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Pseudocapacitive Material for Energy Storage Application: PEDOT and PEDOT:PSS

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Abstract. The total volume of solar energy reaching the earth in every second is equivalent to the total energy usage by the entire human race for three days. With this vast amount of clean energy freely available to humanity, there is still heavy dependence on fossil resources for energy. The major challenge with the use of fossil-based fuel is the generation of both land and atmospheric pollutants, which adversely affect the ecosystem. However, an essential requirement in transitioning from fossil energy to clean energy is the use of effective energy storage systems. Poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(4-styrene sulfonate) (PSS) PEDOT:PSS is currently one of the highly researched semi-conducting polymers that form the vast and expanding literature on energy application. Owing to its high electrical conductivity, thermal stability, and film-forming ability, PEDOT and its derivatives are employed for pseudocapacitive storage applications. This review will present a detailed discussion on the synthesis, properties, and application of PEDOT:PSS for battery and ultracapacitors. Highlights on the recent development and outlook in the use of PEDOT and its derivatives for energy application will also be provided.

INTRODUCTION

The increasing market demand to provide efficient electricity generation for smart grid transmission and distribution has stimulated intensive efforts to store an excess supply of it during off-peak hours. Likewise, providing

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environmentally benign energy storage devices for electric cars and innovative portable electronics further heightens the importance of low-cost, high power/energy density, rapid charging, and long lifespan energy storage. To address these challenges, the development of new electrode material and high-performance storage devices is desirable to meet the urgent energy demands for large-scale applications[1].

Batteries and supercapacitors devices are among the common energy storage devices developed to provide a temporary solution. While both devices can store energy, they, however, function on a dissimilar mechanism which results in significant variation in their energy and power densities. Materials capable of providing high energy density as well as high power density are the pseudocapacitive materials. They provide energy storage through the redox process like a battery, however, at a rapid pace like electrochemical double-layer capacitors[2]. A well-researched pseudo-capacitive material is poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(4-styrene sulfonate) (PSS), PEDOT:PSS due to its high conductivity, high storage capacity, and stability in the oxidized state [3]

PEDOT:PSS is an organic semi-conductor composed of ion-containing polymers which are also called ionomers- namely poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(4-styrene sulfonate) (PSS). PEDOT is a derivative of thiophene synthesized to minimize α–β and β–β couplings that takes place during oxidative polymerization of thiophene[4]. It is often doped to enhance its properties, such as solubility, and electrical conductivity. A 3D structure of PEDOT:PSS is shown in **Fig. 1** below. PEDOT:PSS is soluble and solution-processed to useful products using various techniques such as spin casting, doctor blade, inkjet printing, spray deposition, slot die coating, and screen printing. It is mostly employed in flexible, portable and stretchable electronics, photovoltaics, OFET, actuators, biosensors, thermoelectric devices, and energy harvesting materials. PEDOT: PSS is a highly conducting polymer with an electrical conductivity of up to 4600 S/cm[5]. This value can be improved to higher orders of magnitude, by pre-treating with solvents, such as sorbitol, methyl pyrrolidone, ionic liquids, surfactants, and dimethyl sulfoxide, or post-treating with compounds, such as salts, amphiphilic fluoro-compounds, ethylene glycol, zwitterions, co-solvents, phenol, acids, dimethyl sulfoxide (DMSO), geminal diols and alcohols [6, 7].

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In this mini-review, we explain the synthesis of PEDOT:PSS and further discuss its properties. A section of the write up expatiates the electron conductivity of the polymer. Finally, its application for energy storage particularly for battery storage systems and ultracapacitors are provided.

