ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

REVIEW ON POLYANILINE:TIO2 NANOCOMPOSITE FOR ENERGY STORAGE APPLICATION

K. S. Patil, P. H. Zope
SSBT's COET, Bambhori Jalgaon, India
North Maharashtra University

ABSTRACT

Conducting polymers has widely been explored in energy storage application since long time. Many attractive properties which make conducting polymers a very suitable material for the use of energy storage devices consist of its high conductivity, electroactivity, doping levels, excellent environmental stability and specific capacitance. Numerous techniques have been developed for synthesis and characterization of nanocomposite materials to improve the specific capacitance (248-897.35F/g), current density (0.21-20A/g), energy density (10-181.3 Wh/kg) and power density(300-6000 W/kg)with different scan rate(2-100 mV/s) for energy storage devices. In this review, our aim is to compare different types of Polyaniline, nano-TiO2 composite for electrode materials used in supercapacitors application.

KEYWORDS: Conducting polymer; TiO2; Transition Metal Oxides; Supercapacitor.

INTRODUCTION

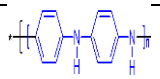
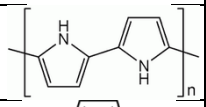
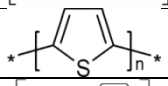
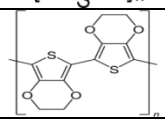
Energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor, also known as ultracapacitors or electrochemical supercapacitor (ES), has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. They are attracting much attention because of their high power density (2-5 kW kg^{-1}), fast charge discharge properties, long life cycle, and their ability to function as a bridge for the power/energy gap between traditional dielectric capacitors and batteries/fuel cells[1-10]. They utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors [1-5]. Supercapacitors can be divided into three general classes: electrochemical double-layer capacitors (EDLC), pseudocapacitors, and hybrid capacitors. Each class is characterized by its unique mechanism for storing charge. In EDLCs, the energy is stored electrostatically at the electrode–electrolyte interface in the double layer, while in pseudocapacitors charge storage occurs via fast redox reactions on the electrode surface. In contrast to EDLCs, which store charge electrostatically, pseudocapacitors store charge Faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes [1, 11-12]. These Faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs [13-15]. The electrode material is one of the most important components that improve capacitance and their operational parameters, particularly voltage range and power rating [16-19]. This review is focused toward the typical electrode active materials based on pseudocapacitor are transition metal oxides and electrically conducting polymers.

CONDUCTING POLYMER

Conducting polymers are promising materials in supercapacitors, rechargeable batteries, chemical sensors, biosensors, actuators, electroluminescent devices, polymer-based electronics, and organic photovoltaic cells. To exploit nanostructural effects in these devices, researchers have developed several methods for fabricating conducting polymers as thin films, nanospheres, nanowires, nanotubes, and core-shell structures. Conducting polymers can offer relatively cost-effective alternative to the conventional electrode materials as a result of their high capacitance, high conductivity, low equivalent series resistance (ESR), fast doping/dedoping capabilities, excellent electrochemical reversibility's in a doped state [20,21]. The conductivity of conducting polymer was first reported in 1963 by McNeill and co-workers [23]. They exhibit the pseudocapacitive and conductive behavior via

electron delocalization in conjugated chemical bond system along the polymer backbone. Among various conducting polymers, polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly (3, 4-ethylenedioxythiophene) (PEDOT) and poly(styrene sulfonate) (PSS) are most commonly studied for supercapacitors. The experimental specific capacitance values of PANI, PPy, PTh and PEDOT are compared in table 1 [21].

Table 1 Experimental capacitance values

Conductive polymers	Structure	Method for doping	Mw (g mol-1)	Dopant level	Potential range (V)	Theoretical capacitance (F/g)	Conductivity (S/cm)
PANI		HCL,DBSA	93	0.5	0.7	750	0.1-5
Ppy		BF_4^-,ClO_4^-	67	0.33	0.8	620	10-50
PTh		BF_4^-,ClO_4^-	84	0.33	0.8	485	300-400
PEDOT		PSS	142	0.33	1.2	210	300-500

