAN/TiO<sub>2</sub> (1:2), (5) PAN/TiO<sub>2</sub> (1:1.5), (6) undoped PAN, (7) TiO<sub>2</sub>.

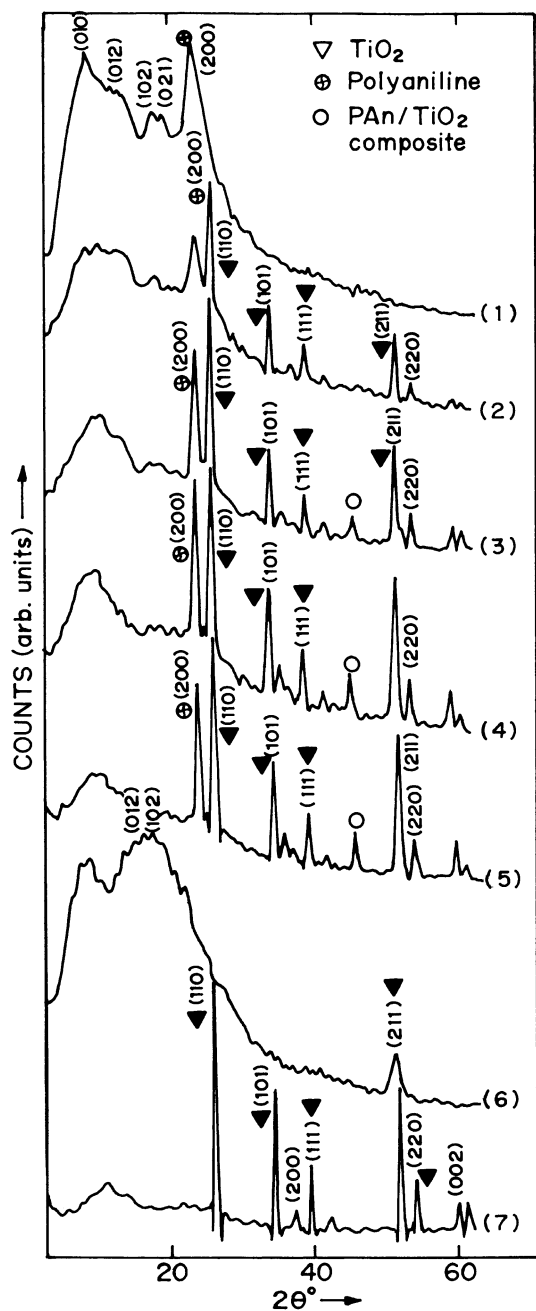


Fig. 3. XRD pattern of (1) polyaniline, (2) PAN/TiO<sub>2</sub> (1:6), (3) PAN/TiO<sub>2</sub> (1:3), (4) PAN/TiO<sub>2</sub> (1:2), (5) PAN/TiO<sub>2</sub> (1:1.5), (6) PAN/TiO<sub>2</sub> (1:1.4), (7) undoped polyaniline (E.B), (8) TiO<sub>2</sub>.

