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Asymmetric supercapacitor devices based on dendritic conducting polymer and activated carbon

Darshna D. Potphode, Sarada P. Mishra, P. Sivaraman, Manoranjan Patri*

Polymer Science and Technology Centre, Naval Materials Research Laboratory (DRDO), Shill-Badlapur Road, Anand Nagar P.O., Ambernath (E) 421506, Maharastra, India

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ABSTRACT

Dendritic conducting polymers(CPs) are a novel class of porous pseudocapacitive electrode materials assembled with the combination of highly reversible redox active triphenylamine(TPA) and thiophene, 3-methylthiophene, selenophene and thieno[3,2-b]thiophen moieties. Due to the unique combination of three dimensional conducting network, fast redox reversible reactions, porous morphology, high thermal and electrochemical stability have fetched these pseudocapacitive polymers to exhibit high specific capacitance and emerged as an ideal candidate for energy storage devices. The electrochemical performance of as-prepared polymers showed specific capacitance of 278, 257, 246 and 315 Fg^{-1} for poly tris[4-(2-thienyl)phenyl]amine (P1), poly tris(4-(3-methylthiophene-2-yl)phenyl)amine (P2), poly tris (4-(selenophen-2-yl)phenyl)amine (P3) and poly tris(4-thieno[3,2-b]thiophen-2-yl) phenyl)amine (P4) respectively with low internal resistance. An insertion of selenophene and thieno(3,2-b)thiophene linkers in TPA block showed enhanced electrochemical performance than the thiophene-TPA pair. Furthermore, asymmetric supercapacitors were assembled with the polymer as cathode and activated carbon as an anode and the detailed electrochemical characterizations has been investigated. This research may shed light on designing new redox active psuedocapacitors and other electrochemical devices.

1. Introduction

Supercapacitors are energy storage devices having capacity of bridging the gap between high energy density batteries and high power density conventional capacitors [1]. It can be used for harvesting energy and delivering high pulse power for short periods [2,3]. Depending upon the level and duration of the storage the electrode materials can be modified and used in many applications like hybrid vehicles, telecommunications, military weapons, spaceships etc [4–8]. For large scale practical application supercapacitors still suffer for low energy density as a major bottleneck. To overcome this, an asymmetric hybridization is considered as one of the most promising tact with psuedocapacitive material as the energy source and electric double layer capacitance material as the power source. This combination can offer outstanding energy density for whole system [9].

The rapid growth in energy storage system demands advances in electrode materials for high specific capacitance and adequate stability. Carbon based electrode materials limits their use due to the non faradiac charge storage at the electrode-electrolyte interface which exhibits lower specific capacitance (~200 Fg^{-1}) than pseudocapacitive materials like metal oxides and CPs [10,11]. Pseudocapacitive materials are most promising materials since the charge storage in those can be induced by reversible redox reactions taking place at surface and bulk of the electrode [12,13]. Among pseudocapacitive materials, metal oxides are potential candidates for higher specific capacitance (upto1200 Fg^{-1}) and high stability than the CPs but polymeric materials can compete them interms of low cost, easy route of synthesis, light weight etc as long as commercialization concern [14–16]. Further, the electrochemical properties of the conducting polymers can be tuned by controlling the chemical structure of the polymer by inexpensive ways than the metal oxides. The CPs, such as polyaniline, polypyrrole, polythiophene and their derivatives are widely studied for electrochemical energy storage in both aqueous and non aqueous systems [13,17]. Polyaniline, being most used polymer in electrochemical strorage, showed highest specific capacitance upto 815 Fg^{-1} with good environmental stability than the polypyrrole and polythiophenes [16]. Polythiophenes and its various derivatives have been well explored as electrode materials

* Corresponding author.
E-mail addresses: mrpatri@gmail.com, patri@nmrl.drdo.in (M. Patri).

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in supercapacitors with specific capacitance range of 180-250 Fg^{-1} in non-aqueous system [18,19]. Three dimentional structured TPA based materials are known for fast charge transfer and reversibly redox activity and have been utilized in various applications viz. organic field effect transistors, electrochromic devices, solar cells etc [20,21]. Moreover combination of TPA core with electron rich thiophene moiety to form a conducting polymer has been proved a potential electrode material for electrochemical storage [22]. Robert et al. have reported electrochemically polymerized poly tris (4-(thiophene-2-yl) phenyl)amine based electrode material for energy storage. Nevertheless these kind of materials have not been fully explored for energy storage application. As polymeric structure and morphology plays an important role in energy storage [23], incorporation of such kind of materials in device fabrication has been receiving more attention due to their inherent redox properties and unusual high specific capacitance [22].