From the table-1 the polyaniline is a particularly interesting conducting polymer because it has good stability in air and in water, high conductivity in its oxidized/protonated form, acid-base properties, electrochromic behavior, and electrochemical capacitance [25]. Polyaniline has been used in sensors and biosensors [26-29], solar cells [30], batteries [31], electrochromic devices [32] and antistatic coatings [33]. Because of its high specific capacitance, [34] polyaniline is also one of the most promising materials for electrochemical supercapacitors [35-36].
Electrical conductivity of polyaniline is a very important parameter and it could be modified by the addition of inorganic fillers [17]. Additionally, electrical conductivity of polyaniline depends on dopant ions. The properties of conducting polymers can be modified by the addition of transition metal oxides. Recently, considerable efforts have been placed by researchers to develop all kinds of nanocomposite capacitive materials, such as mixed metal oxides, conducting polymers mixed with metal oxides, carbon nanotubes mixed with conducting polymers, or metal oxides, and graphene mixed with metal oxides or conducting polymers. It is necessary to compare and study the effect of different type of transition metal oxide when mixed with conducting polymer for the fabrication and synthesis of electrode materials for supercapacitor.

NANOCOMPOSITE

The nanocomposite materials are those that combine two or more individual components in order to improve performance properties in which at least one dimension of the dispersed particles of a component is in the nanometer range. Use of conducting polymers to form conducting nanocomposites has successfully been achieved and has been an area of interest for the past few years. One of the most promising nanocomposites system would be the hybrids based on organic Pani and nanoparticles like TiO2, CNT and GR. These nanostructured particles combined with Pani can give rise a polymer nanocomposite with interesting physical properties and thus potential materials for newer and novel applications. The resulting nanocomposites can be produced in the form of nanofibres, nanorods, thin films etc. As a result, a large number of publications on research and development of nanocomposites came out within a short span of time. The review is focused toward different structures of PANI:TiO2 nanocomposite electrode in supercapacitor application.

POLYANILINE/NANO-TIO2 COMPOSITE AS AN ELECTRODE MATERIAL

Most of the polymers reported in literature are insulators, but after the synthesis they exhibit semiconducting behavior. Polymers possess unique optical, electronic and mechanical properties and they have broad spectrum of application. Besides other conducting polymers, polyaniline (PANI) has been extensively studied due to its non-redox doping, good environmental and thermal stability, high conductivity and economic feasibility. In particular, the PANI filled with materials like magnetic particles (e.g. Fe_2O_3, Fe_3O_4, $BaFe_{12}O_{19}$ etc.) or dielectric particles (e.g.

$BaTiO_3$, TiO_2, $SrTiO_3$ etc.) or carbonaceous fillers (carbon black, graphite, carbon nanotubes, graphene etc.) display combination of dielectric/magnetic and electrical properties. Researchers shown that the conductivity of PANI changes significantly upon adding TiO_2. Subsequently, efforts have been made to improve the conducting properties of these materials. In composite form, the properties of PANI change significantly. Till now, a number of studies on composites of PANI/TiO_2 have been reported in table 2 and majority of the researchers are still focusing on their synthesis and characterization.

Table 2: comparison of Pani/Nanocomposites

Composite	specific capacitance (F/g)	Current Density (A/g)	energy density (Wh/kg)	power density (W/kg)	scan rate (mV/s)	Method	Reference
TiO2 coated MWCNTs /PANI	443.57	--	6.2-120.75	621-3152	2	chemical reduction	Reddy*et al.[48]*
TiO2 coated MWCNTs/ PANI/ graphene	666.3	--	10-181.3	932-5142.85	2	chemical reduction	Reddy*et al.[48]*
polyaniline/nano-TiO2	330	1.5	--	--	--	one-step in situ oxidation	C.Bianet al [49]
PANI-f-HEG	355	10	--	--	10-100	hydrogen-exfoliated graphene	A. K. Mishra and S. Ramaph-rabu [50]
A-MWCNT/PANI	248	0.5	--	--	--	ultrasonic polymerization	Li et al[52]
PANI-TiO2/Ti	732-543	1-20	27.2-36.6	300-6000	100	Anodization	Xie et al.[53]
PANI and TiO2@PANI core-shell	732	--	10	--	20	Hydrothermal and chemical polymerization	Li et al[54]
PANI/TiO2/Ti	897.35	0.21	--	--	20	Anodization, Electrodeposition	Z. Shao et al.[55]

Reddy *et al*. specific capacitance obtained for the TiO2 coated MWCNTs/PANI nanocomposite was 443.57 F/g at 2 mV/s scan rate by chemical reduction method. Upon addition of graphene nanosheet to the TiO2 coated MWCNTs in a weight ratio of (9:1) the specific capacitance value increased to 666.3 F/g at the same scan rate, also resulting in an increase in energy density and power density [48].