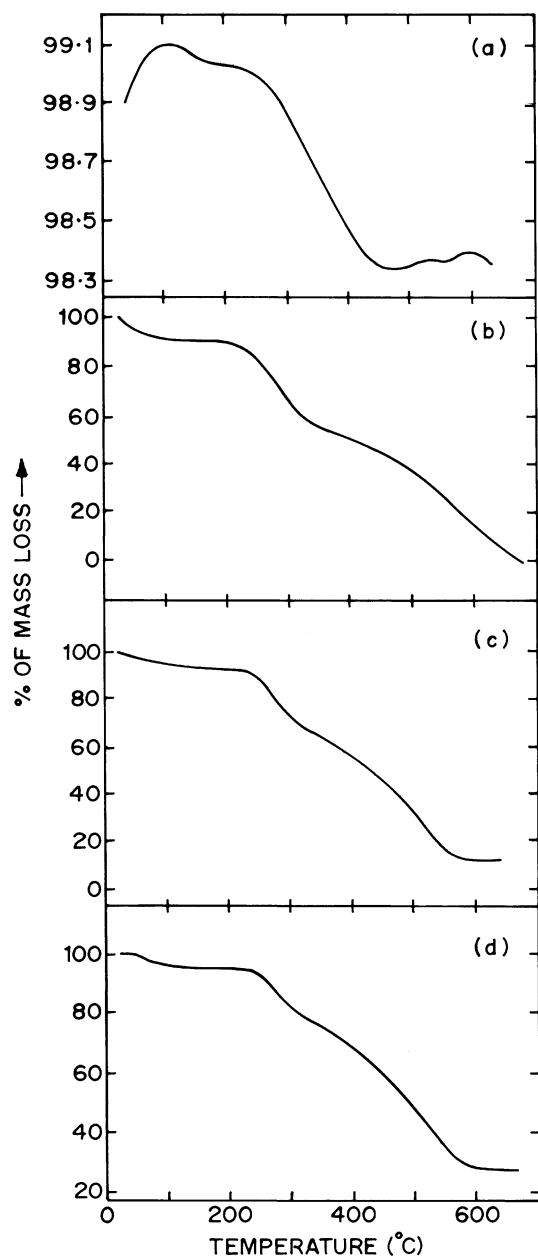


Fig. 4. TGA of (a) TiO<sub>2</sub>, (b) PAN/SSA, (c) PAN/TiO<sub>2</sub> (1:6), (d) PAN/TiO<sub>2</sub> (1:3).

reported values. The XRD patterns reveal the occurrence of orthorhombic structure in pure polyaniline and that of tetragonal in TiO<sub>2</sub>. From the XRD patterns of PAN/TiO<sub>2</sub>, a new reflection is observed at a  $2\theta$

value of  $48^\circ$  in addition to 'd' spacings of  $\text{TiO}_2$  and polyaniline.

Typical thermogram (TG) curves of  $\text{TiO}_2$  powder, polyaniline and  $\text{PAn/TiO}_2$  composite are shown in Fig. 4. From these figures, it is evident that the dehydration of the material occurs from  $80$  to  $100^\circ\text{C}$ , and thereafter exists a plateau up to  $245^\circ\text{C}$ . A mass loss of 28% occurred between  $245$  and  $305^\circ\text{C}$  with an exothermic peak probably due to the expulsion of the dopant. From  $305^\circ\text{C}$ , the decomposition of polyaniline starts.

The main FTIR characteristic bands observed in KBr medium of polyaniline,  $\text{TiO}_2$ , deprotonated polyaniline and  $\text{PAn/TiO}_2$  composite are shown in Fig. 5. The bands at  $2343\text{ cm}^{-1}$  is assigned to O–H stretching,  $1581\text{ cm}^{-1}$  to nitrogen benzenoid–quinoid,  $1474\text{ cm}^{-1}$  to N–H stretching,  $1124\text{ cm}^{-1}$  to C–H band,  $1022\text{ cm}^{-1}$  to  $\text{SO}_3^-$ ,  $803\text{ cm}^{-1}$  to C–H out of plane and  $667\text{ cm}^{-1}$  for Ti–O stretching.

### 3.2. Conductivity studies

The pellets of polyaniline,  $\text{PAn/acetylene black}$ ,  $\text{PAn/TiO}_2$  composite and  $\text{PAn/TiO}_2$  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  $\text{PAn/TiO}_2$  composite

Sample	Conductivity ( $\text{S/cm}^2$ )
Polyaniline (PAn)	0.10
$\text{PAn/acetylene mixture}$	10.00
$\text{PAn/TiO}_2$ composite	0.04
$\text{PAn/TiO}_2$ 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