In this work, the newer supercapacitor electrode materials have been developed by synthesizing of structurally homologous dendritic conducting polymers differing in the density of electron rich linkers (3-methyl thiophene, selenophene and thieno(3,2-b) thiophene) in direct conjugation with TPA core. As per aromaticity of the selenophene and thieno(3,2-b)thiophene concern, these polymer have been prepared following the idea that an aromatic system similar to the thiophene-TPA pair to exhibit superiority in contributing more quinoidal character and inter-ring π-electron delocalization in polymer backbone to enhance the electrochemical performance. The dendritic nature of the polymer plays an important role in enhancing electrochemical storage to achieve highly porous morphology in the solid state by preventing close packing unlike linear chains. Moreover, our approach to creating the dendritic polymers through easy synthetic route by oxidative chemical polymerization has general applicability for large scale production at a very low cost and easy processible to use as electrode material in energy storage application.

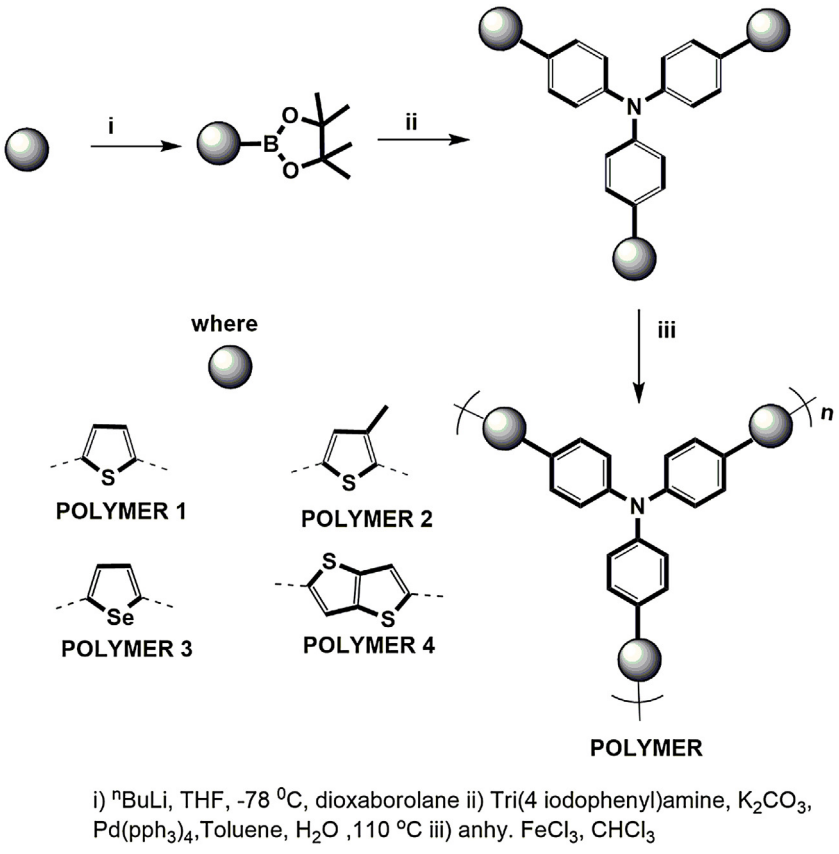
2. Experimental

2.1. Materials

Thiophene, 3-methyl thiophene, selenophene, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, ^{n}butyl lithium, tetrakis (triphenyl phosphine)palladium(0) ($Pd(PPh_3)_4$), unhydrous ferric chloride (anh.$FeCl_3$), potassium carbonate (K_2CO_3), acetonitrile (ACN) and tetraethylammonium tetrafluoroborate ($TEABF_4$) were purchased from Sigma Aldrich and used as received. All solvents were dried by conventional methods prior to use. Activated carbon (AC) (surface area: 1990 $m^2 g^{-1}$) used in this work was procured from PICA, France, grade:BP10. Conducting carbon (CC) powder (Vulcan XC-72) and carbon paper were procured from Cabot Corp., Japan and Toray, Japan respectively. Teflon (PTFE) suspension was supplied by Hindustan Flurocarbon Corp., India.

2.2. Instrumentation

The ^{1}H NMR spectra were recorded in a Brucker 400 FT-NMR spectrometer with chloroform -*d* as solvent. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra of polymers were recorded in JASCO FT/IR–4200 over a scanning range from 500 to 4000 cm^{-1} using KBr pallets. Raman spectroscopy of the



Scheme 1. Schematic of monomer synthesis and polymerization.