C. Bian *et al.* studied the Fibriform polyaniline/nano-TiO2 composite is prepared by one-step in situ oxidation polymerization of aniline in the presence of nano-TiO2 particles, which contains 80% conducting polyaniline by mass, with a conductivity of 2.45S/cm at 25°C. Its maximum specific capacitance is 330F/g at a constant current density of 1.5A/g, and can be subjected to charge/discharge over 10,000 cycles in the voltage range of 0.05–0.55V [49].

Further, A. K. Mishra and S. Ramaphrabu found a maximum specific capacitance of 265 F/g for TiO2 decorated functionalised graphene [50].

Lee et al. prepared carbon nanotubes/PANI composite shows the best capacitance performance, with a specific capacitance of 248 F/g at 0.5 A/g reported [51].

Xie et al. demonstrated that PANI nanowires encapsulated inside TiO2 nanotube arrays exhibit excellent electrochemical performances, with a specific capacitance of 732 F g_1 in 1 M HCl reported [52].

Li et al. prepared TiO2@PANI coreeshell nanorod arrays using a combination of hydrothermal and in situ chemical polymerization methods [53].

Li et al synthesized PANI and PANI/TiO_2 composites using oxidative polymerization of aniline hydrochloride in the presence of different wt% of TiO_2 with ammonium persulphate. The FTIR results confirm the presence of PANI in the composite and in case of composites of PANI/TiO_2, there exists small shifting in frequencies of the bands as observed in PANI. The SEM study of PANI-TiO_2 composites revealed uniform distribution of TiO_2 particles in PANI matrix. Although PANI/TiO_2 composites show lower *dc* electrical conductivity as compared to PANI, and it decreases regularly with increasing content of TiO_2. But the composites show a higher thermal stability than that of pure PANI, which can also be shown by comparing values of activation energy. The *dc* electrical conductivity of

PANI and PANI/TiO_2 composites increases with increase of temperature. This work opens new perspectives for the use of PANI/TiO_2 composites as a conducting material at high temperature [54].
Z. Shao et al. found Supercapacitor based on the PANI nanowire/TiO2 nanotube array/Ti film electrodes exhibited a high specific capacitance of 897.35 F/g at a current density of 0.21 A/g and a super cycling stability of 86.2% specific capacitance retention over 1500 cycles. Because of the strong synergistic effect between the PANI nanowire networks and TiO2 nanotube array in this study, these high performance porous electrode materials are expected to have potential applications in electrochemical energy storage devices [55].
In the present decade the researchers are turns towards H-TiO2 X. H. Lu demonstrated a flexible solid-state ASC device with H-TiO2@MnO2 core–shell NWs as the positive electrode and the H-TiO2 @C core–shell NWs as the negative electrode. This device operates in a 1.8 V voltage window and is able to deliver a high specific capacitance of 139.6 F/g , maximum volumetric energy density of 0.30 mWh/cm (59 Wh/kg) and volumetric power density of 0.23 W/cm (45 kW kg/1). Also, the device exhibits excellent cycling performance (8.8% capacitance loss after 5000 cycles) and good flexibility. The capability of developing complex nanostuctured electrodes could advance the design and fabrication of high-performance and flexible ASCs.

Application of Electrochemical Supercapacitor

ECs have potential applications in wide range of fields and industries. For example in the application of electric vehicles and hybrid electric vehicles when high power delivery and long cycle life were needed, supercapacitors can supply pulse power for batteries or fuel cells in engine starting, acceleration, and also can store energy during braking within a short time [56, 57]. The stored energy can be reused when the vehicle starts moving again. In particular, supercapacitors may also replace or be combined with batteries as the electric power source of electric vehicles and hybrid electric vehicles [57] due to their high power delivery or uptake and relatively high energy stored [58].

CONCLUSION

The embedded structure of conducting polymers and transition metal oxides represent new advanced material as a key issue for the development of new devices and their structures offers various properties required in advanced application. The researcher reported maximum specific capacitance 248-897.35F/g, current density 0.21-20A/g, energy density 10-181.3 Wh/kg, power density 300-6000 W/kg with scan rate varies between 2-100 mV/s for supercapacitors. Synthesis and characterization result promising electrode materials for high performance electrical energy storage devices.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of this project from Shram Sadhana Research Proposal Scheme No. COET/SSRPS/1626/019/13 Dated 6-sept-2013 started in SSBT's COET Bambhori Jalgaon India for promoting research activity in the departments.

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