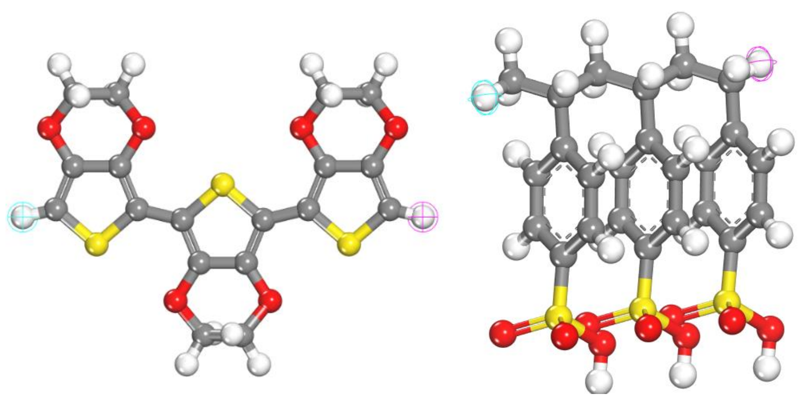

Figure 1: 3D chemical structure showing the repeating unit of PEDOT:PSS

Synthesis of PEDOT:PSS

PEDOT:PSS is a p-conjugated organic semi-conductor, that is obtained chemically through oxidative polymerization[8] or by electro-polymerization[9] of EDOT. Owing to the atomic substitution at the 3 and 4 positions of the thiophene molecule, PEDOT is insoluble in water and stable in the oxidative atmosphere. However, to ease fabrication of PEDOT for various application such as wearable, flexible, stretchable and implantable devices, it is often complexed with a hydrophilic counter ion, PSS, which promote the hydrophilicity of PEDOT. This is made possible due to the presence of sulfonate groups (SO_3^-) and sulfonic acid groups ($SO_3^- H^+$) in PSS. PSS is a salt $(CH_2CHC_6H_4SO_3H)_n$ synthesized through sulfonation of polystyrene. This method, however, produces a crosslinking defect [4]. PEDOT:PSS is soluble and solution-processed to a useful product using various techniques such as spin casting, slot die coating, doctor blade, inkjet printing, spray deposition, and screen printing [10].

$$\underset{\textbf{EDOT}}{n\ C_2H_4O_2C_4H_2S} + \underset{\textbf{Polyoxydisulfate}}{n\ (OSO_3)_2^{2-}} \longrightarrow \underset{\textbf{PEDOT}}{[C_2H_4O_2C_4S]n} + 2n\ HOSO^{3-}$$

$$\underset{\textbf{Polystyrene}}{(CH_2CHC_6H_5)_n} + \underset{\textbf{Sulfonate}}{n\ SO_3} \longrightarrow \underset{\textbf{Polystyrene sulfonate}}{(CH_2CHC_6H_4SO_3H)_n}$$

Properties of PEDOT:PSS

PEDOT:PSS exhibits a desirable combination of excellent properties such as flexibility, high electrical conductivity (10^{-2} to 10^3 S cm^{-1}), excellent environmental stability, superior electrochemical properties (33.9 F g^{-1} at 0.1 Ag^{-1}), facile process scalability, and cycling stability, which make the material a promising candidate for energy storage application[10]. The surface roughness is estimated to be approximately 5 nm. Depending on the relative humidity, PEDOT:PSS film exhibits mechanical between 25-55MPa, the elastic modulus of 1-2.7GPa, and strain at a break between 3-5% [11, 12]. Anisotropic thermal conductivity of PEDOT: PSS films was reported to be $\Lambda\perp = 0.76 \pm 0.41$ W m^{-1} K^{-1} and $\Lambda\| = 0.30 \pm 0.2$ W m^{-1} K^{-1} [13-15]. A nanoscale PEDOT that was developed using the oxidative chemical vapor deposition (oCVD) method exhibited a thermal conductivity of 0.16 W m^{-1} K^{-1} at room temperature [15].

Electronic Conductivity of PEDOT:PSS

The electrical properties of a material depend on its electronic structure.[16]. However, the energy band theory is insufficient in explaining the electronic conduction in organic semiconductors such as PEDOT:PSS. PEDOT:PSS is a *p*-conjugated conducting polymer characterized by localized single σ -bonds alternating with the double bond of localized σ-bonds (which forms a strong chemical bonding) and delocalized π-bonds(which is weakly bonded). Conduction proceeds with π-electrons moving to a neighboring site along the skeleton of the polymer chain leaving a hole(vacant site) behind for another π-electrons to fill. This movement of electron results in electric conduction in PEDOT:PSS. It is expected according to band theory that once an electron is dislodged from the top of the valence band of PEDOT:PSS, the hole left behind becomes completely delocalize[17]. However, for organic molecules like PEDOT:PSS, once an electron is extracted from or added to a carbon atom, radical ions are formed. The radicals formed becomes the charge carrier.

The addition and removal of electrons from the polymer is achieved through a redox process called doping. A stable radical cation called polaron is obtained when PEDOD:PSS becomes positively doped(p-doped) through the removal of an electron from the HOMO of the polymer. This is an oxidation process. While for a reduction process to occur, an unstable radical PEDOT:PSS anion is produced when the polymer becomes negatively doped(n-doped) by the addition of an electron to the LUMO of its molecular orbital. Again, it is imperative to note that PEDOT is often further doped with a counter ion PSS to improve its solubility in aqueous media. Although, this counter ion is not the charge carrier but rather the charges on PEDOT that are the mobile charge carriers. Moreover, if a second electron is removed from a p-doped PEDOT:PSS, either a second independent polaron is formed with a spin of 1/2 or a bipolaron with a spin of 0 if the extracted electron is the unpair-electron of the first polaron. The charges created on the bipolaron are dependent and propagate as a pair. The conductivity of PEDOT:PSS then depends on the amount of these charge carriers and their mobility -how fast their movement is within the bulk polymer[18].