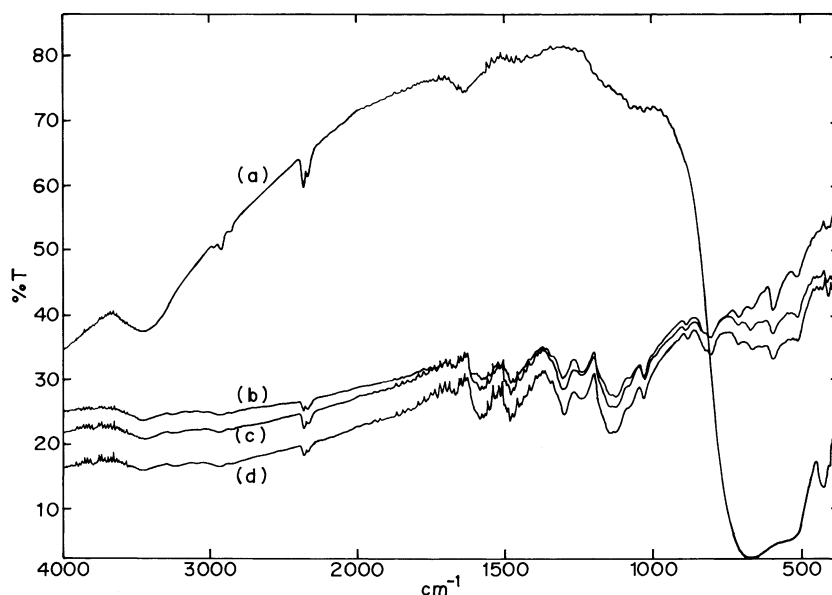


Fig. 5. FTIR spectra of (a)  $\text{TiO}_2$ , (b) polyaniline, (c)  $\text{PAn/TiO}_2$ , (d)  $\text{PAn/TiO}_2$ .

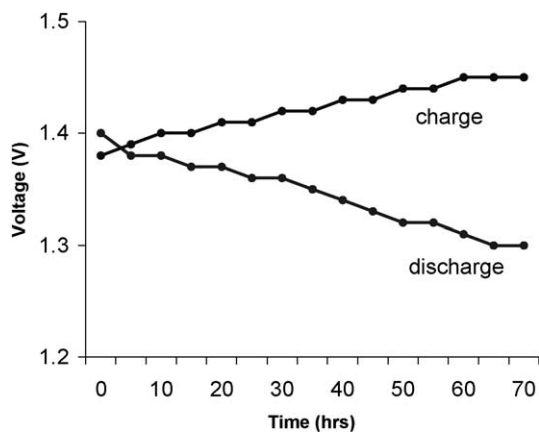


Fig. 6. Charge–discharge characteristics of PAN/TiO<sub>2</sub> composite at constant current.

aqueous solution of H<sub>2</sub>SO<sub>4</sub> saturated with lead sulfate between lead electrodes.

#### 3.4. Advantages of conducting polymer composite battery

Assembly of PAN/TiO<sub>2</sub>-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 TiO<sub>2</sub>, polyaniline and polyaniline/TiO<sub>2</sub> composite are re-

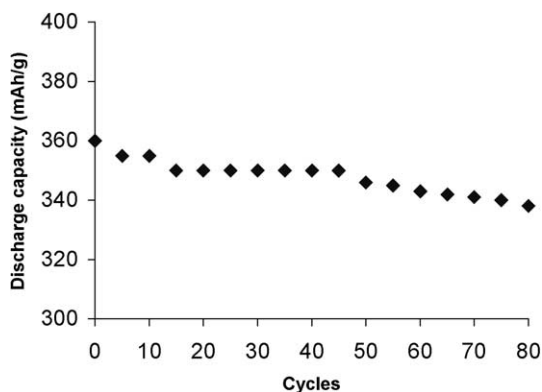


Fig. 7. Capacity as a function of cycles.

Table 2  
Electrochemical parameter for battery application

Parameter	Value	
	Polyaniline	PAN/TiO <sub>2</sub> 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/TiO<sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> and 0.5 M NH <sub>4</sub> 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/TiO<sub>2</sub> composite as a cathode material than the polyaniline. This can be attributed to the fact that transparent conducting oxide TiO<sub>2</sub> 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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