Application of PEDOT:PSS for Energy Storage

PEDOT:PSS has found wide application, particularly as electrode material for energy storage systems. In a battery, PEDOT:PSS can function as a binder and as an anode material to store electrical charges. Its superior capacitance and conductivity allow for bulk charge storage through faradaic charging [19-22]. Recently, an anode material was developed for the lithium-ion battery using a composite of PEDOT:PSS with nanostructured Ge particles. The electrode was prepared using a facile solution impregnation technique. And the electrochemical properties of the composite were found to exhibit a reversible capacity of 405 $mAhg^{-1}$ after 200 cycles at 0.2C. Also, the anode display a rate capability of 800 and 700 $mAhg^{-1}$ at 2C and 4C respectively with initial discharge capacity of ~1400 $mAhg^{-1}$ and Coulomb efficiencies of 89% [19].

PEDOT:PSS is shown to mitigate electrode and electrolyte instability and display stability for oxygen reduction in Li-air batteries in the presence of lithium peroxide (Li_2O_2) under a nonaqueous environment. Lithium peroxide (Li_2O_2) is a superoxide intermediate discharge during cycling which reacts with a conventional electrode such as carbon to form an insulating product like lithium carbonate (Li_2CO_3) which is difficult to oxidize during charge and require high overpotentials[23].

Besides, PEDOT:PSS has found use as a conductive binder material for cathodes in a lithium-ion battery. Cathode materials in Li-ion batteries are composites made of redox-active components such as metal oxide, e.g. $LiCoO_2$ and $LiMn_2O_4$, or metal phosphates ($LiFePO_4$), with the inactive component having different functionalities. Literature shows that PEDOT:PSS, when used as a binder, is a stable material under multiple cycling in the operating potential range up to 4.2 V and shows no change in the impedance after 200 cycles [24]. Additionally, it can function as conductive additives to ensure electronic conductivity in the cathode. Moreover, increasing PEDOT:PSS content results in a decrease in the overvoltage and improved rate capability[25].

Furthermore, it can also be used as anode and cathode materials for supercapacitors[21, 22, 26-28]. Driven by the need to develop portable, flexible, and lightweight energy storage devices for wearable electronics, Hee and colleagues developed cheap, flexible, and high-performance electrode using PEDOT:PSS wrapped MWNT/MnO composite for supercapacitor applications. The developed electrode possesses electrochemical stability, the high specific capacitance of 428.2 F/g, a high energy density of 63.8 Wh kg^{-1}, and good cycle stability [27]. Dawei et. al. 2017, demonstrated the use of MWCNT-reinforced cellulose/PEDOT:PSS film (MCPP) to fabricate a high-performance electrode for supercapacitor. The electrode exhibits excellent electrochemical properties which include low resistance of 0.45 Ω, a high specific capacitance of 485 F g^{-1} at 1 A g^{-1}. The capacity retention of the electrode was 95% after 2000 cycles at 2 A g^{-1} which indicates good cycling stability [28]. Dan et al. [26] investigated the electrochemical performance of PEDOT nanowire films for solid-state supercapacitors. They developed flexible and freestanding PEDOT nanowire (NW) films using a facile modified self-assembled micellar soft-template technique accompanied by vacuum-assisted filtration. The resulting film electrode exhibited conductivity as high as 1340 S cm^{-1} with a specific capacitance of 667.5 mF cm^{-2} at 1 mA cm^{-2}. Using the film for supercapacitor, specific capacitance as high as 413.5 mF cm^{-2} at 1 mA cm^{-2} and 306.0 mF cm^{-2} at 50 mA cm^{-2} were recorded. The supercapacitor also displayed outstanding energy density of 48.3 mWh cm^{-2} and 19.1 mWh cm^{-2} at a power density of 0.22 mW cm^{-2} and 16.77 mW cm^{-2} respectively [26].

CONCLUSION

PEDOT:PSS is a potential pseudocapacitive matrix for high throughput energy storage applications. Its properties can be easily tuned by doping and/or by reinforcing it with suitable nanofillers. Its high electrical conductivity, specific capacity, and facile fabrication process have made it a suitable electrode material for batteries and supercapacitors. PEDOT:PSS exhibits superior electrochemical properties compared to conventional anode(graphite) material for Li-ion batteries. However, for supercapacitors, there is a trade-off, increasing the specific capacitance of PEDOT:PSS is at the expense of the charging and discharging cycling stability. An increase in capacitance leads to a reduction in the cycling life of the polymer.

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